

CARINA data synthesis project: pH data scale unification and cruise adjustments

A. Velo¹, F. F. Pérez¹, X. Lin², R. M. Key², T. Tanhua³, M. de la Paz¹, A. Olsen^{6,5}, S. van Heuven⁴, S. Jutterström⁵, and A. F. Ríos¹

¹Instituto de Investigaciones Marinas, CSIC, Eduardo Cabello, 6, 36208 Vigo, Spain

²Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, NJ, USA

³Leibniz-Institute für Meereswissenschaften, Marine Biogeochemie, Kiel, Germany

⁴Netherlands Institute for Sea Research, Texel, The Netherlands

⁵Institutionen för kemi, Göteborgs universitet, Göteborg, Sweden

⁶Bjerknes Centre for Climate Research, UNIFOB AS, Allégaten 55, 5007 Bergen, Norway

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Abstract. Data on carbon and carbon-relevant hydrographic and hydrochemical parameters from 188 previously non-publicly available cruise data sets in the Arctic Mediterranean Seas (AMS), Atlantic Ocean and Southern Ocean have been retrieved and merged to a new database: CARINA (CARbon IN the Atlantic Ocean).

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 database were objectively examined in order to quantify systematic differences in the reported values. Systematic biases found in the data have been corrected in the data products, three merged data files with measured, calculated and interpolated data for each of the three CARINA regions; AMS, Atlantic Ocean and Southern Ocean. Out of a total of 188 cruise entries in the CARINA database, 59 reported pH measured values. All reported pH data have been unified to the Sea-Water Scale (SWS) at 25 °C.

Here we present details of the secondary QC of pH in the CARINA database and the scale unification to SWS at 25 °C. The pH scale has been converted for 36 cruises. Procedures of quality control, including crossover analysis between cruises and inversion analysis are described. Adjustments were applied to the pH values for 21 of the cruises in the CARINA dataset. With these adjustments the CARINA database is consistent both internally as well as with the GLODAP data, an oceanographic data set based on the World Hydrographic Program in the 1990s. Based on our analysis we estimate the internal consistency of the CARINA pH data to be 0.005 pH units. The CARINA data are now suitable for accurate assessments of, for example, oceanic carbon inventories and uptake rates, for ocean acidification assessment and for model validation.

Data coverage and parameter measured

Repository-Reference:

doi:10.3334/CDIAC/otg.CARINA.AMS.V1.2

doi:10.3334/CDIAC/otg.CARINA.ATL.V1.0

doi:10.3334/CDIAC/otg.CARINA.SO.V1.0

Available at:

http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA.AMS.V1.2/

http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA.ATL.V1.0/

http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA.SO.V1.0/

Coverage: 78° S–90° N; 180° W–180° E

Location Name: Arctic Mediterranean Seas, Atlantic Ocean and Southern Ocean

Date/Time Start: 1977-10-7

Date/Time End: 2006-02-10



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

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 degree
longitude		LONGITUDE		decimal degree
cruiseno				
depth				meter
temperature		CTDTMP		°C
salinity	sf	SALNTY	SALNTY_FLAG_W	
pressure		CTDPRS		decibar
phsws25	phsws25f	PH_SWS	PH_SWS_FLAG_W	

For an introduction to this work and a complete list of parameters in the CARINA data base, see Key et al. (2010) and Tanhua 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

Carbon-related data from both historical and recent hydrographic cruises in the Arctic Mediterranean Seas (AMS, includes Arctic Ocean and Nordic Seas), Atlantic and Southern Oceans have been brought together to form the CARINA database. The major aim of this project was to produce an internally consistent dataset of carbon-related parameters that can be used to assess and quantify carbon uptake and storage in these regions. Focus was placed not only on the collection of relevant data but also ensuring quality. The CARINA working group has performed both primary and secondary quality control (QC). This report is a summary of the pH data in the CARINA data set and describes the data consistency analysis (secondary QC) and scale conversions undertaken. For an introduction to and overview of the work done in the CARINA project see Key et al. (2010), Tanhua et al. (2010) as well as the other more specialized papers of this special issue.

1.1 Description of parameter (pH)

pH is one of the four parameters that define the carbonate system in sea water. The term pH describes the acidity of a liquid and it is defined as: $\text{pH} = -\log_{10} [\text{H}^+]$. The pH of seawater has become a valuable oceanographic parameter, particularly since problems with its measurement and interpretation have been resolved through the development of rational pH scales (Dickson, 1993), photometric measurement methods (Clayton and Byrne, 1993) and reliable pH buffer standards of seawater (Dickson, 1993; Millero et al., 1993).

Oceanic pH reflects the thermodynamics state of the acid-base system in seawater, especially of the geochemically important carbonate system. The equilibrium between carbonate species and CO_2 , the carbonate buffering, helps to mitigate to a large extent the changes that can be induced to seawater pH by several causes (Millero, 2007; Raven et al., 2005; Wootton et al., 2008). Uptake of CO_2 from the atmo-

sphere can incur changes in pH, but the carbonate buffering acts to stabilize these changes by consumption of carbonate ions present in the seawater, and ultimately by taking carbonate ions through dissolution of CaCO_3 sediments, shifting the equilibrium.

1.2 Distribution

The primary factors governing the spatial and temporal distribution of ocean pH are temperature, because of the dependence of the dissociation constant on this parameter, and partial pressure of CO_2 ($p\text{CO}_2$), total alkalinity (A_T) and total carbon (C_T), due to carbonate equilibrium. Surface ocean pH is mainly affected by temperature, biology, uptake/release of CO_2 from/to atmosphere, and uptake/release of CO_2 from/to deeper waters by upwelling or sinking. There are changes and cycles that contribute to fluctuations in the surface ocean pH, on timescales of days to years and including seasons (Raven et al., 2005; Wootton et al., 2008). It is estimated that the global surface ocean has already acidified by roughly 0.1 pH units (from 8.2 to 8.1 in SWS scale at 25 °C) since pre-industrial times (Caldeira and Wickett, 2003; Olafsson et al., 2009; Orr et al., 2005; Raven et al., 2005) due to anthropogenic CO_2 emission, and its uptake by the ocean. In the deep oceans, the CO_2 concentration increases by decomposition of organic matter that sinks, and these additions of CO_2 cause its pH to decrease, but because CaCO_3 is abundant in sediments, the pH of the deep oceans is very stable, and changes are minimal even on timescales of 10 000 years (Raven et al., 2005).

1.3 Different pH scales

The first pH definition ($\text{pH} = -\log_{10} [\text{H}^+]$) from Sørensen (1909) presents some operational problems since free protons $[\text{H}^+]$ do not exist in any significant amount in aqueous solutions. Thus, the symbol “ H^+ ” represents hydrate complexes rather than the concentration of free hydrogen

Table 1. pH scales used on seawater measurements, definitions, and relationships (Dickson, 1993; Dickson et al., 2007; Millero, 2007).

Scale	pH definition
NBS	$\text{pH}_{\text{NBS}} = -\log a_{\text{H}}$
Free	$\text{pH}_{\text{F}} = -\log [\text{H}^+]_{\text{F}}$
Total	$\text{pH}_{\text{T}} = -\log[\text{H}^+]_{\text{T}} = -\log([\text{H}^+]_{\text{F}} \cdot (1 + [\text{SO}_4^{2-}]/K_{\text{S}})) \approx -\log([\text{H}^+]_{\text{F}} + [\text{HSO}_4^-])$
Seawater	$\text{pH}_{\text{SWS}} = -\log[\text{H}^+]_{\text{SWS}} = -\log([\text{H}^+]_{\text{F}} \cdot (1 + [\text{SO}_4^{2-}]/K_{\text{S}} + [\text{F}^-]/K_{\text{F}})) = -\log([\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}])$

ions. The first operational definition was the NBS pH scale (Bates and Vijh, 1973). NBS pH scale is defined by a series of standard buffer solutions with assigned pH values close to the best estimates of the proton activity (a_{H^+}), so that $\text{pH}_{\text{NBS}} = -\log a_{\text{H}^+}$. The reference state for pH_{NBS} scale is the indefinitely diluted solution, which is very useful in dilute natural waters such as rivers and lakes. However, this scale is not recommended for seawater because of its large ionic strength (Dickson, 1984; Millero et al., 1993).

In addition to the NBS pH scale, three other scales have been suggested for seawater, the free hydrogen ion scale (pH_{F}), the total hydrogen ion scale (pH_{T}) and the seawater scale (pH_{SWS}). The reason for the existence of four simultaneous pH scales is primarily historical. They reflect the gradual refinement of the experimentally determined pH in seawater. The definitions of the different scales are summarized in Table 1.

The free pH scale is conceptually the clearest being explicitly defined only by the H^+ concentration. The drawback is that the H^+ cannot be directly measured. This operational inconvenience is resolved with the total and seawater scales. The total pH scale (Hansson, 1973) accounts for the dissociation of HSO_4^- ion (including SO_4^{2-} in its calibration solutions), avoiding the definition of the HSO_4^- dissociation constant whose accurate value is difficult to obtain in seawater. The seawater scale (Dickson and Riley, 1979) includes besides bisulphate, the dissociation reaction for hydrogen fluoride. The differences between the total and the seawater scales thus arise from the fact whether the medium in which the scale is based includes fluoride or not. However, this difference is numerically small (about ~ 0.01 pH units at salinity 35) because the concentration of HSO_4^- is much larger than that of HF in the seawater. Contrarily, the pH reported on the free scale is about 0.11 and 0.12 pH units higher than on the total and the seawater scale (Zeebe and Wolf-Gladrow, 2001). These differences are much larger than the present precision achieved in the pH measurements, which is on the order of ± 0.0004 – 0.001 pH units (Clayton and Byrne, 1993).

Confusion may arise when the pH scale is not explicitly stated, and significant errors can be introduced in the calculation of the carbonic acid speciation because the first and second dissociation constant of H_2CO_3 are defined for a specific pH scale; thus, if the pH scale is ignored, serious errors in the $p\text{CO}_2$ calculation can occur that can reach $100 \mu\text{atm}$, specially whenever pH is a master variable of the carbonic system.

1.4 Methodology of pH measurements

Two analysis techniques are routinely used to get precise measurements of pH in seawater. These are potentiometric methods with electrodes, and spectrophotometric methods with an indicator.

The potentiometric method is based on the hydrogen ion sensitivity of an electrode (Dickson, 1993). It has fewer requirements on equipment, but is prone to problems due to electrode drift, susceptibility to electromagnetic interferences or problems with reference electrodes (Dickson, 1993). The accuracy of the measurement relies on the preparation of the calibration buffers. These, together with the precision of the temperature control, are common sources of biases/noise. The reproducibility of the potentiometric method is no better than ± 0.02 pH units (Dickson, 1993).

Spectrophotometric methods are based on the absorbance of a pH indicator, thus eliminating problems associated with buffer preparation and handling. Furthermore, errors due to poor temperature control can be partially reduced by using m-cresol (meta-cresol) as the indicator, since its pK value is centered in the typical range of the oceanic pH, and the temperature dependence follows that of pH along this range (Clayton and Byrne, 1993; Friis et al., 2004). The reproducibility with this method can reach to ± 0.0004 pH units (Clayton and Byrne, 1993).

