Earth Syst. Sci. Data Discuss., 2, 137–180, 2009
www.earth-syst-sci-data-discuss.net/2/137/2009/

Earth System Science Data Discussions

Earth System Science Data Discussions is the access reviewed discussion forum of *Earth System Science Data*

CARINA alkalinity data in the Atlantic Ocean

A. Velo[1], F. F. Perez[1], P. Brown[2], T. Tanhua[3], U. Schuster[2], and R. M. Key[4]

[1]Instituto de Investigaciones Marinas, CSIC, Eduardo Cabello, 6, 36208 Vigo, Spain
[2]School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[3]Leibniz-Institut für Meereswissenschaften, Marine Biogeochemie, Kiel, Germany
[4]Princeton University, Program in Atmospheric and Oceanic Science, Forrestal Campus/ Sayre Hall, Princeton, NJ 08544, USA

Received: 25 June 2009 – Accepted: 3 July 2009 – Published: 3 August 2009

Correspondence to: A. Velo (avelo@iim.csic.es)

Published by Copernicus Publications.

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: This will be provided by CDIAC soon.
Available at: http://cdiac.ornl.gov/oceans/CARINA/Carina_table.html
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

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.

ESSDD
2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

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 consists of 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 nor 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 consists of 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); 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 2 and described in Sect. 5. In many cases there are more reported parameters in the individual cruise files than has been included in the secondary QC, such as ^{14}C, ^{13}C and SF_6.

ESSDD
2, 137–180, 2009
CARINA alkalinity data in the Atlantic Ocean
A. Velo et al.

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), for an overview of the North Atlantic CARINA data, see Tanhua et al. (2009a).

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

2 Data Provenance and Structure

As derived by 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. 1a, 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.

ESSDD
2, 137–180, 2009

Near surface formation of water masses is the main process that affects A_T variability. In Fig. 1b, the variation of A_T versus salinity for the subset of surface waters (depth < 200 m) is plotted. The correlation for this data set is higher than in Fig. 1a, giving a R^2 of 0.94 due to most of the variability in both salt and alkalinity occuring in the upper few hundred meters, where there is a strong salt-alkalinity correlation. This enforces the idea of the interdependence of both parameters.

Alkalinity data included in the CARINA 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 and Goyet, 1994), many measurements were also made by potentiometric titration at end-point in open cell (Mintrop et al., 2000).

In total, data from 98 cruises were included in the dataset for CARINA-ATL, of which 75 reported A_T data, totaling 65531 unique alkalinity measurements from 4774 stations. After the 1st QC check, 59793 data points (4580 stations from 73 cruises) remained flagged as good. However, crossover comparisons were performed on only 2562 stations (15 706 data points) as the remainder had insufficient deep water samples located sufficiently close together to enable station-station analyses. The results of the comparison exercise (2nd QC) are used for a total of 46593 A_T data points from 4696 stations sampled on 51 cruises, ensuring their quality regardless of the application of a correction or not. This is equivalent to 71% of the original data.

Of the 51 cruises included in the analysis, alkalinity data from 31 had been generated using certified reference materials (CRMs) to test or calibrate the titration system. The remaining 21 did not use CRM at all, instead using an alternative solution for standardization (DOE, 1994). 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 of 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 $\pm 6\,\mu\text{mol kg}^{-1}$, 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. Only data that were flagged "good" during the primary QC procedure (Key et al., 2009) are 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.

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 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

ESSDD
2, 137–180, 2009

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 followed 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 was 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 L crossovers with the uncertainty (σ):

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

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 results for cruises in this exercise with A_T data in Atlantic Ocean, i.e. cruises with at least two acceptable crossovers.

The following data is presented in the table:

- Region: Location of the cruise. All cruises in Table 1 belong to Atlantic Ocean (NA), but some overlap with the Arctic Mediterranean Seas (AMS) or Southern Ocean (SO) areas.
- 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).
- 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 $\pm 6\,\mu\text{mol}\,\text{kg}^{-1}$ are applied.
- Core cruises are highlighted in bold types.

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.

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.

5.1 Cruise 06MT19941012 (12)

This is the WOCE leg A02 cruise, with 53 stations and 24 sampling levels using a 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 ±3 μmol kg^{-1} and an accuracy ±6 μmol kg^{-1}. This cruise has 19 crossovers. The inversions suggest a correction of −25.1 μmol kg^{-1}. Most of the residuals fit within ±10 μmol kg^{-1}, with half part of them inside ±5 μmol 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 μmol kg^{-1}. Based on this evidence, an adjustment of −25 μmol kg^{-1} was applied to the alkalinity data.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

5.2 Cruise 18HU19970509 (44)

This is AR07Wh, a CCHDO cruise with 13 stations using a Rosette system with 24 ten-liter bottles. CRM analyses were used for standardization and precision was 2.7 μmol kg^{-1}. There are eight crossovers giving a fitted correction of 6.2 μmol kg^{-1}. The suggested adjustment for this cruise is therefore 6 μmol kg^{-1}. Most of the residuals fits very close to 0 and keep inside ±5 μmol kg^{-1} after offsets applied. 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)

This is WOCE line AR16e, also called 29CSMORENA_1. 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 shows 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)

This cruise has 33 stations in a hydrocast with 1.7 liter Niskin bottles. A precision of 0.1% and accuracy of 1.4 μmol kg^{-1} is 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.

5.5 Cruise 29GD19860904 (57)

This cruise has 50 stations in a hydrocast with 1.7 liter Niskin bottles. A precision of 0.1% and accuracy of 1.4 μmol kg^{-1} are 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 ±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)

This is the Hesperides FICARAM II cruise HE073. It is an A17 repeat section in the western South Atlantic region. The cruise has 29 full depth stations and 24 sampling levels using a 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 between the offset error and is better supported than no adjustment. All residuals fit very close to 0 and keep inside ±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.

5.7 Cruise 316N19971005 (65)

This is the Knorr cruise KN154/2 on the WOCE AR24b section. 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 μmol kg^{-1}. The

ESSDD
2, 137–180, 2009
CARINA alkalinity data in the Atlantic Ocean
A. Velo et al.

suggested adjustment is +8 μmol kg^{-1}. Excepting one, all inversion residuals fit inside ±6 μmol kg^{-1}. The cruise has a good fit with three core-cruises. Based on this evidence, an adjustment of 8 μmol kg^{-1} was applied to the alkalinity data

5.8 Cruise 31AN19890420 (64)

This cruise has 51 stations taken with a rosette system. Values seem to be about 5 to 10 μmol kg^{-1} too high in relation to OACES93 and A16N2003. CRMs were not used. The fitted correction is −9.6 μmol kg^{-1}. The inversions suggest an adjustment of −10 μmol 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 μmol kg^{-1} was applied to the alkalinity data

5.9 Cruise 323019940104

This is the CITHER2 cruise along the WOCE A17 section. In the cruise report, an offset for alkalinity of −8 μmol kg^{-1} was stated. There are eight crossovers that give a fitted correction of −8.9 μmol kg^{-1}. The suggested adjustment is −8 μmol kg^{-1} because it agrees with both the fitted result and the cruise report. Most of the inversion residuals fit inside ±5 μmol kg^{-1}. There are very good fits with four GLODAP cruises.

Based on this evidence, an adjustment of −8 μmol kg^{-1} was applied to the alkalinity data.

5.10 Cruise 35TH19990712 (106)

This is EQUALANT99 cruise, in the Equatorial Atlantic region. It has 102 stations and 24 sampling levels using a rosette system. .Precision is reported as 1.7 μmol kg^{-1}. A comparison with WOCE A15 data implies offset values as high as 12.7 μmol kg^{-1}. There are six crossovers, giving a fitted correction of -6.8 μmol kg^{-1}. The suggested

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

adjustment is $-6\,\mu$mol kg^{-1}. All inversion residuals fit inside ±6 μmol kg^{-1} after corrections are applied. There are very good fits with two GLODAP cruises.

Based on this evidence, an adjustment of $-6\,\mu$mol kg^{-1} was applied to the alkalinity data

5.11 Cruise 64TR19890731 (153)

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)

This is a meridional section from 30° N to 60° N along 20° W. This cruise has 23 stations with multiple casts on most of them. Method of Bradshaw et al. (1981), and calculations with constants of Goyet and Poisson (1989). 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.

5.13 Cruise 74AB19910501 (160)

This is the 74AB058 VIVALDI cruise. It has 34 deep stations and 24 sampling levels using a rosette system. 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.

ESSDD
2, 137–180, 2009

Title Page
Abstract Instruments
Data Provenance & Structure
Tables Figures
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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)

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.

5.15 Cruise 74DI19980423 (172)

This is the 74DI233 cruise, a meridional section along 20° W from 20° N to 60° N. Data is generally good, with a few data high relative to neighbors and GLODAP. CRMs were used. There are 24 crossovers giving a fitted correction of -8.5 μmol kg^{-1}. The suggested adjustment is -9 μmol kg^{-1}. Most of the residuals fit very close to zero and keep inside ± 5 μmol kg^{-1} after corrections are applied. There are very good fits with core and GLODAP cruises. Based on this evidence, an adjustment of -9 μmol kg^{-1} was applied to the alkalinity data.

5.16 Cruise OMEX2 (188)

There are nine crossovers giving a fitted correction of -8.1 μmol kg^{-1}. The suggested adjustment is -8 μmol kg^{-1}. Excepting one, all inversion residuals fit inside

$\pm 6\,\mu$mol kg^{-1}. There are many uncertainties. 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.

6 Data quality evaluation

In order to make an overall evaluation of alkalinity data quality, a Multi-Linear Regression (MLR) was done.

For improving the quality of the evaluation, the MLR analysis was applied in four density layers. Density at 1000 db (σ_1) was used to divide the ocean in four layers. 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 attends for depths 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 for this evaluation.

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

$$A_{T\_\mathrm{MLR}} = \sum_{i=1}^{8} a_i \cdot X_i$$

$$A_{T\_\mathrm{residuals}} = A_{T\_\mathrm{measured}} - A_{T\_\mathrm{MLR}} \quad (2)$$

where X_i stand for Theta, 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. 23. This shows a box plot of alkalinity residuals cruise data for each cruise. The width of individual boxes attends to the number of samples for that cruise.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

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 original ones. Most of the cruises have the alkalinity residuals median inside of the ±6 μmol kg^{-1} boundary. 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 observed variability of alkalinity; and secondly, the predictor parameters have their own inherent measurement errors.

Acknowledgements. This work has been performed and funded as part of the EU project CarboOcean (Project 511176). Additional support from the International Ocean Carbon Coordination Project IOCCP (Maria Hood) and the Hanse Institute for Advanced Study (HWK Delmenhorst, Germany) are gratefully acknowledged. Additional support provided as follows: for A. Velo, F. F. Perez PGIDIT05OXIC40203PM Xunta de Galicia and CTM200627116E/MAR MEC; P. J. Brown Award NER/S/A/2004/12255; T. Tanhua EU FP6 CARBOOCEAN Integrated Project, Contract no. 511176; and R. M. Key, NOAA grant NA08OAR4320752 and NA08OAR4310820. We want also to thank the hard work and dedication of analysts and investigators that collect the data at the sea; without them, this work would not be possible. We gratefully acknowledge also those who have contributed their data to the CARINA project.

References

Bradshaw, A., Brewer, P., Shafer, D., and Williams, R.: Measurements of total carbon dioxide and alkalinity by potentiometric titration in the geosecs program, Earth Planet. Sci. Lett, 55, 99–115, 1981.

Dickson, A.: An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, Deep-Sea Res,, 28, 609–623, 1981.

Dickson, A. and Goyet, C.: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, Version 2, 1994.

Feely, R., Sabine, C., Lee, K., Millero, F., Lamb, M., Greeley, D., Bullister, J., Key, R., Peng, T., and Kozyr, A.: In situ calcium carbonate dissolution in the pacific ocean, Global Biogeochem. Cy., 16, 1144, doi:10.1029/2002GB001866, 2002.

Goyet, C. and Poisson, A.: New determination of carbonic acid dissociation constants in sea-water as a function of temperature and salinity, Deep-Sea Res., 36, 1635–1654, 1989.

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T.-H.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18, GB4031, doi:10.1029/2004GB002247, 2004.

Key, R. M., Tanhua, T., Olsen, A., Hoppema, M., Jutterström, S., Schirnick, C., van Heuven, S., Lin, X., Wallace, D. W. R., and Mintrop, L.: The carina data synthesis project: Introduction and overview, Earth Syst. Sci. Data Discuss., in preparation, 2009.

Mintrop, L., Pérez, F., González-Dávila, M., Santana-Casiano, J., Körtzinger, A., Geowissenschaften, F., Weg, D., and Cabello, E.: Alkalinity determination by potentiometry: Intercalibration using three different methods determinación potenciométrica de la alcalinidad: Intercalibración usando tres métodos diferentes, Ciencias Marinas, 26, 23–37, 2000.

Sabine, C., Key, R., Kozyr, A., Feely, R., Wanninkhof, R., Millero, F., Peng, T., Bullister, J., and Lee, K.: Global ocean data analysis project (glodap): Results and data, ndp-083, 110 pp., Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 2005.

Tanhua, T., Steinfeldt, R., Key, R. M., Brown, P., Gruber, N., Wanninkhof, R., Perez, F. F., Körtzinger, A., Velo, A., Schuster, U., van Heuven, S., Bullister, J. L., Stendardo, I., Hoppema, M., Olsen, A., Kozyr, A., Pierrot, D., Schirnick, C., and Wallace, D. W. R.: Overview of the atlantic ocean carina data and salinity measurements, Earth Syst. Sci. Data Discuss., in preparation, 2009a.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

Tanhua, T., van Heuven, S., Key, R. M., Velo, A., Olsen, A., and Schirnick, C.: Quality control procedures and methods of the carina database, Earth Syst. Sci. Data Discuss., in preparation, 2009b.
Wanninkhof, R., Kozyr, A., and Energy, D. O.: Comparison of inorganic carbon system parameters measured in the atlantic ocean from 1990 to 1998 and recommended adjustments, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, 2003.

ESSDD
2, 137–180, 2009

Table 1. Alkalinity adjustments applied to dataset.