2 Data

The pH data included in the CARINA dataset comes from a recompilation of cruise data from a multitude of international research groups until 2005. The data includes measurements obtained using both the potentiometric and spectrophotometric methods. Totalizing, CARINA dataset has pH data from 3761 stations on 59 cruises, resulting in 49 915 pH measurements. Figure 1 shows the location of the stations with pH data in CARINA (all ATL, SO and AMS datasets joined).

3 Conversions to pH SWS 25 °C

As a first step, all pH values were converted to the seawater scale at 25 °C (SWS 25). The conversion was done by using the CO2SYS (Lewis et al., 1998) routines converted to MATLAB code (van Heuven et al., 2009). This toolbox can be accessed at <http://cdiac.ornl.gov/oceans/co2rprt.html> and does all calculations needed to get the full solution of the

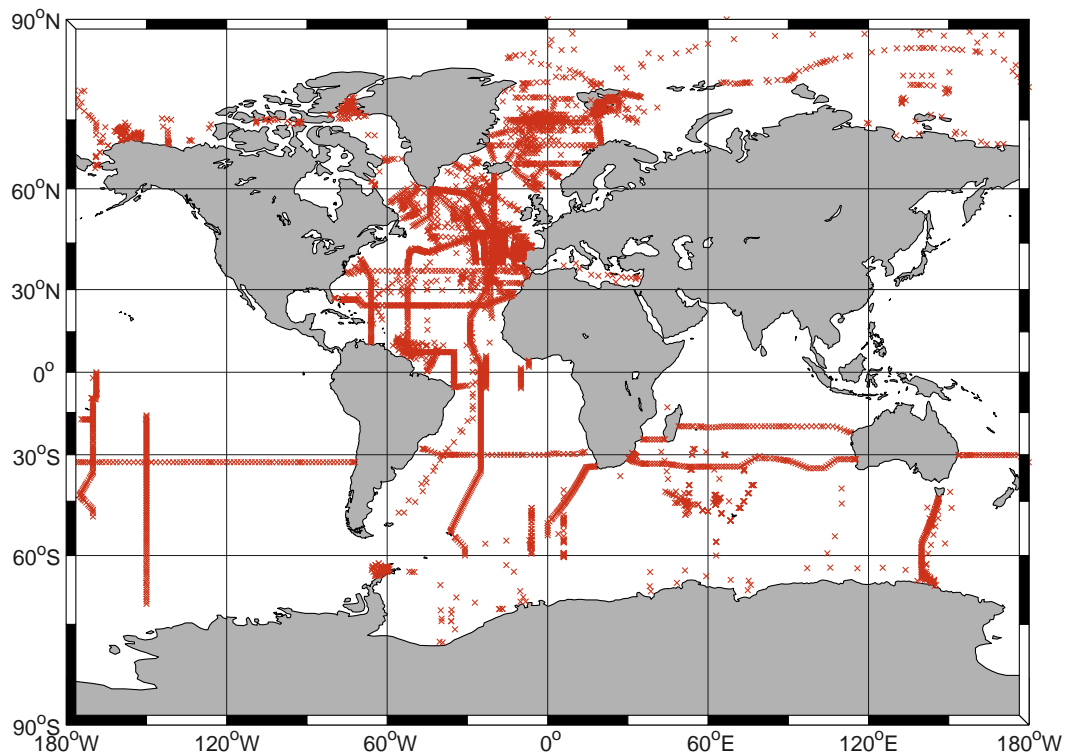


Figure 1. Map of stations with pH data in the full CARINA dataset (ATL, AMS and SO merged).

Table 2. Equations used by CO2SYS matlab software routines for conversion on pH scales. The routines use Total Scale internally for CO₂ calculations.

Equations used for pH scale conversion
$\text{pH}_T = \text{pH}_{\text{SWS}} - \log\left(\frac{1+S_T/K_S}{1+S_T/K_S+F_T/K_F}\right)$
$\text{pH}_T = \text{pH}_F - \log(1+S_T/K_S)$
$\text{pH}_T = \text{pH}_{\text{NBS}} - (\log(1+S_T/K_S) + \log(f_H))$

carbonate system in seawater. The code calculates the pH in all of the four scales used in seawater, and allows the user to choose which set of constants to use for the carbonate and sulfate systems.

Additional parameters required for these calculations are pressure, salinity, silicate, phosphate, and alkalinity. For the conversions, the following constants were used: Mehrbach refitted by Dickson and Millero (Dickson and Millero, 1987; Mehrbach et al., 1973) for carbonate, and Dickson (Dickson, 1990) for sulphate. The matlab routine converts all pH values to the total scale using the equations summarized in Table 2, which, in turn, are based on the definitions summarized in Table 1.

The next step taken by the CO2SYS routines is to calculate all four parameters of the CO₂ system (C_T, A_T, pH and

pCO₂) to the output temperature of 25 °C (still on the total scale). This is achieved by recalculating the constants, solving the system, and calculating the pH again.

As the last step, these values are used to calculate the pH on the other three scales. The output in pH_{SWS} is calculated from pH_T by reversing the first equation in Table 2:

$$\text{pH}_{\text{SWS}} = \text{pH}_T + \log\left(\frac{1 + \frac{S_T}{K_S}}{1 + \frac{S_T}{K_S} + \frac{F_T}{K_F}}\right) \quad (1)$$

Where: S_T is the Total Sulfate, calculated with the equations from Morris and Riley (1966), F_T is the Total Fluorine, calculated with the equations from Riley (1965), K_S is the bisulfate ion dissociation constant, from Dickson (1990), K_F is the hydrogen fluoride dissociation constant, from Dickson (1979), and f_H is the activity coefficient of hydrogen ion in seawater (Pérez and Fraga, 1987), calculated according to Takahashi et al. equations (1982).

Table 3 shows the cruises identified to be in a scale different than SWS at 25 °C. Original scale is noted in the second column and the reported temperature in the third.

4 Methods

The methods and techniques for the quality control are described in detail in the methods paper of this special issue (Tanhua et al., 2010). This secondary quality control (2nd

Table 3. Scale conversions. Note for cruise 165: Temperature specified for each sample, between 16.42 and 22.04 °C; Note for cruise 187: data quality low.

Cruise ID	Cruise Expocode	Scale	Temperature (°C)
3	06AQ19960712	T	15
20	06MT19990610	T	22
21	06MT19990711	T	22
23	06MT20010507	T	21
25	06MT20010717	T	21
30	06MT20030723	T	21
51	29CS19771007	NBS	15
52	29CS19930510	NBS	15
58	29HE19951203	NBS	15
59	29HE19960117	NBS	15
61	29HE20010305	T	25
62	29HE20020304	T	25
84	33LK19960415	T	in situ T/P
92	35A320010203	T	25
93	35A320010322	T	25
95	35LU19950909	T	in situ T/P
99	35MF19990104	T	in situ T
107	35TH20010823	T	25
108	35TH20020611	T	25
109	35TH20040604	T	25
110	49HH19941213	NBS	25
115	49ZS19921203	NBS	in situ T
119	58AA19950217	T	15
141	58JH19970414	T	15
142	58JH19980801	T	15
148	58LA19860719	T	25
160	74AB19910501	NBS	15
163	74AB20020301	T	25
165	74DI19890511	SWS	lab
172	74DI19980423	T	25
168	74DI19900425	NBS	25
170	74DI19900612	NBS	25
179	77DN20020420	T	15
182	90AV20041104	T	25
183	91AA19971204	T	15
187	OMEX1NA	NBS	in situ T

QC) starts after the unification of the pH data to SWS scale at 25 °C for all cruises. Next, an overview of the terminology is presented for improved readability.

- Crossover: Comparison of any parameter between a pair of cruises (A and B) located near or that cross each other. The comparison is done by station profiles.
- Offset: The numeric result of the crossover. Can be additive or multiplicative, and represents the quantity that cruise B data is biased (offset) from cruise A data. The crossover procedure returns also a statistical uncertainty for the offset.

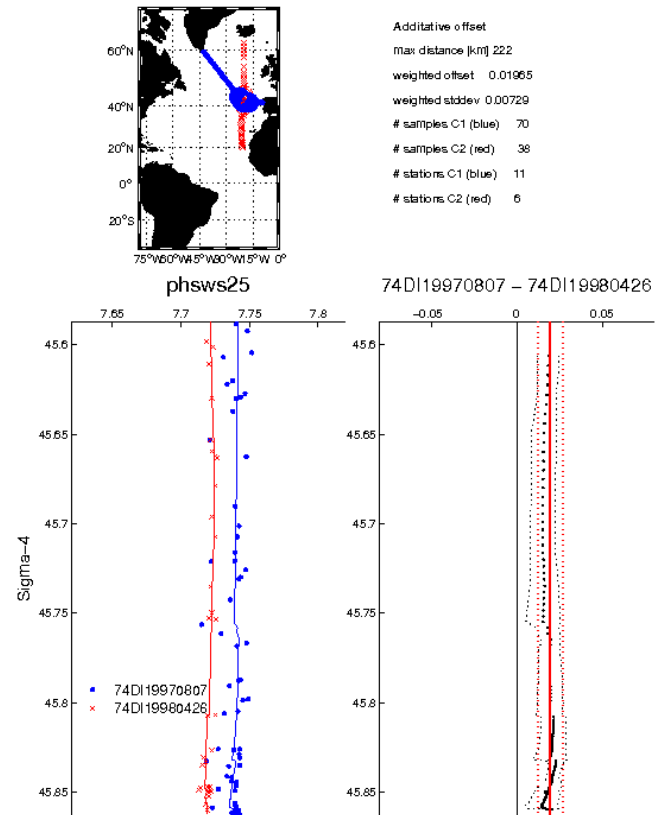


Figure 2. Crossover made with Running-Cluster Routines.

- Inversions: Weighted and Weighted Damped Least Squares (WLSQ and WDLSQ) procedure. It uses the collection of offsets and their uncertainties as input, and calculates the optimal corrections for the individual cruise files needed in order to minimize the offsets.
- Corrections: The value of correction for each cruise directly returned by the inversions.
- Minimum adjustment: Not all corrections proposed by the inversions were applied. A minimum threshold was defined for each parameter. Below this limit, no adjustment was performed.
- Adjustments: Final adjustment value applied to the cruise. The correction given by inversions was taken as reference, but manual supervision and agreement was done by the CARINA group for each adjustment.

4.1 Crossovers (offsets)

The secondary QC procedure starts with comparisons of data from pairs of cruises that are either co-located or “near” each other. Only data that were flagged “good” during the primary QC procedure (Key et al., 2010) were considered.

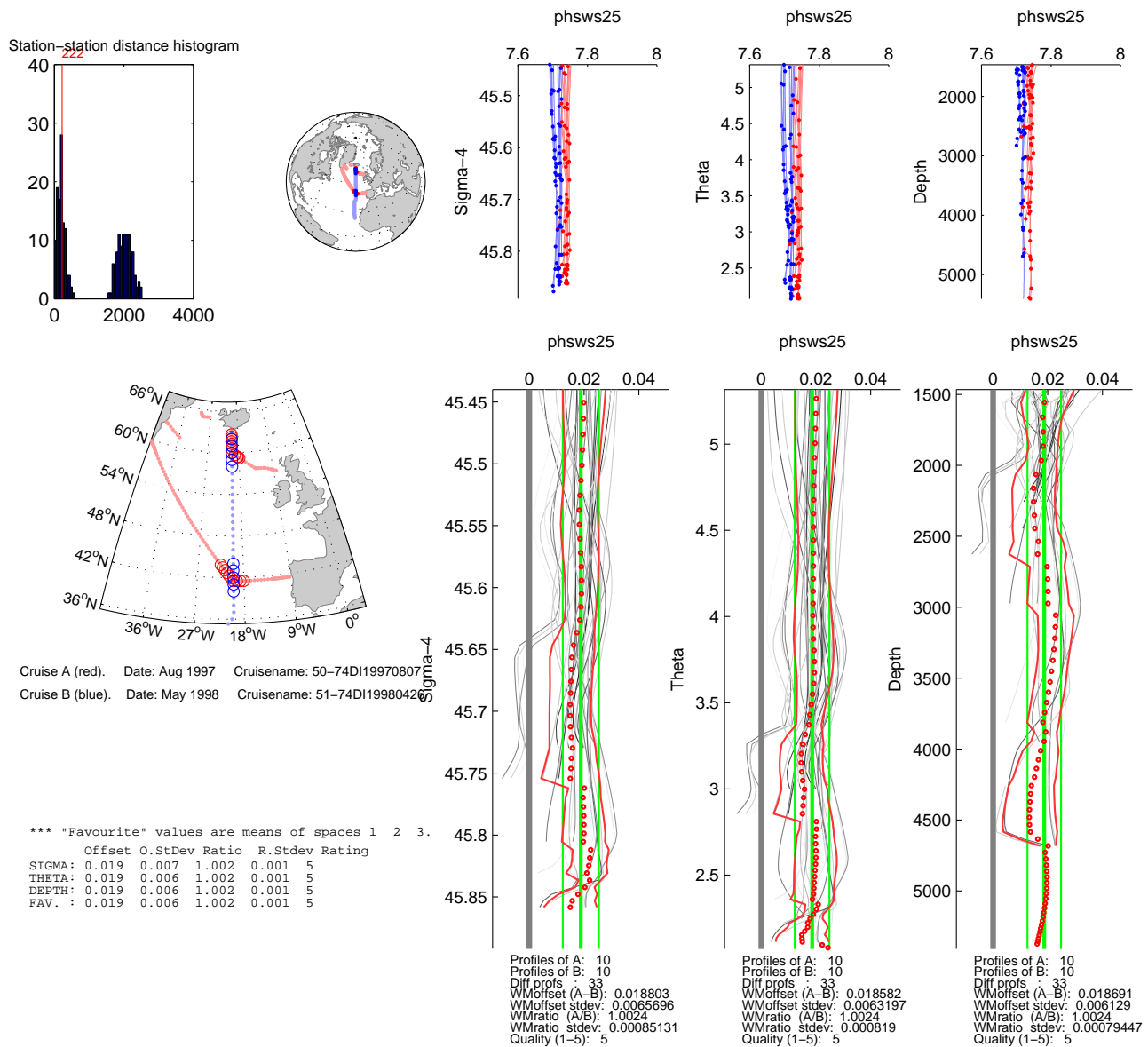


Figure 3. Crossover made with cnaX routines.

The application of various software packages (Tanhua et al., 2010) generated statistical and objective information about the differences between pairs of cruises, as well as the graphics needed to visually verify the computer determined differences. Each crossover analysis established the difference (i.e. the offset) between station profiles of two cruises that were located close to each other (2 degrees of Latitude was the typical distance). Only samples deeper than 1500 m were considered. The code returned the value of the offset as well as its uncertainty, and the number of contributing stations and samples.

In this work, manual, running-cluster and cnaX crossover procedures were applied on all possible pairs of CARINA cruises. Next, the crossover results were visually inspected in

order to ensure quality. Only “good” quality crossovers were selected, and those results were used for subsequent cruise correction calculations. Good crossovers were the ones with enough samples to produce reasonably uniform data profiles over the entire area included in the crossover. As additive offsets were being used for pH analysis, care was taken to verify that the profiles of both cruises flowed in parallel, so that the offset could be determined. Uncertainty as standard deviation was also used to provide more information about crossover quality.

In Figs. 2 and 3, two examples of pH crossovers are shown; Fig. 2 was produced by Running Cluster routines, and Fig. 3 was produced by cnaX routines (Tanhua et al., 2010).

4.2 Inversions (cruise corrections)

A weighted damped least squares inversion procedure (WDLSQ) was applied to the collection of accepted crossover offsets and their uncertainties, to get the the solution of cruise corrections that would minimize the offsets (Gouretski and Jancke, 2001; Johnson et al., 2001). Uncertainties were used as weighting factors or data covariance matrix in this procedure. In order to ensure the highest quality results from the inversion and to get a more accurate and consistent solution, a small subset of cruises were a priori defined as “core”, giving to them a weighting factor of 2 in the inversion. 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 that involve “core” cruises received a higher weighting (double if only one cruise is “core”, and four times if both are “core”) in the inversion (Tanhua et al., 2010).

A second round of quality control was carried out by calculating pH from C_T and A_T for cruises with no pH measured, and including them into the crossover and inversion procedures. This was done to improve the confidence of corrections for cruises without so many crossovers, as pH data are sparse in some areas. An accuracy of ± 0.006 in calculated pH is accomplished from typical accuracies in on-boat measurement analysis of $\pm 3\text{--}4\ \mu\text{mol kg}^{-1}$ in A_T and $\pm 2\ \mu\text{mol kg}^{-1}$ in C_T (Millero, 2007; Zeebe and Wolf-Gladrow, 2001). The expected error in CARINA dataset is about $\pm 6\ \mu\text{mol kg}^{-1}$ in A_T and $\pm 4\ \mu\text{mol kg}^{-1}$ in C_T , so calculated pH accuracy could be lower than ± 0.006 here.

A total of 217 crossovers were used as input for the inversion procedure when using only measured pH data, and 311 when using also calculated pH from A_T and C_T .

Figure 4 shows the pH offsets for all individual crossovers before any adjustment (red dots), and after applying the full inversion solution to all cruises (i.e. all the corrections). As can be shown, after applying the corrections, the offsets are lower, and most of them fit between the ± 0.005 pH units boundary.

4.3 Adjustments

A minimum threshold of 0.005 pH units was defined and only corrections greater than this value has been taken into account by the CARINA group to decide the final adjustments for the cruises.

Corrections proposed by WDLSQ inversion of running-cluster, cnaX and manual crossover offsets have been analyzed by the CARINA group to get an agreement upon the value of adjustment proposed and applied to the cruises.

4.4 Quality control

Once the adjustments were determined and applied for all analyzed parameters, a final crossover and inversion analysis

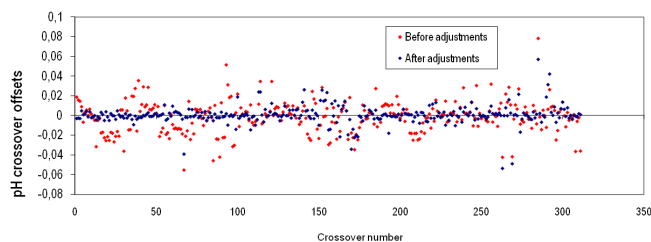


Figure 4. Crossover pH offsets obtained with original database and after adjustments were applied.

was performed for all cruises in CARINA database. Some additional regression analyses and statistical checks were also done in order to ensure the consistency of cruise data within their region and the internal consistency of carbon parameters. During this analysis, two Nordic Seas cruises, not previously adjusted by the crossover exercise because of too few data, evidently needed adjustments based on regional consistency and internal carbon consistency, so adjustments were calculated and applied to these data.

5 Assessment of applied adjustments

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

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

- Green dots: “Offsets”. These values are the offsets taken directly from each selected crossover. The standard deviation is shown as error bars on these dots. Mixed crossovers from running-cluster, cnaX, and manual crossovers have been used here
- Yellow line indicates the additive correction for the cruise calculated by WDLSQ inversion. Note that the correction and offsets are of opposite sign.
- Black stars indicate the correction calculated by WDLSQ inversion 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.

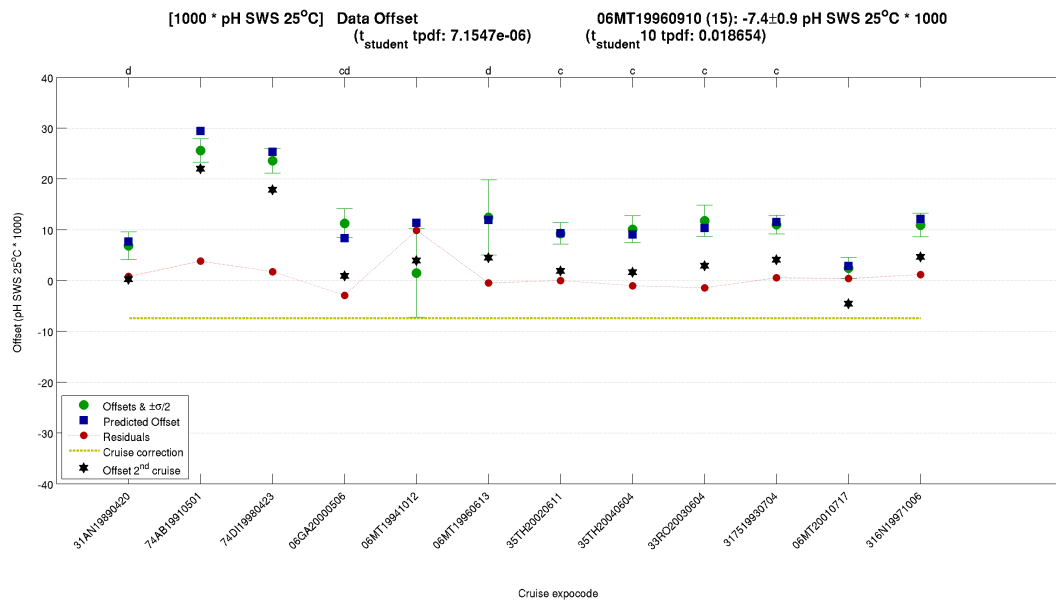


Figure 5. Cruise crossover information plot for 06MT19960910 (15).

- d suffix in the upper x-axis labels stands for cruises with pH derived from A_T and C_T .

5.1 Cruise 06MT19960910 (15) (Fig. 5)

This is the so called M36/5 cruise, carried out on board R/V Meteor, in the North Atlantic. It has 62 stations sampled with a 24 position rosette system. The cruise has 12 crossovers. The inversion suggests a correction of -0.007 ± 0.001 . Except one, all residuals are very low and fit inside ± 0.003 after the full solution of the inversion is applied. Very good fit exists with 5 core cruises. Based on this evidence, an adjustment of -0.007 was applied to the pH data.