Carina ID	Expocode	Region	CRM	WLSQ adj ±STD	WDLSQ adj ±95%CI	Adjustment μmol kg^{-1}
12	06MT19941012	NA	x	−27.9±1.3	−25.1±1.6	−25
44	18HU19970509	NA	x	7.4±0.8	6.2±1.2	6
52	29CS19930510	NA		6.7±1.0	7.1±1.0	7
55	29GD19840218	NA		6.7±0.9	6.5±1.3	6
57	29GD19860904	NA		4.8±0.9	4.3±1.7	6
61	29HE20010305	NA+SO	x	−3.9±1.8	−5.1±0.8	−6
65	316N19971005	NA		5.5±0.8	8.1±0.9	8
64	31AN19890420	NA		−10.2±0.9	−9.6±1.1	−10
	323019940104	NA+SO	x	−10.9±2.8	−8.9±0.8	−8
106	35TH19990712	NA	x	−4.6±2.6	−6.8±1.6	−6
153	64TR19890731	NA		13.7±0.9	13.8±0.7	14
154	64TR19900417	NA		15.2±0.7	14.4±1.4	14
160	74AB19910501	NA		4.1±0.7	5.2±0.7	5
170	74DI19900612	NA		11.9±0.4	14.9±1.6	15
172	74DI19980423	NA	x	−5.3±0.6	−8.5±0.6	−9
188	OMEX2	NA		−9.3±1.0	−8.1±2.0	−8

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

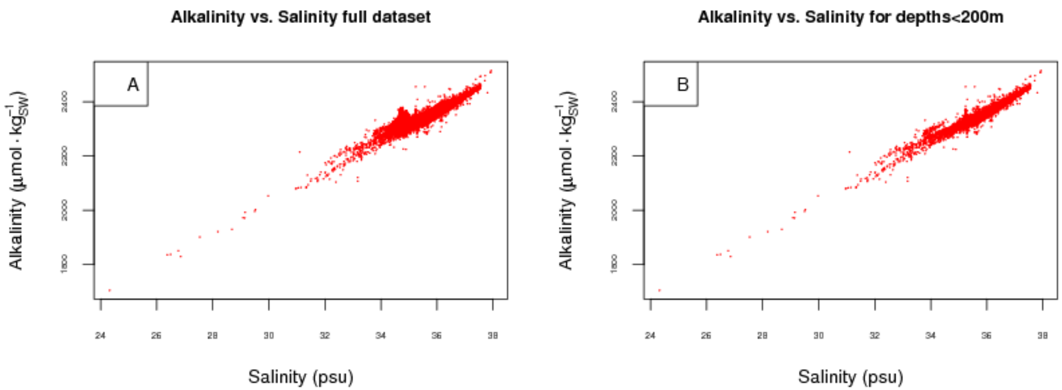

Fig. 1. Alkalinity data in CARINA final database versus salinity for: **(A)** data deeper than 200 m **(B)** depths <200 m.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

Title Page

Abstract | Instruments

Data Provenance & Structure

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

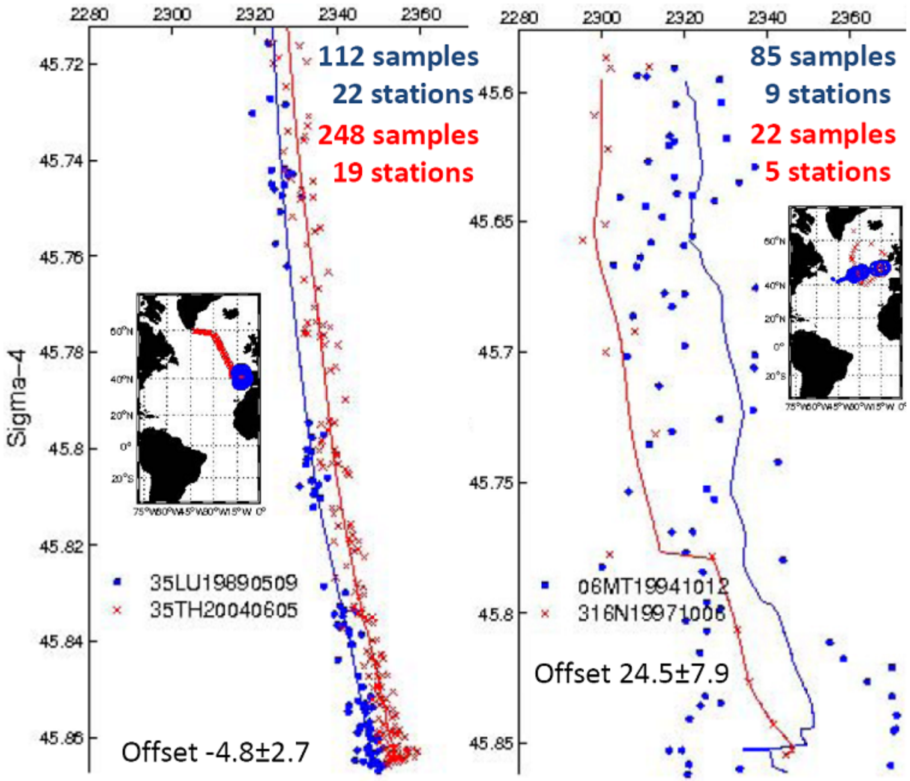

Fig. 2. Crossover between the cruises 35LU19890509 and 35TH20040605 **(a)** and the cruises 06MT19941012 and 316N19971006 **(b)**.

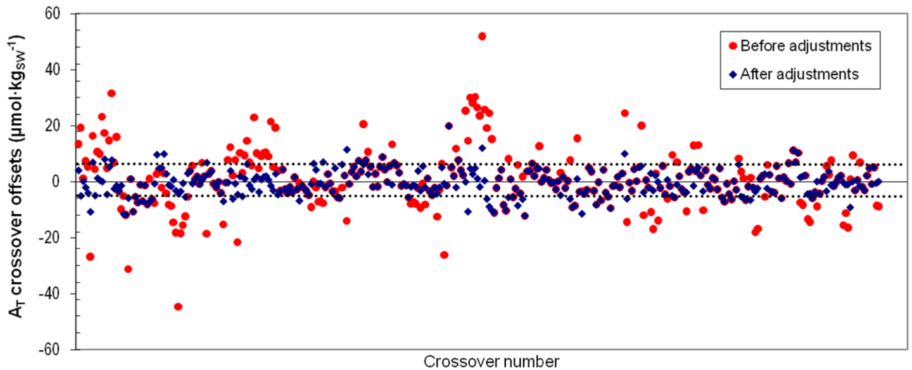

Fig. 3. Crossover alkalinity offsets obtained with original database and after adjustments were applied.

ESSDD
2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

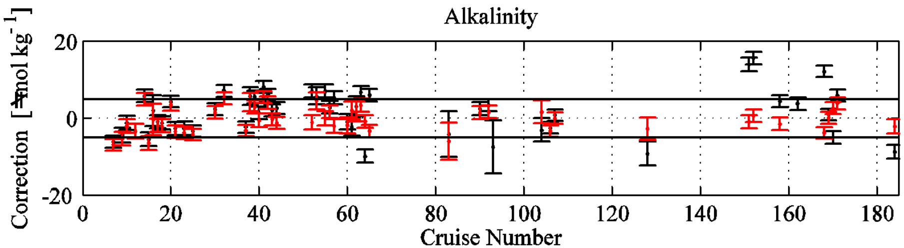

Fig. 4. Mean and standard deviation of the offset for each cruise before (black) and after (red) the adjustments were applied.

ESSDD
2, 137–180, 2009
CARINA alkalinity data in the Atlantic Ocean
A. Velo et al.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

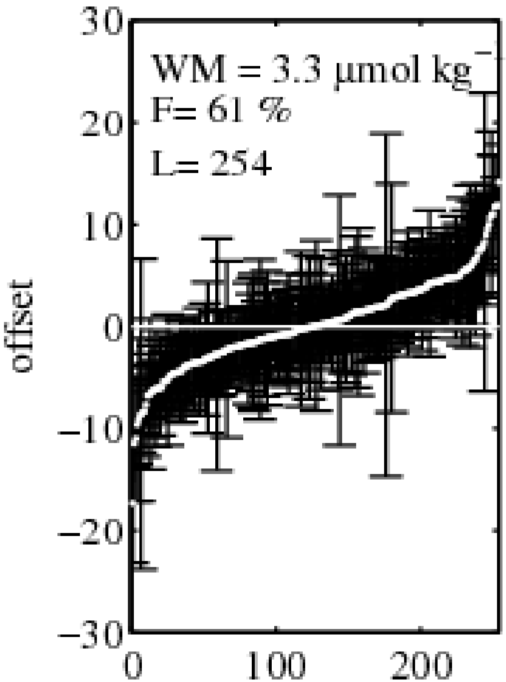

Fig. 5. Sorted offsets calculated for the crossovers in the CARINA-ATL data after adjustments have been applied. *WL*: the weighted mean of the offsets (see text); *F*: the percentage of offsets indistinguishable from 1 within their uncertainty; *L*: the number of crossovers.

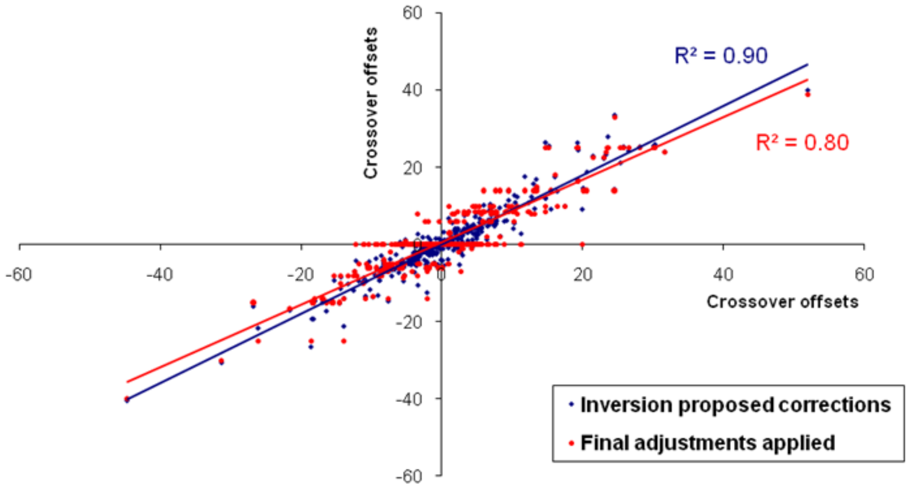

Fig. 6. Original versus post-adjust offsets for the all crossover in the Atlantic Ocean after applying the full solution (blue) or the final applied solution given in the last column of Table 1 (pink).

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

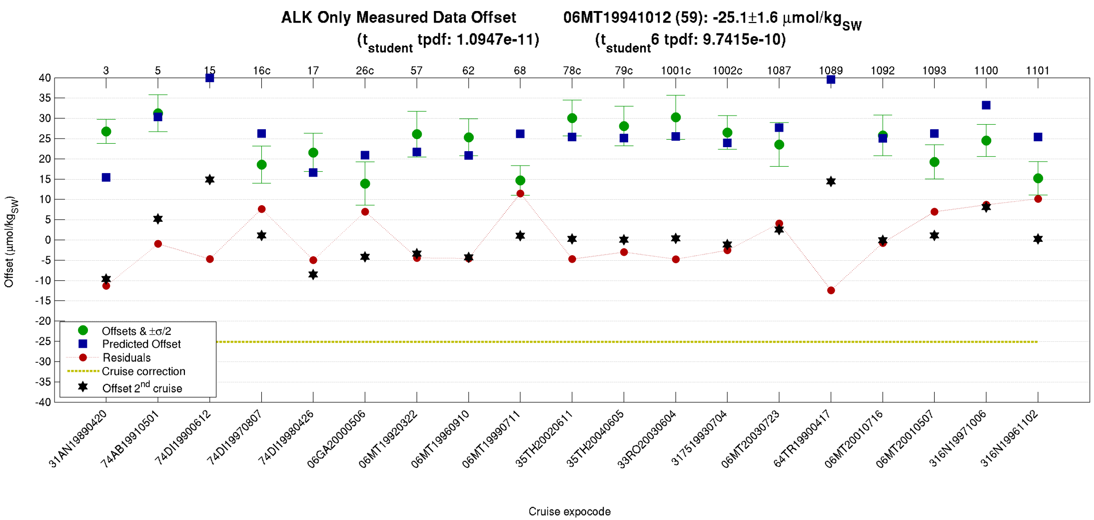

Fig. 7. Cruise crossover information plot for 06MT19941012.

ESSDD
2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

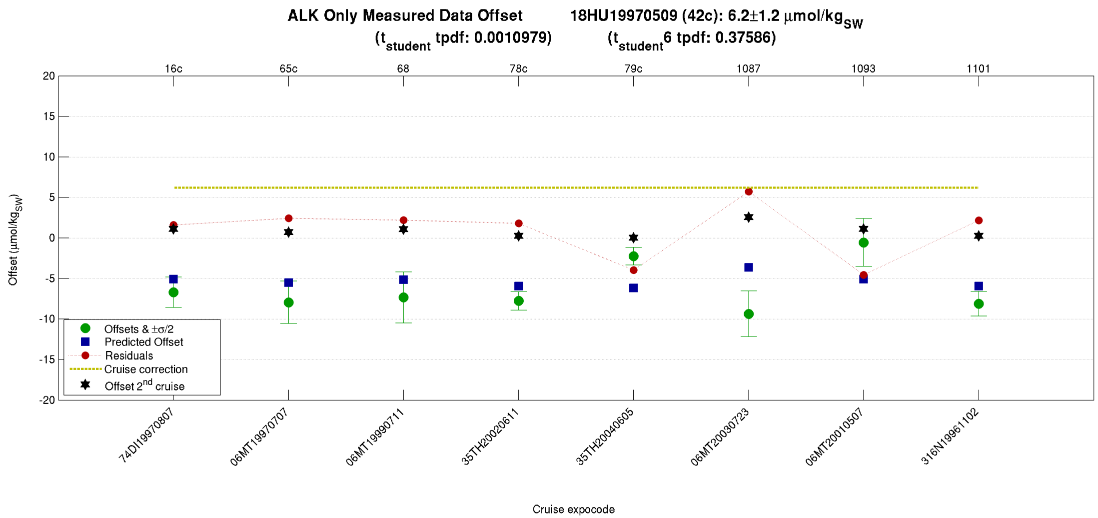

Fig. 8. Cruise crossover information plot for 18HU19970509.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