5.2 Cruise 06MT20010507 (23) (Fig. 6)

This is leg 1 of the experiment called SFB460 (M50/1), carried out on board R/V Meteor in the subpolar North Atlantic. It has 53 stations sampled with a 24 position rosette system. The analysis of pH was done using spectrophotometric method with precision of ± 0.002 . Original data were reported on the Total pH scale at 21°C . The cruise has 7 crossovers. The inversion suggests a correction of -0.008 ± 0.005 . Except for two crossovers, all residuals are very low and fit inside ± 0.005 after the full solution of the inversion is applied. Very good fit also exists with two core cruises. Based on this evidence, an adjustment of -0.008 was applied to the pH data.

5.3 Cruise 06MT20010717 (25) (Fig. 7)

This is leg 4 of the experiment called SFB460 (M50/4), carried out on board R/V Meteor in the North Atlantic. It has

139 stations sampled with a 22 position rosette system. The analysis of pH was done using spectrophotometric method with precision of ± 0.002 and a standard deviation of replicates of ± 0.0009 , given an estimated uncertainty of ± 0.002 . Original data were reported on the Total pH scale at 21°C . The cruise has 16 crossovers. The inversion suggests a correction of -0.005 ± 0.001 . Except for two crossovers, all residuals are very low and fit inside ± 0.003 after the full solution of the inversion is applied. Very good fit exists with four core cruises and two GLODAP cruises (317519930704 and 06MT20030723). Based on this evidence, an adjustment of -0.005 was applied to the pH data.

5.4 Cruise 29CS19930510 (52) (Fig. 8)

This cruise is called MORENA-I, carried out on board R/V Cornide de Saavedra. It is a cruise along WOCE line AR16e. It has 92 stations sampled with a 24 position rosette system. Original data were reported on the NBS pH scale at 15°C . The cruise has 8 crossovers. The inversion suggests a correction of 0.017 ± 0.001 . All residuals are very low and fit inside ± 0.002 after the full solution of the inversion is applied. Very good fit also exists with three core cruises. Based on this evidence, an adjustment of 0.017 was applied to the pH data.

5.5 Cruise 29GD19821110 (53) (Fig. 9)

This is the so called GALICIA-V cruise, carried out on board R/V Garcia del Cid on Atlantic close to NW of Spain. It has 19 stations sampled on hydrocasts with 5L Niskin bottles. The analysis of pH was done using potentiometric method

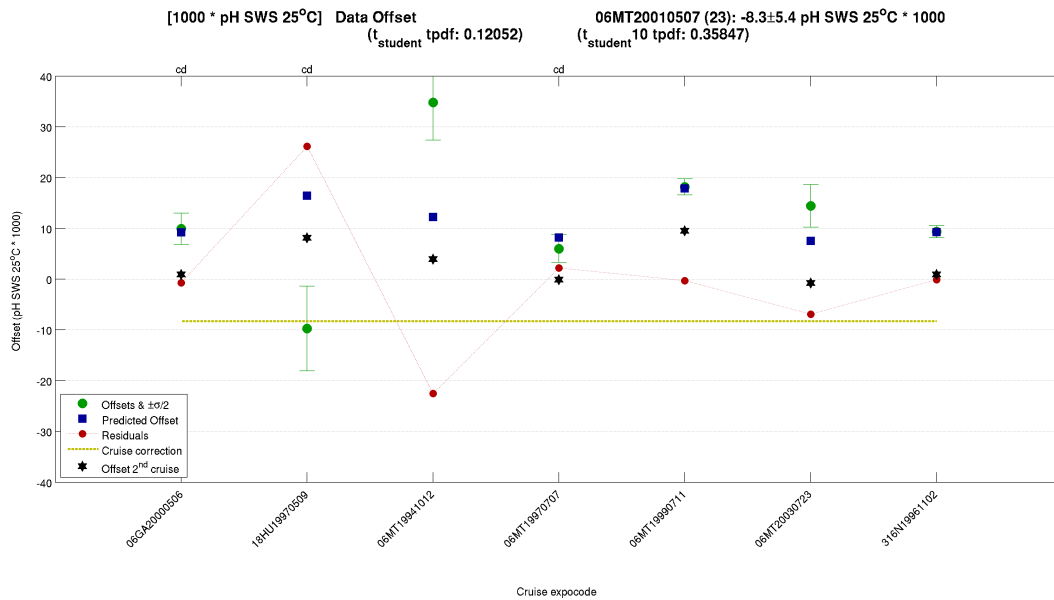


Figure 6. Cruise crossover information plot for 06MT20010507 (23).

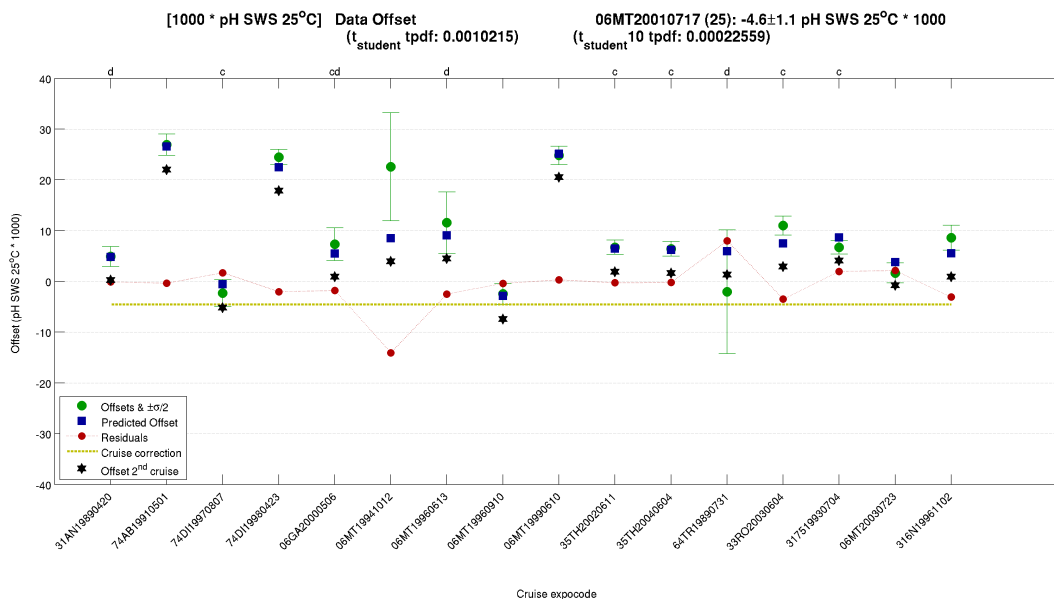


Figure 7. Cruise crossover information plot for 06MT20010717 (25).

with a glass electrode. The claimed accuracy is 0.003. The cruise has 7 crossovers. The inversion suggests a correction of 0.024 ± 0.002 . Except one, all residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Good fit exits with 3 core cruises. Based on this evidence, an adjustment of 0.024 was applied to the pH data.

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

This is the so called GALICIA-VII cruise, carried out on board R/V Garcia del Cid on Atlantic close to NW of Spain. It has 33 stations sampled on hydrocasts with 1.7L Niskin bottles. The analysis of pH was done using potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 8 crossovers. The inversion suggests a correction of 0.023 ± 0.001 . All residuals are low and fit inside ± 0.002 after the full solution of the inversion is applied.

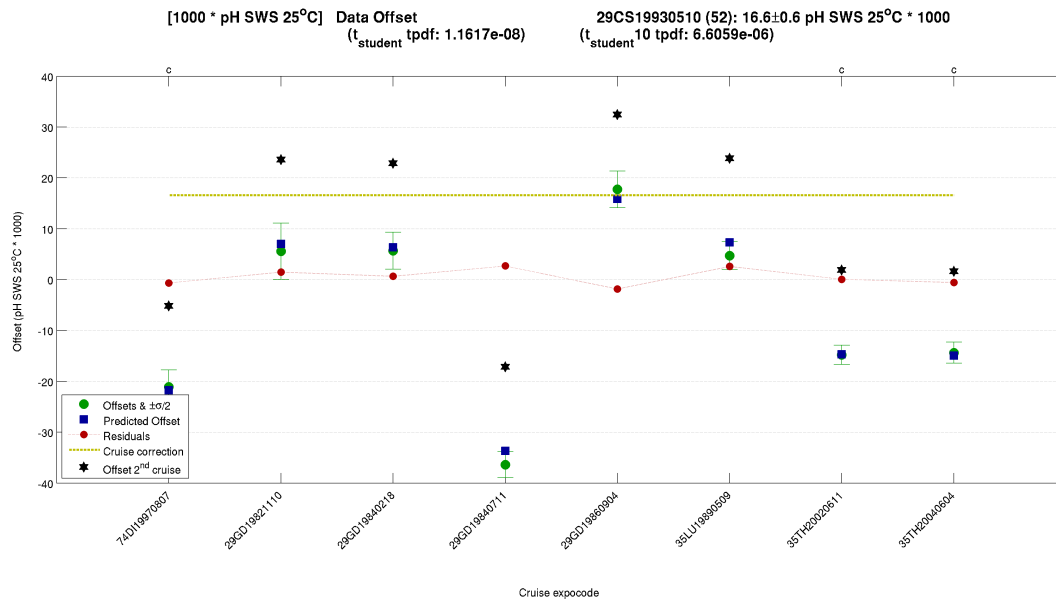


Figure 8. Cruise crossover information plot for 29CS19930510 (52).

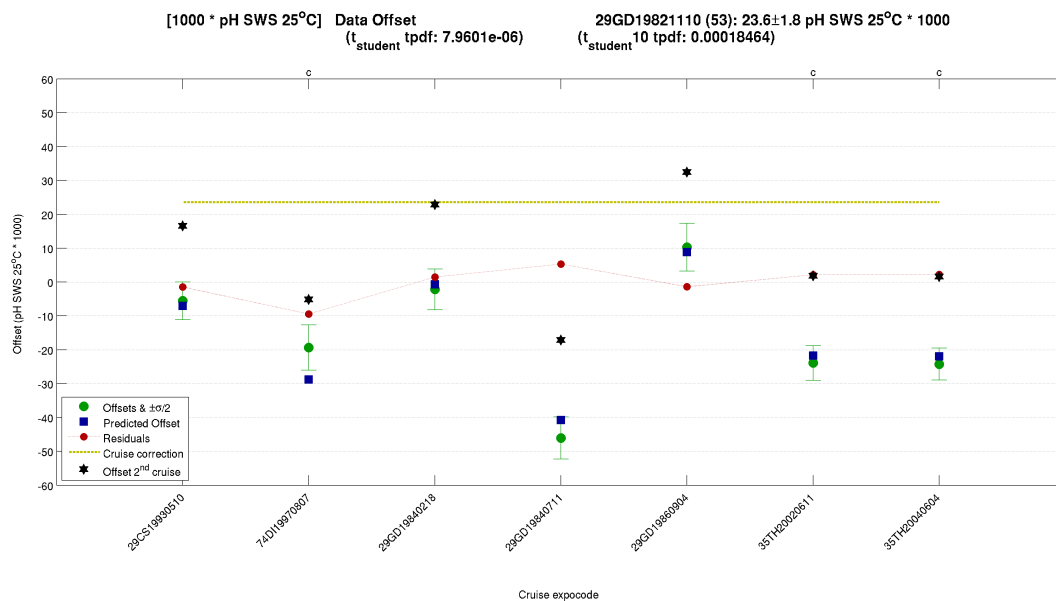


Figure 9. Cruise crossover information plot for 29GD19821110 (53).

Good fit exists with 3 core cruises. Based on this evidence, an adjustment of 0.023 was applied to the pH data.

5.7 Cruise 29GD19840711 (56) (Fig. 11)

This is the so called GALICIA-VIII cruise, carried out on board R/V Garcia del Cid on Atlantic close to NW of Spain. It has 118 stations sampled on hydrocasts with 1.7L Niskin bottles. The analysis of pH was done using potentiometric method with a glass electrode. The claimed accuracy is

0.003. The cruise has 8 crossovers. The inversion suggests a correction of -0.017 ± 0.002 . Except one, all residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Good fit also exists with 3 core cruises. Based on this evidence, an adjustment of -0.017 was applied to the pH data.

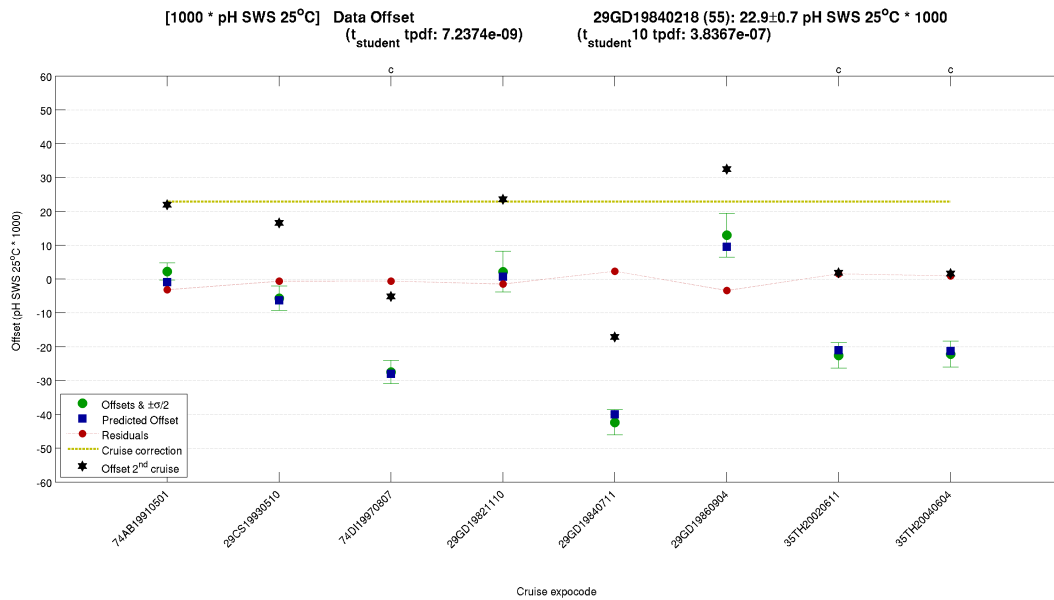


Figure 10. Cruise crossover information plot for 29GD19840218 (55).

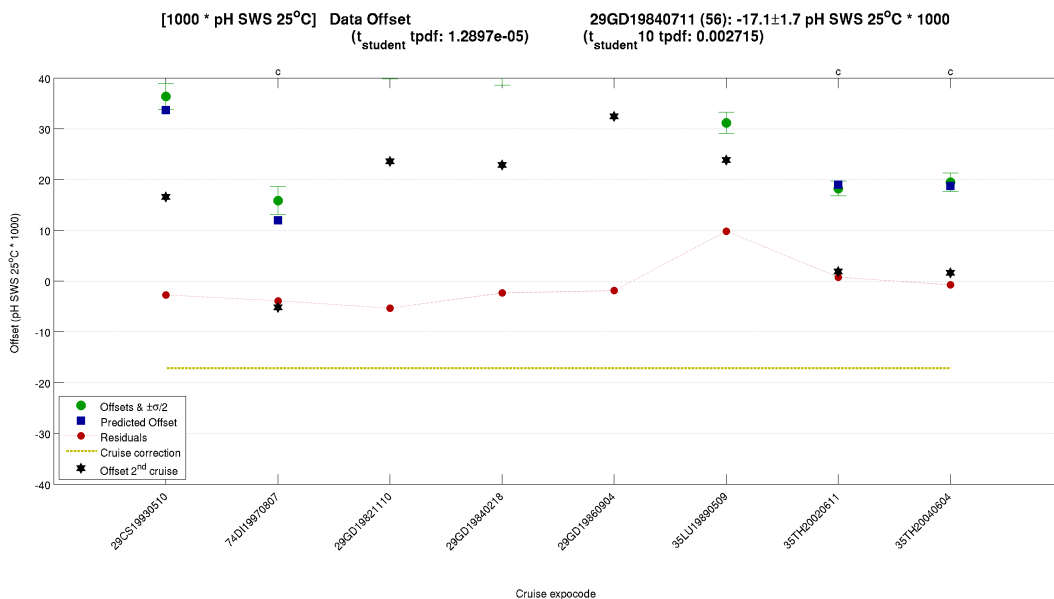


Figure 11. Cruise crossover information plot for 29GD19840711 (56).

5.8 Cruise 29GD19860904 (57) (Fig. 12)

This is the so called GALICIA-IX cruise, carried out on board R/V Garcia del Cid on Atlantic close to NW of Spain. It has 50 stations sampled on hydrocasts with 1.7L Niskin bottles. The analysis of pH was done using potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 7 crossovers. The inversion suggests a correction of 0.032 ± 0.001 . All residuals are very low and fit inside ± 0.005 after the full solution of the inversion is ap-

plied. Very good fit also exists with 3 core cruises. Based on this evidence, an adjustment of 0.032 was applied to the pH data.

5.9 Cruise 29HE20010305 (61) (Fig. 13)

This is the so called FICARAM II cruise, carried out on board R/V Hesperides along WOCE section A17 in the western South Atlantic. It has 29 full depth stations sampled with a 24 position rosette system. The analysis of pH was

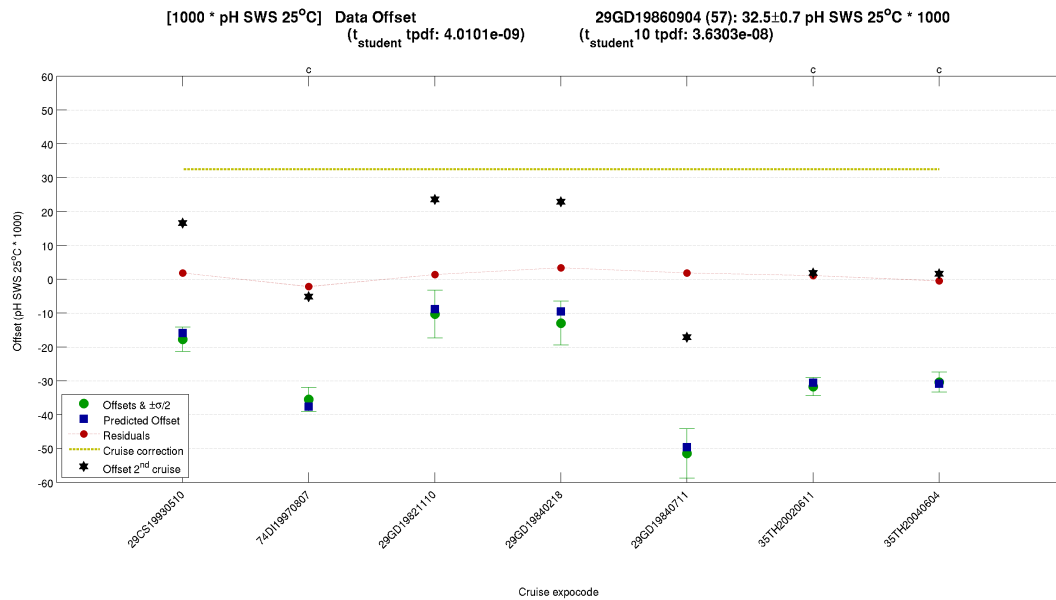


Figure 12. Cruise crossover information plot for 29GD19860904 (57).

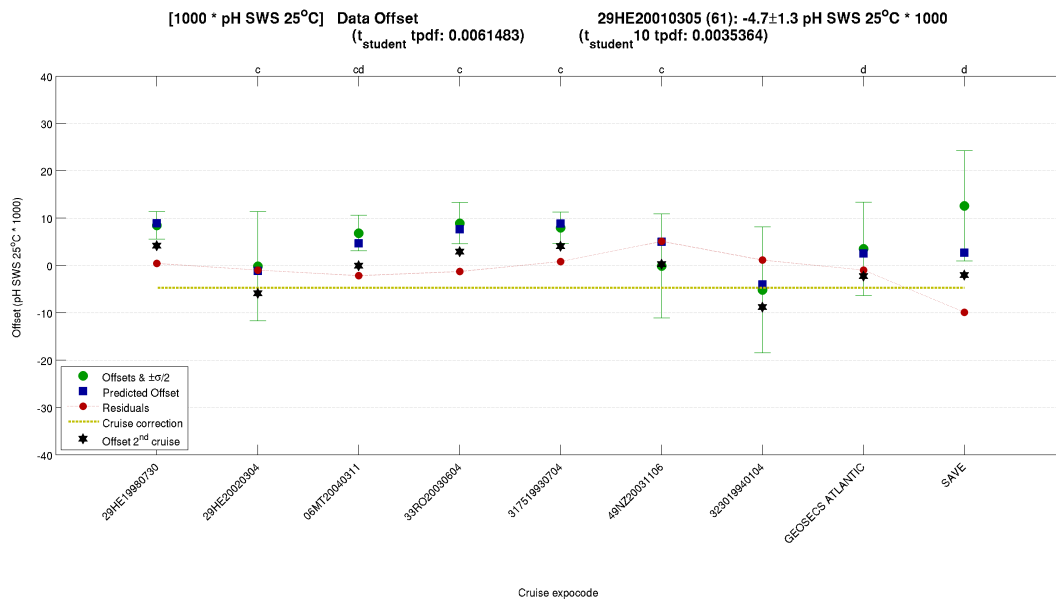


Figure 13. Cruise crossover information plot for 29HE20010305 (61).

done using spectrophotometric method. CRM batch 41 and 51 were used, with an uncertainty of 0.002. Original data were reported on the Total pH scale at 25 °C. The cruise has 9 crossovers. The inversion suggests a correction of $+0.005 \pm 0.001$. Except one, all residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Very good fit also exists with 5 core cruises. Based on this evidence, an adjustment of $+0.005$ was applied to the pH data.