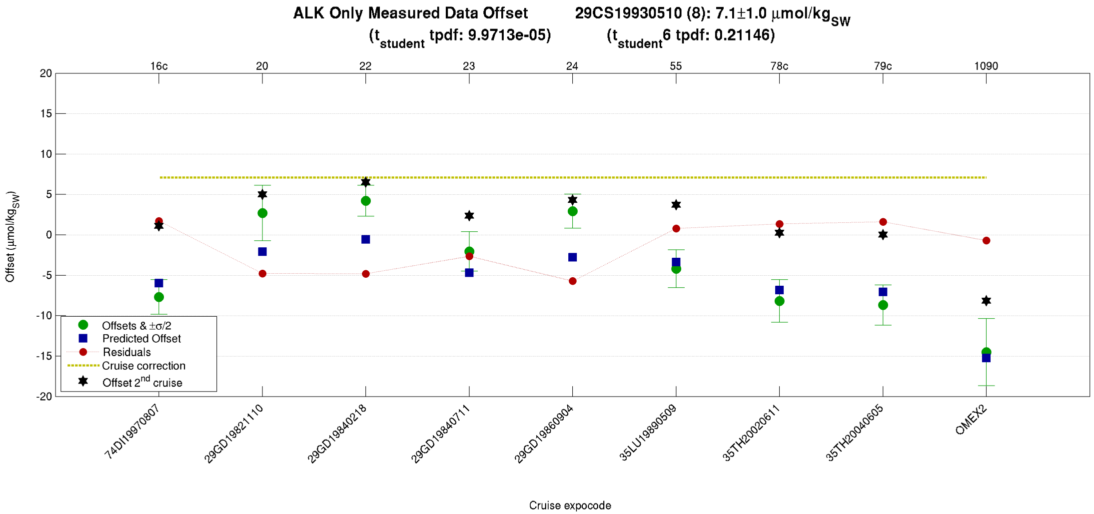

Fig. 9. Cruise crossover information plot for 29CS19930510.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

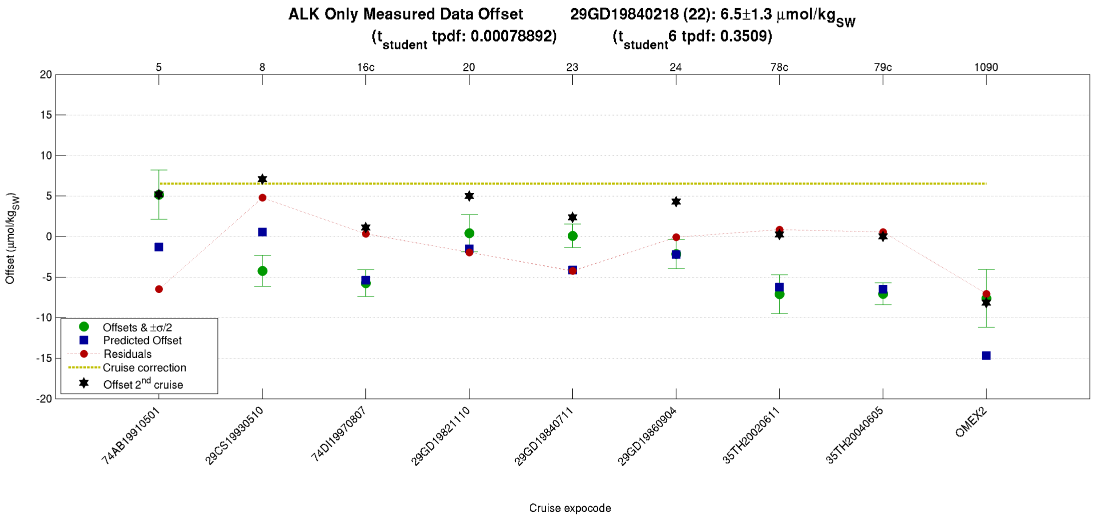

Fig. 10. Cruise crossover information plot for 29GD19840218.

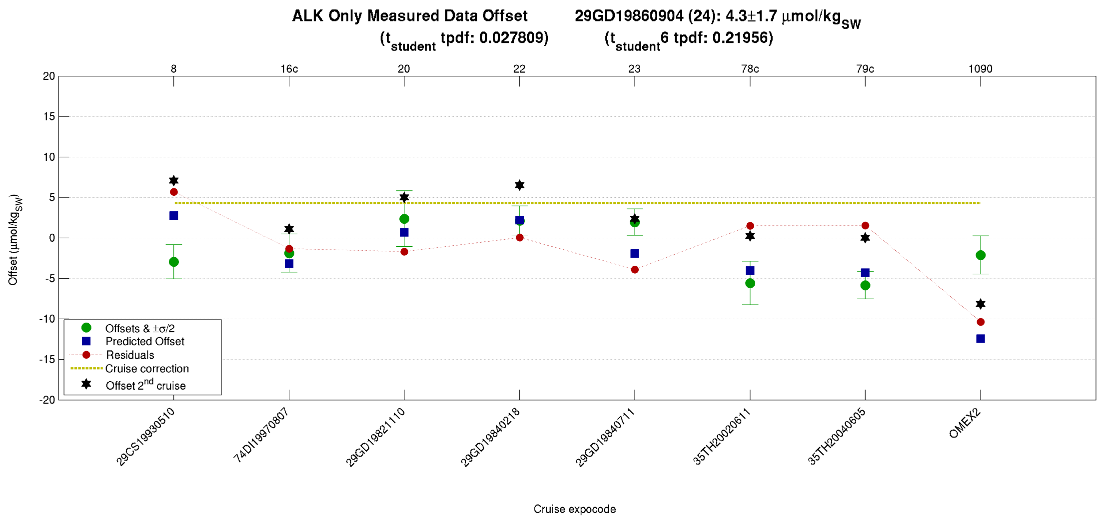

Fig. 11. Cruise crossover information plot for 29GD19860904.

ESSDD
2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

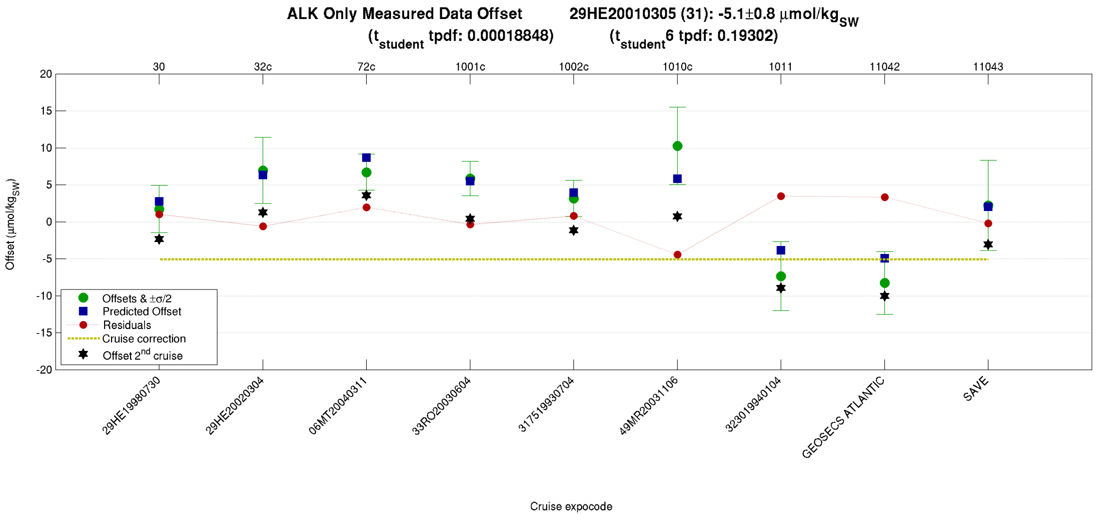

Fig. 12. Cruise crossover information plot for 29HE20010305.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