5.10 Cruise 33LK19960415 (84) (Fig. 14)

This is the so called ETAMBOT2 cruise, carried out on board R/V Edwin Link along WOCE section AR04h, in the west equatorial Atlantic, near Brazil. It has 94 stations sampled with a 24 position rosette system. The analysis of pH was done using the potentiometric method with a standard deviation of replicates of 0.003. Original data were reported on the Total pH scale at in-situ conditions of temperature and pressure. Data were measured at 25 °C.

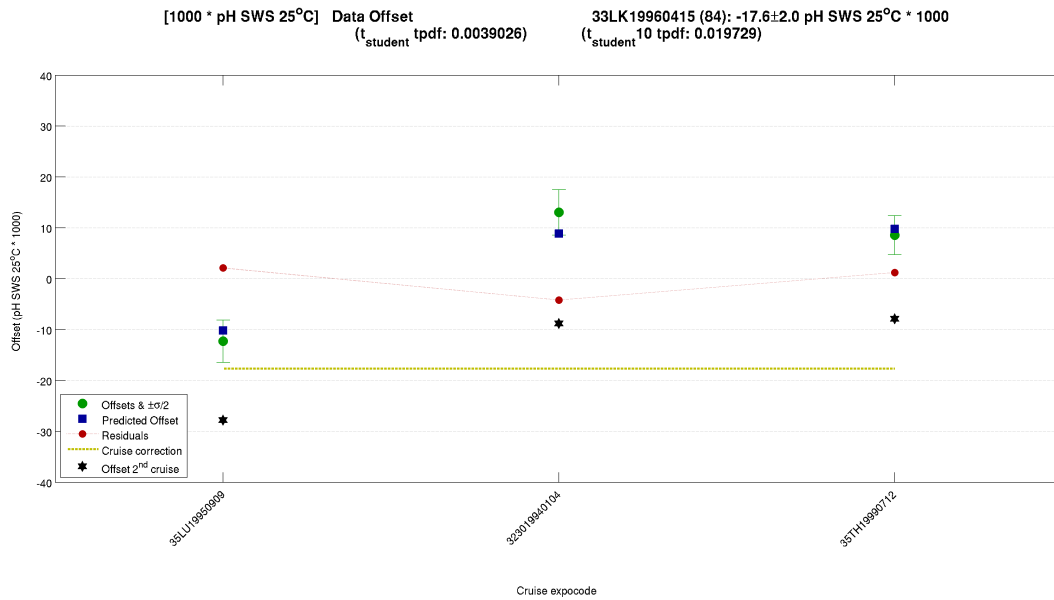


Figure 14. Cruise crossover information plot for 33LK19960415 (84).

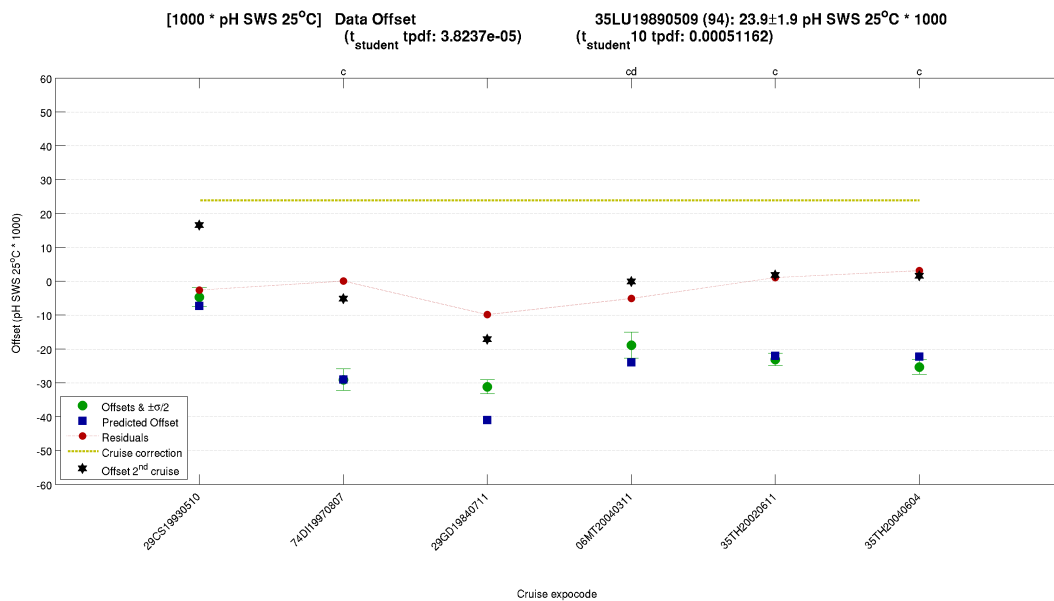


Figure 15. Cruise crossover information plot for 35LU19890509 (94).

The cruise has 3 crossovers. The inversion suggests a correction of -0.018 ± 0.003 . All residuals are very low and fit inside ± 0.005 after the full solution of the inversion is applied. Good fit also exists with one GLODAP cruise (323019940104). Based on this evidence, an adjustment of -0.018 was applied to the pH data.

5.11 Cruise 35LU19890509 (94) (Fig. 15)

This is the so called BORDEST-3 cruise carried out on board R/V “Le Noroit”, on a rectangular grid in the Atlantic west of the Iberian Peninsula. It has 47 full depth stations sampled with a rosette system. The cruise has 6 crossovers. The inversion suggests a correction of 0.024 ± 0.002 . Very good fit also exists with 4 core cruises. Based on this evidence, an adjustment of 0.024 was applied to the pH data.

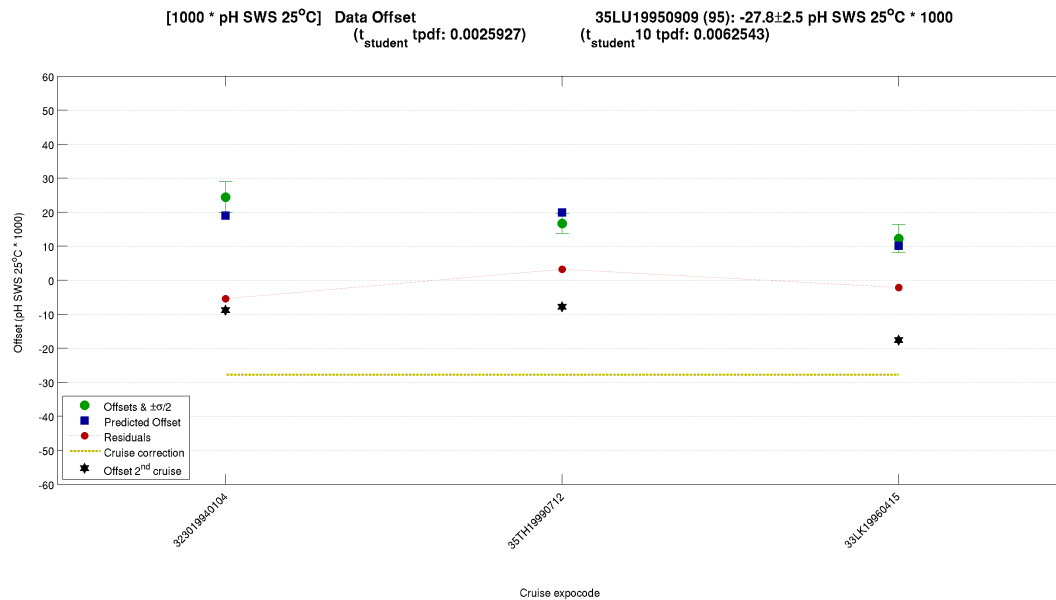


Figure 16. Cruise crossover information plot for 35LU19950909 (95).

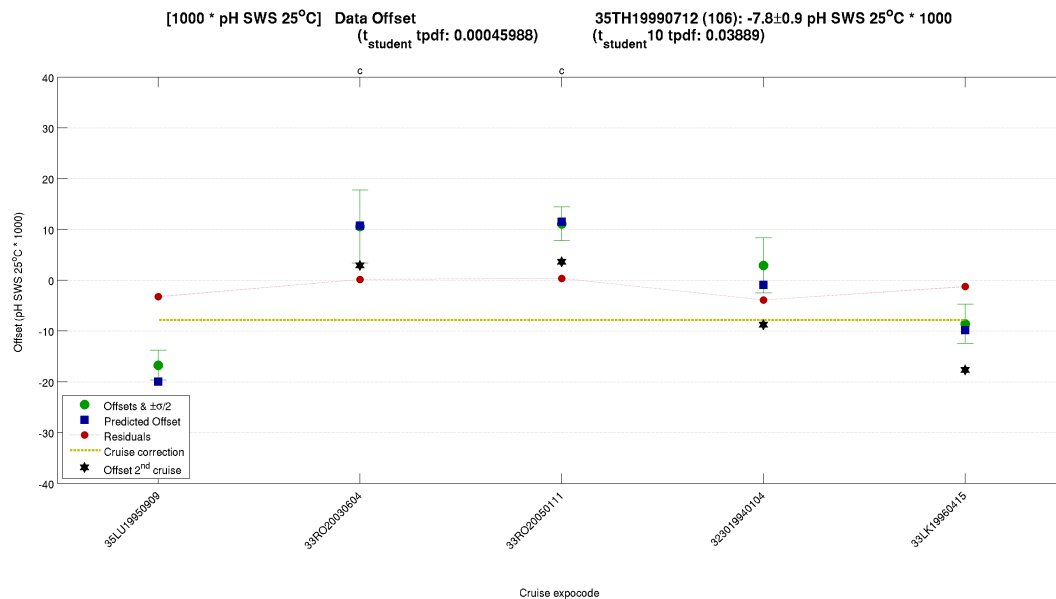


Figure 17. Cruise crossover information plot for 35TH19990712 (106).

5.12 Cruise 35LU19950909 (95) (Fig. 16)

This is the so called ETAMBOT1 cruise, carried out on board R/V “Le Noroit” along WOCE section AR04g, in the western equatorial Atlantic, near Brazil. It has 85 full depth stations sampled with a 24 position rosette system. The analyses of pH were done using the potentiometric method with a standard deviation of replicates of 0.002. Original data were reported on the Total pH scale at in-situ conditions for temperature and pressure. Data were measured at 25 °C. The

cruise has 3 crossovers. The inversion suggests a correction of -0.028 ± 0.003 . All residuals are very low and fit inside ± 0.005 after the full solution of the inversion is applied. Based on this evidence, an adjustment of -0.028 was applied to the pH data.

5.13 Cruise 35TH19990712 (106) (Fig. 17)

This is the so called EQUALANT99 cruise, carried out on board R/V “Thalassa” in the equatorial Atlantic. It has 102

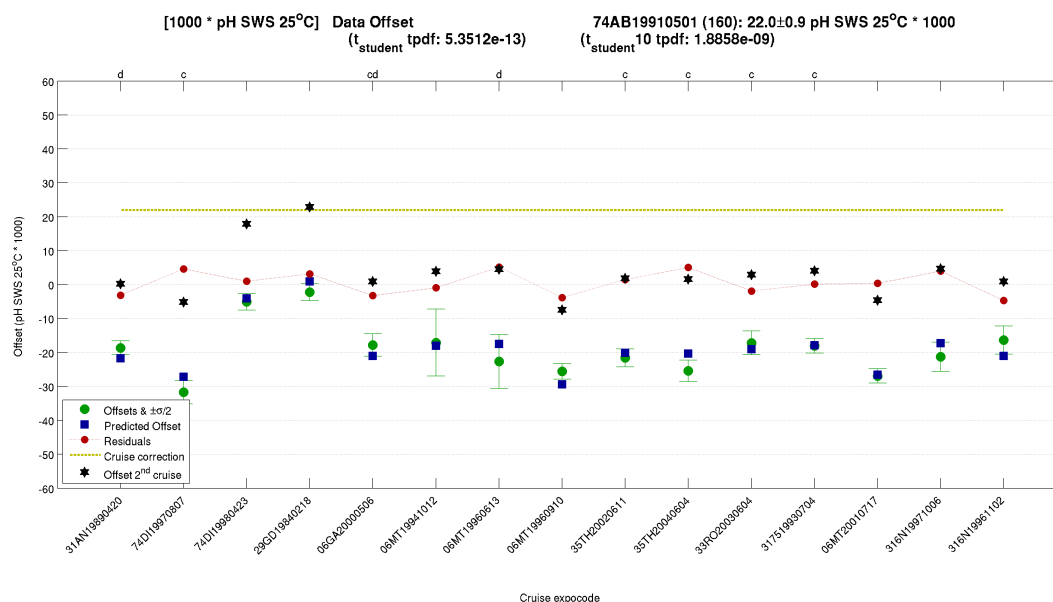


Figure 18. Cruise crossover information plot for 74AB19910501 (160).

stations sampled with a 24 position rosette system. The analysis of pH was done using the potentiometric method with a standard deviation of replicates of 0.003. Original data were reported on the Total pH scale at in-situ conditions of temperature and pressure. Samples were measured at 25 °C. The cruise has 5 crossovers. The inversion suggests a correction of -0.008 ± 0.001 . All residuals are very low and fit inside ± 0.003 after the full solution of the inversion is applied. Very good fit also exists with two GLODAP cruises (33RO20030604 and 33RO20030111). Based on this evidence, an adjustment of -0.008 was applied to the pH data.

5.14 Cruise 58AA19950217 (119)

This is the so called 58AA9502 cruise carried out on board R/V Haakon Mosby in the Nordic Seas. It has 34 stations sampled with a 12 position rosette system. The analysis of pH was done using spectrophotometric method, with a reported accuracy of ± 0.002 and a precision of 0.001. The analysis of the data showed that the scatter on pH is high. The cruise has only a few pH data, so decision here was to flag the measured pH data as questionable, and not include them in the data product.

5.15 Cruise 58JH19970414 (141)

This is the so called 58JH9704 cruise, carried out on board R/V “Johan Hjort” in the Nordic Seas. It has 135 stations sampled with a 12 position rosette system. The analysis of pH was done using spectrophotometric method. Original data were reported on the Total pH scale at 15 °C. Not enough crossovers with other cruises were found to support

an adjustment, but a comparison with Greenland Sea deep waters suggested a need of a correction of $+0.025$. Comparison with pH calculated from adjusted A_T and C_T supports this adjustment, and so does the MLR analysis (see below). Based on this evidence, an adjustment of 0.025 was applied to the pH data.

5.16 Cruise 58JH19980801 (142)

This is the so called 58JH9808 cruise, carried out on board R/V “Johan Hjort” in the Nordic Seas. It has 49 stations sampled with a 12 position rosette system. The analysis of pH was done using spectrophotometric method, with a reported precision of about ~ 0.005 pH units. Original data were reported on the Total pH scale at 15 °C. Not enough crossovers with other cruises were found to support an adjustment, but a comparison with Greenland Sea deep waters suggested a need of a correction of $+0.020$. Intercomparison with pH calculated from adjusted A_T and C_T supports this adjustment, and so does the MLR analysis (see below). Based on this evidence, an adjustment of 0.020 was applied to the pH data.

5.17 Cruise 74AB19910501 (160) (Fig. 18)

This cruise is the so called Vivaldi expedition, carried out on board R/V Charles Darwin. It has 614 stations, from which only 34 are deep stations. The stations were sampled with a 24 position rosette system. Original data were reported on the NBS pH scale at 15 °C. This cruise has 15 crossovers, and the inversion suggests a correction of 0.022 ± 0.001 . All residuals after the full solution of the inversion have been applied are very low and fit

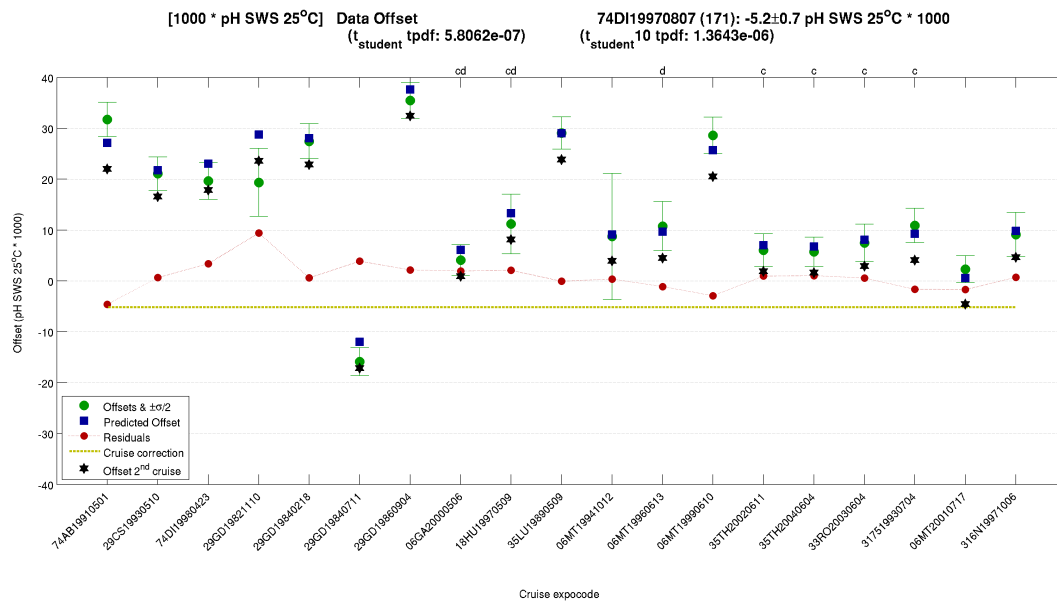


Figure 19. Cruise crossover information plot for 74DI19970807 (171).

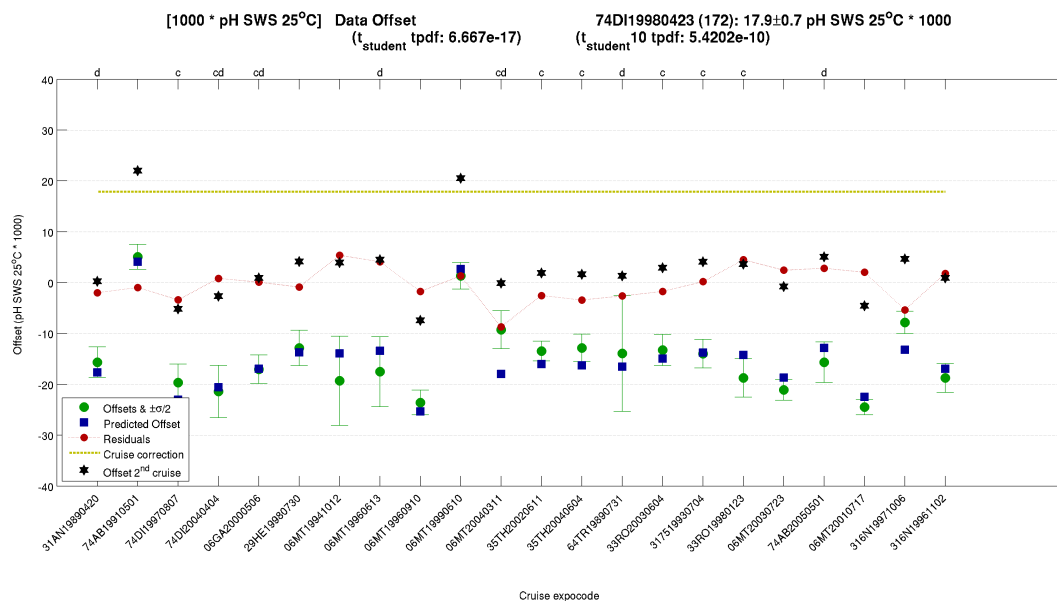


Figure 20. Cruise crossover information plot for 74DI19980423 (172).

inside ± 0.005 . Very good fit also exists with 5 GLODAP cruises (74DI19970807, 06MT19941012, 317519930704, 316N19971006 and 316N19961102). Based on this evidence, an adjustment of 0.022 was applied to the pH data.

5.18 Cruise 74DI19970807 (171) (Fig. 19)

This is the so called FOUREX cruise (IGY section Four Repeat Experiment), carried out on board R/V Discovery, along the WOCE leg A25. It has 143 full depth stations. The cruise

has 19 crossovers. The inversion suggests a correction of -0.005 ± 0.001 . Except one, all residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Very good fit also exists with 6 core cruises. Based on this evidence, an adjustment of -0.005 was applied to the pH data.

5.19 Cruise 74DI19980423 (172) (Fig. 20)

This is a cruise on a meridional section along 20° W from 20° N to 65° N, carried out on board R/V Discovery. It has

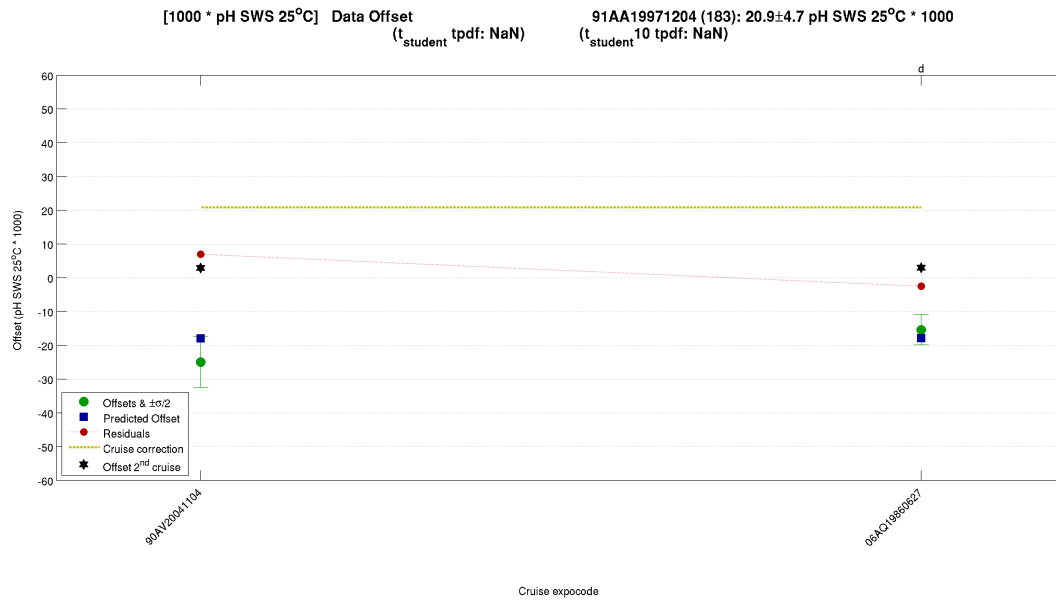


Figure 21. Cruise crossover information plot for 91AA19971204 (183).