Title Page

Abstract | Instruments

Data Provenance & Structure

Tables | Figures

◀| |▶

◀ ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

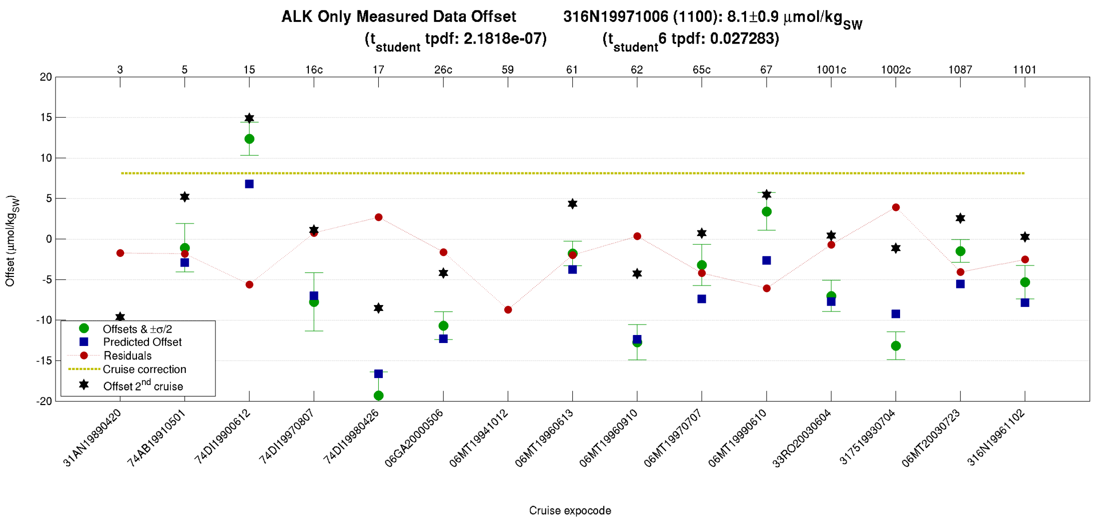

Fig. 13. Cruise crossover information plot for 316N19971005.

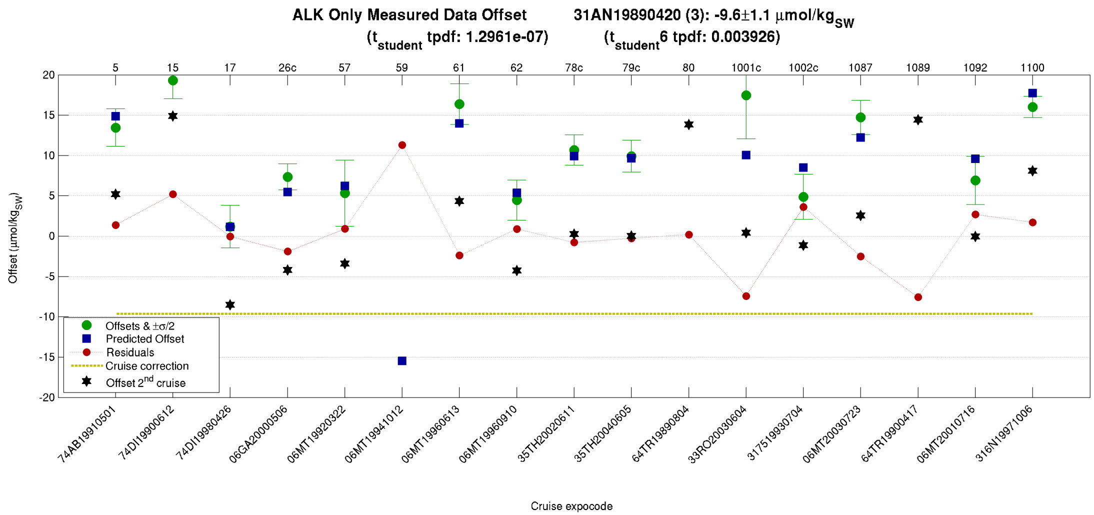

Fig. 14. Cruise crossover information plot for 31AN19890420.

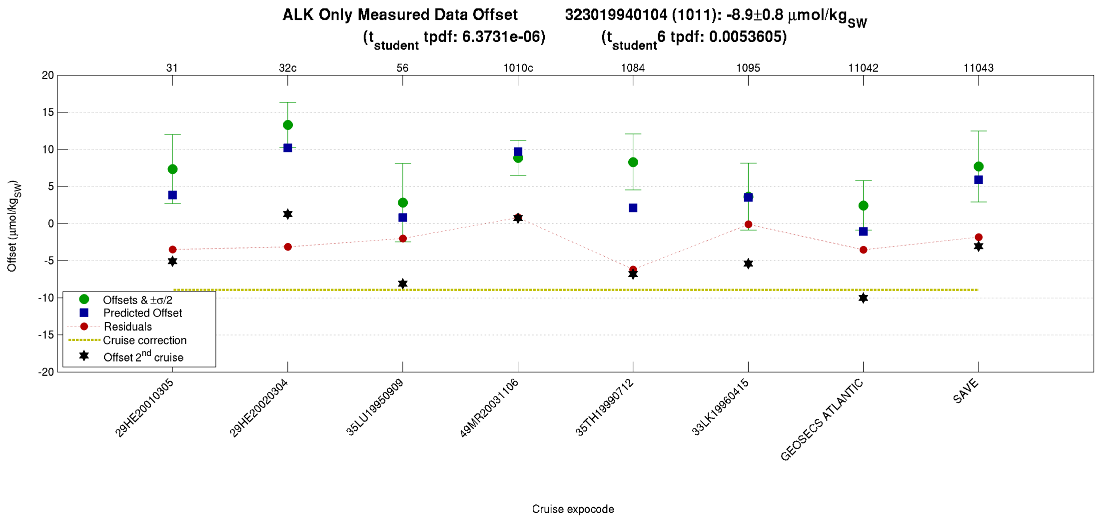

Fig. 15. Cruise crossover information plot for 323019940104.

ESSDD
2, 137–180, 2009

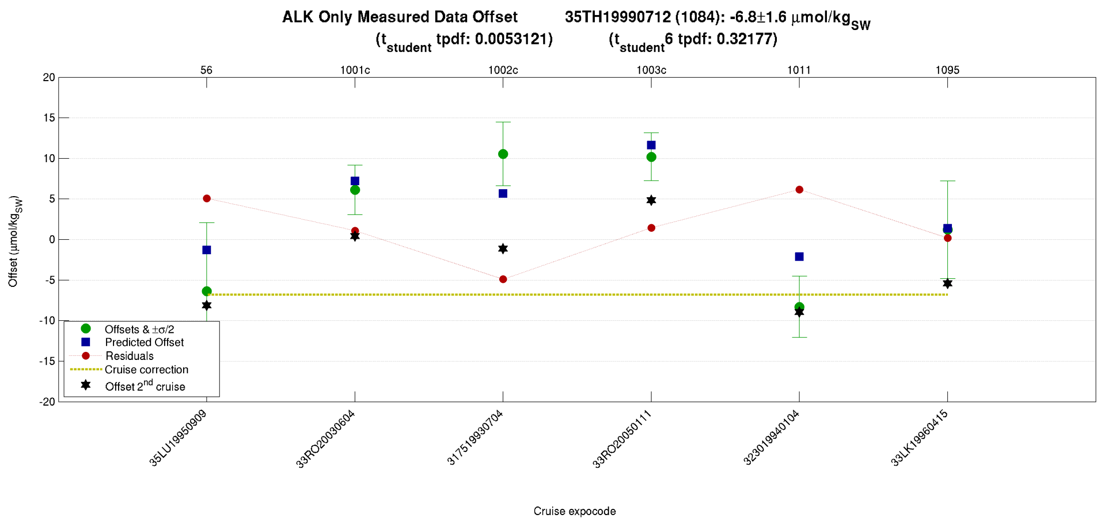

Fig. 16. Cruise crossover information plot for 35TH19990712.