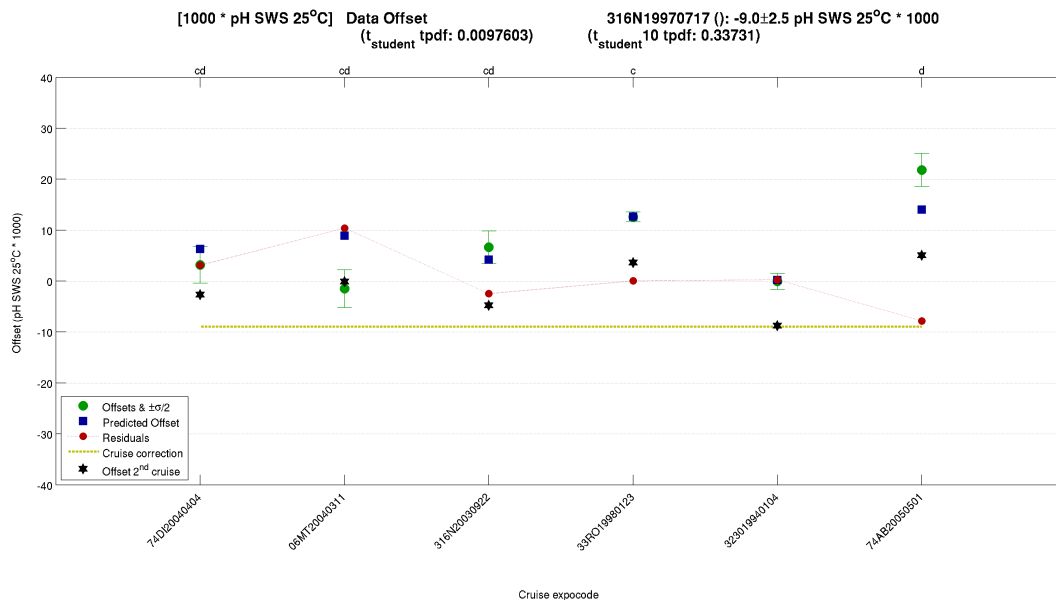


Figure 22. Cruise crossover information plot for 316N19970717.

44 full depth stations sampled with a 24 position rosette system. The cruise has 22 crossovers. The inversion suggests a correction of 0.018 ± 0.001 . Except two, all residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Good fit also exists with 8 core cruises. Based on this evidence, an adjustment of 0.018 was applied to the pH data.

5.20 Cruise 91AA19971204 (183) (Fig. 21)

This is the so called SWEDARP 1997 expedition, carried out on board S.A Agulhas on a meridional section along 6° E , with 40 stations. The analysis of pH was done using spectrophotometric method. Original data were reported on the Total pH scale at 15° C . The cruise has only 2 crossovers. The inversion suggests a correction of 0.021 ± 0.005 . All residuals fit inside ± 0.010 after the full solution of the inversion is applied. Based on this evidence, an adjustment of 0.021 was applied to the pH data.

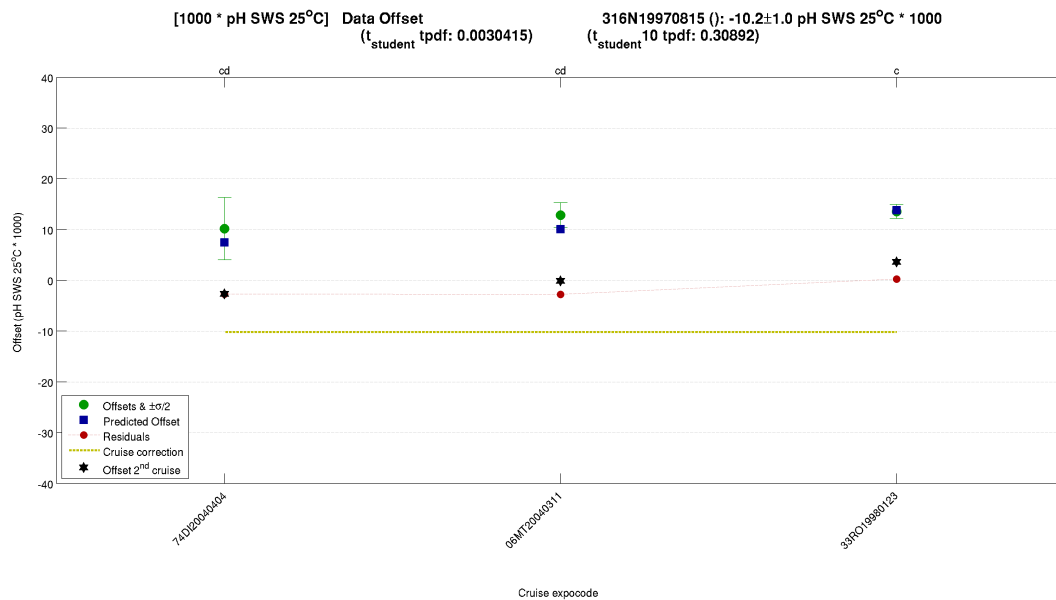


Figure 23. Cruise crossover information plot for 316N19970815.

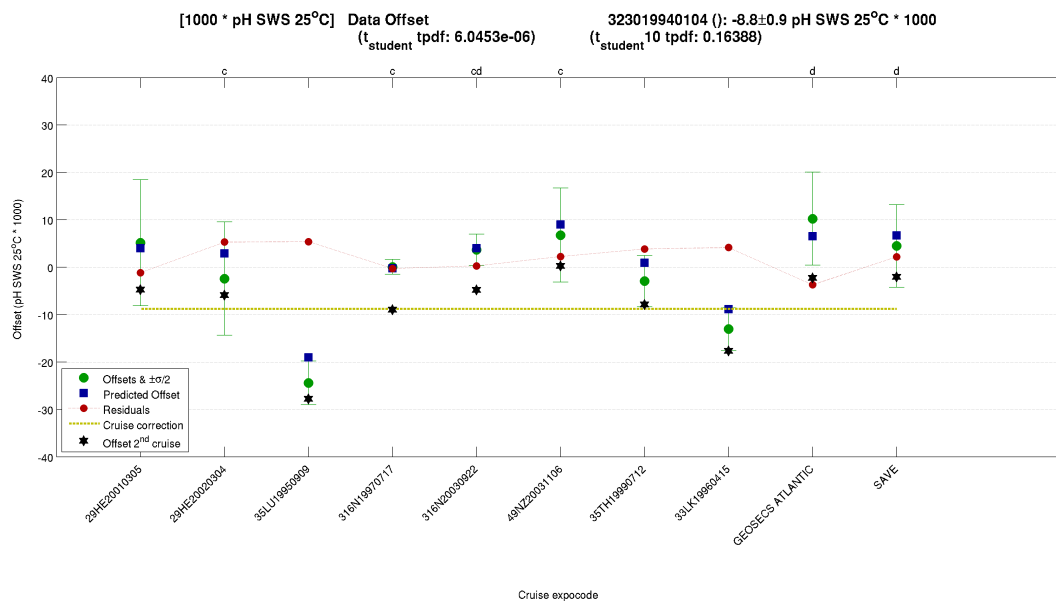


Figure 24. Cruise crossover information plot for 323019940104.

5.21 Cruise 316N19970717 (Fig. 22)

This is a cruise carried out on board R/V Knorr along WOCE section A20 in the North Atlantic. It has 95 stations sampled with a 36 position rosette system. The analysis of pH was done using the potentiometric method. CRM batch 33, 36 and 37 were used. The cruise has 6 crossovers. The inversion suggests a correction of -0.009 ± 0.003 . Except two, all residuals are very low and fit inside ± 0.005 after the full solution of the inversion is applied. Very good fit also exists with

two GLODAP cruises (32019940104 and 33RO19980123). Based on this evidence, an adjustment of -0.009 was applied to the pH data.

5.22 Cruise 316N19970815 (Fig. 23)

This is a cruise carried out on board R/V Knorr along WOCE section A22 in the North Atlantic. It has 7 stations sampled with a 36 position rosette system. The analysis of pH was done using the potentiometric method. CRM batch 33, 36



Figure 25. Cruise crossover information plot for 90MS19811009.

and 37 were used. The cruise has 3 crossovers. The inversion suggests a correction of -0.010 ± 0.001 . Very good fit also exists with two core cruises and one GLODAP cruise (33RO19980123). Based on this evidence, an adjustment of -0.010 was applied to the pH data.

5.23 Cruise 323019940104 (Fig. 24)

This is the so called CITHER 2 cruise carried out on board R/V Maurice Ewing, along WOCE section A17 in the western South Atlantic. It has 235 stations sampled with a 32 position rosette system. The analysis of pH was done using potentiometric method with stated overall precision of ± 0.003 . Original data were reported on the NBS scale at 15°C . The cruise has 10 crossovers. The inversion suggests a correction of -0.009 ± 0.001 . All residuals are low and fit inside ± 0.005 after the full solution of the inversion is applied. Very good fit also exists with 3 GLODAP cruises (316N19970717, GEOSECS_ATLANTIC and SAVE). Based on this evidence, an adjustment of -0.009 was applied to the pH data.

5.24 Cruise 90MS19811009 (Fig. 25)

This is the so called Weddell Polynya Expedition 81 (WE-POLEX 81) cruise carried out on board R/V Mikhail Somov in the Wedell Sea. It has 24 stations sampled with a 12 position rosette system. The analysis of pH was done using potentiometric method. The cruise has only 2 crossovers. The inversion suggests a correction of -0.034 ± 0.001 . All residuals are very low and fit inside ± 0.002 after the full solution of the inversion is applied. Based on this evidence, an adjustment of -0.034 was applied to the pH data.

Table 4. Adjustments applied to individual cruise files. “P” or “S” are acronyms for pH measurement method, and refer to Potentiometric or Spectrophotometric techniques respectively.

Cruise ID	Cruise expocode	Is Core Cruise	pH measurement method	Adjustment Applied
15	06MT19960910		P	-0.007
23	06MT20010507		S	-0.008
25	06MT20010717		S	-0.005
52	29CS19930510		P	0.017
53	29GD19821110		P	0.024
55	29GD19840218		P	0.023
56	29GD19840711		P	-0.017
57	29GD19860904		P	0.032
61	29HE20010305		S	0.005
84	33LK19960415		P	-0.018
94	35LU19890509		P	0.024
95	35LU