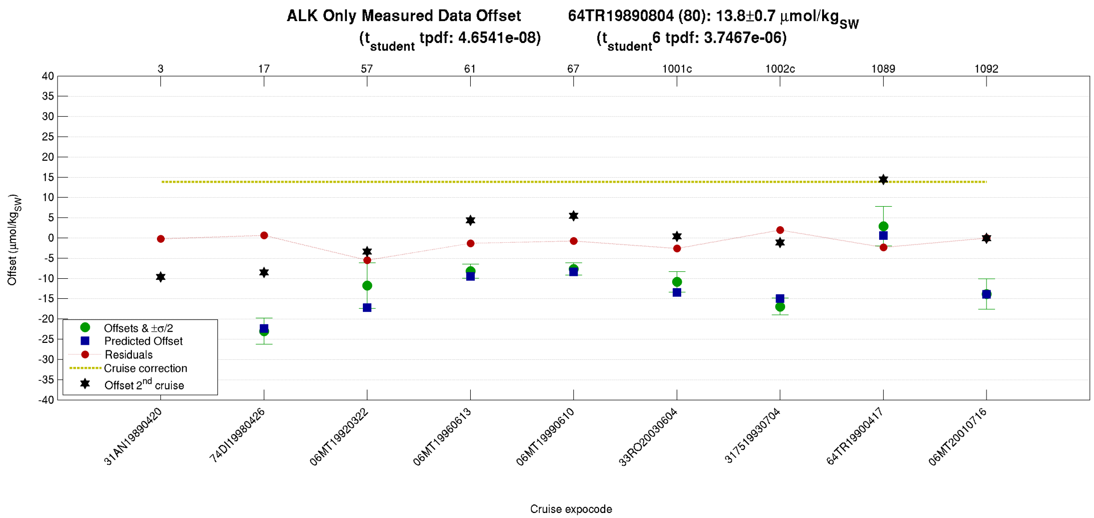

Fig. 17. Cruise crossover information plot for 64TR19890731.

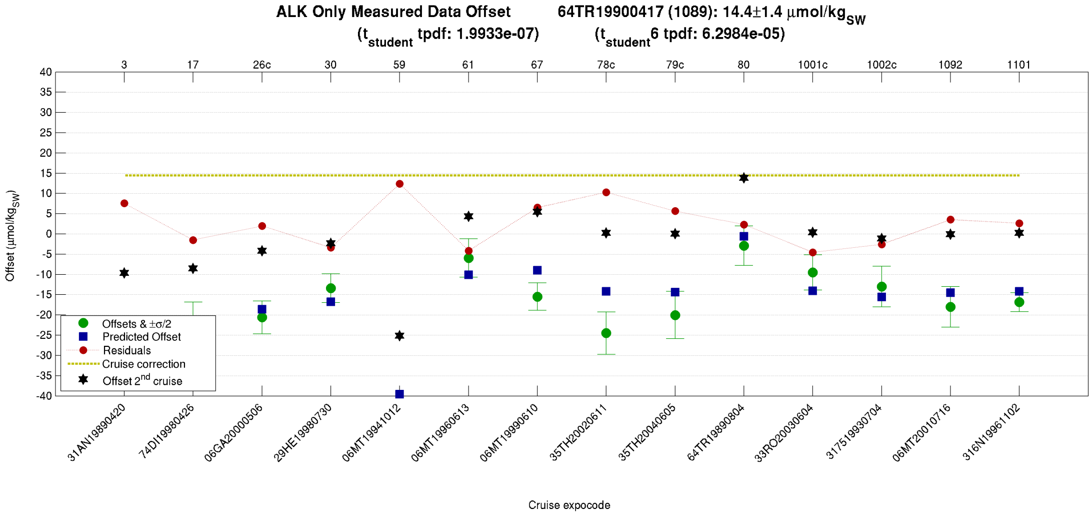

Fig. 18. Cruise crossover information plot for 64TR19900417.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

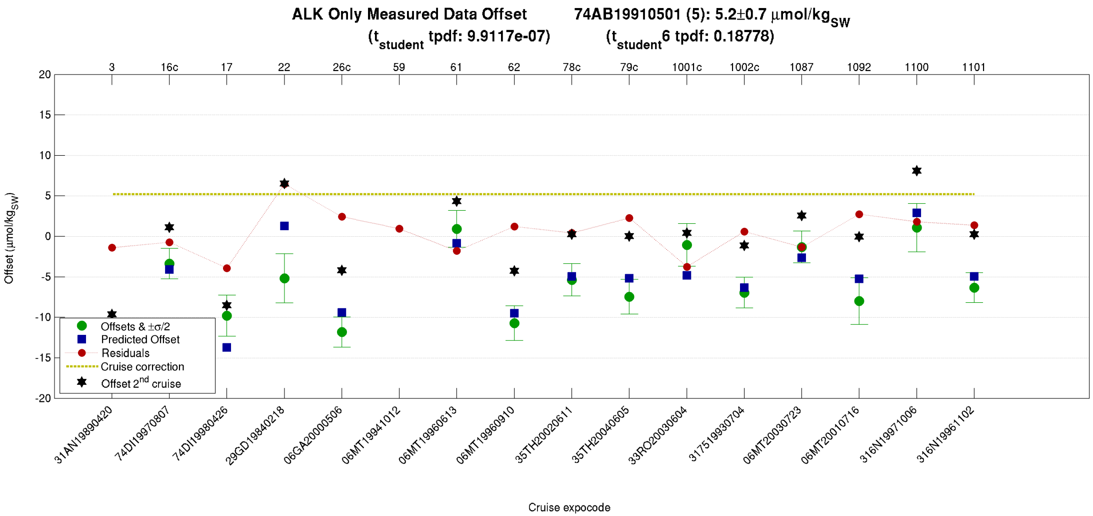

Fig. 19. Cruise crossover information plot for 74AB19910501.

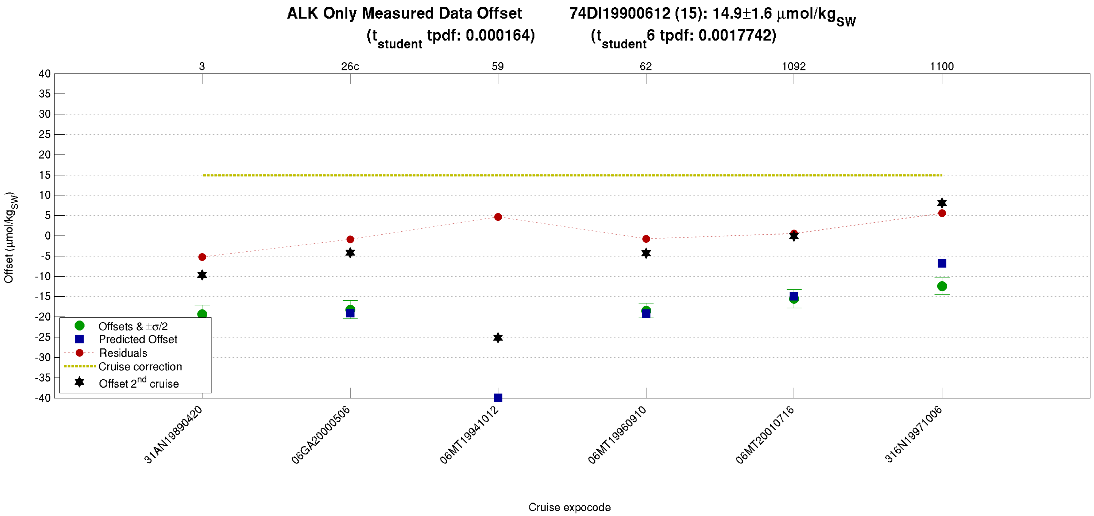

Fig. 20. Cruise crossover information plot for 74DI19900612.

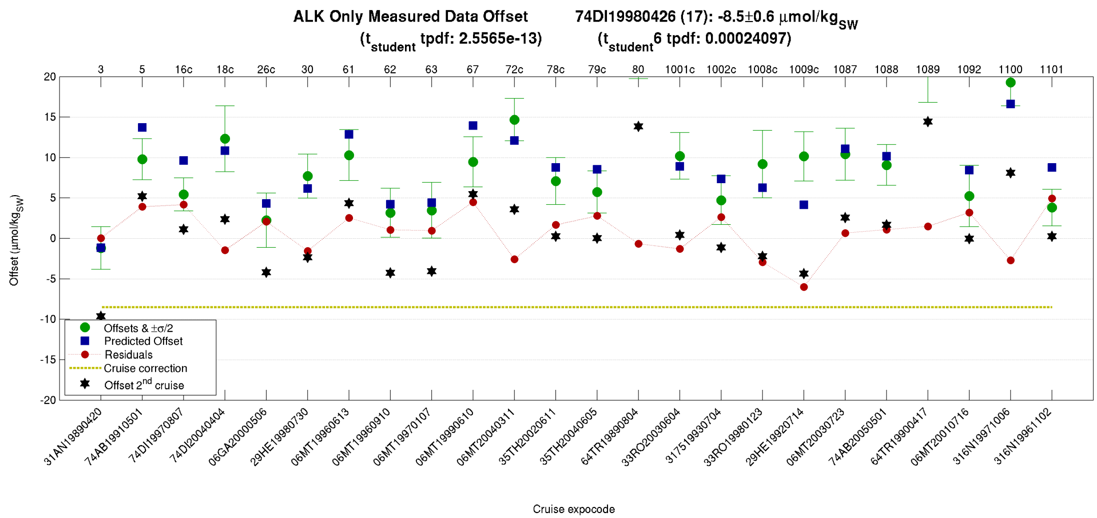

Fig. 21. Cruise crossover information plot for 74DI19980423.

ESSDD

2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

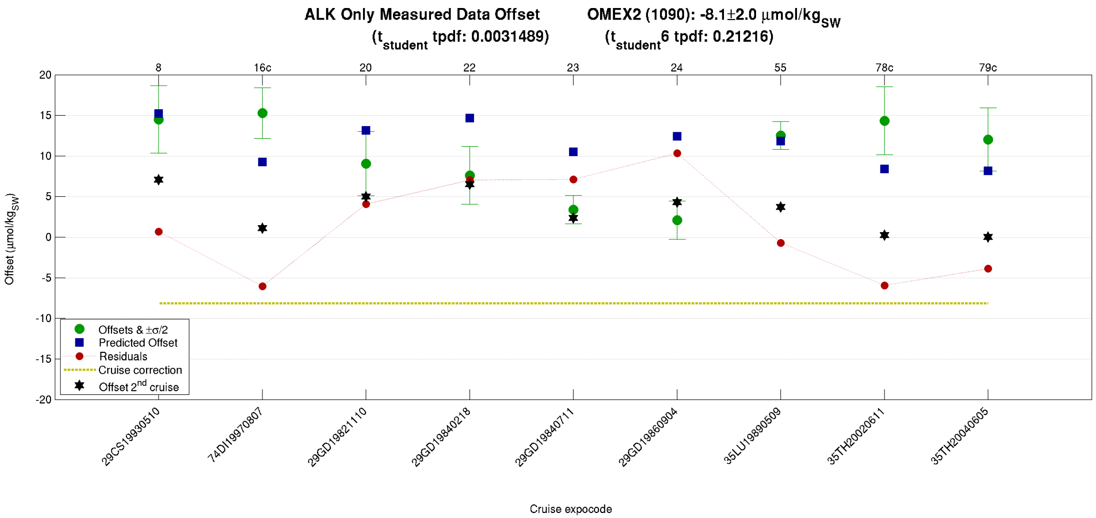

Fig. 22. Cruise crossover information plot for OMEX2.

ESSDD
2, 137–180, 2009

CARINA alkalinity data in the Atlantic Ocean

A. Velo et al.

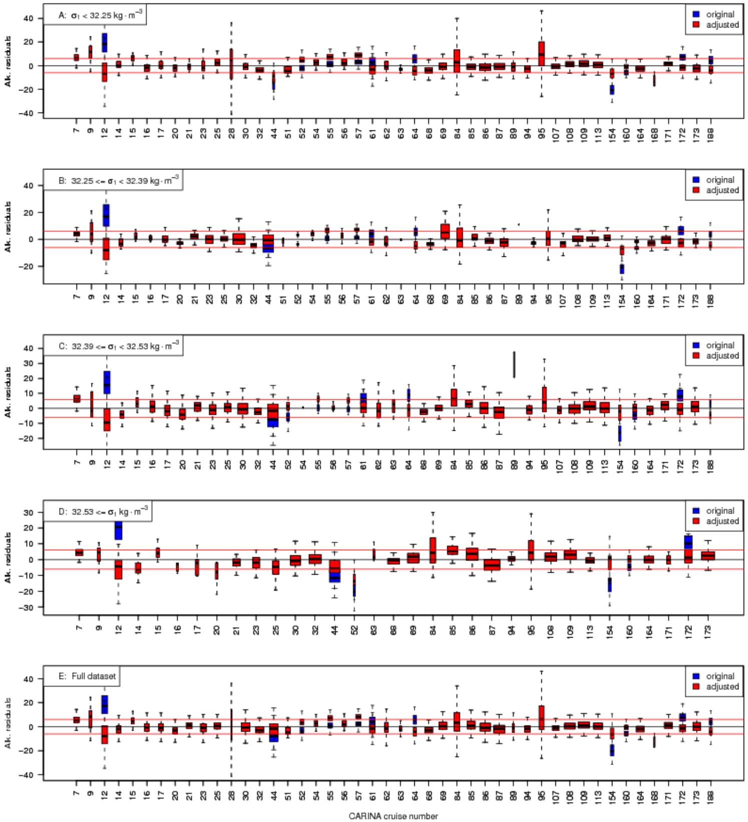

Fig. 23. Alkalinity residuals obtained from CARINA-ATL dataset by applying an MLR for alkalinity data against Theta, Salinity, Latitude, AOU, Nitrate, Phosphate and Silicate. Figures **(A)** to **(D)** are CARINA-ATL subsets for the indicated σ_1 interval, and **(E)** is the join for the full dataset. Blue values are residuals with the original unadjusted alkalinity values, and Red values are the final adjusted alkalinity values. Red lines are the $\pm 6\,\mu\text{mol}\,\text{kg}^{-1}$ of alkalinity used as lower limit for adjustments in the crossover exercise.

ESSDD
2, 137–180, 2009

Title Page
Abstract
Instruments
Data Provenance & Structure
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion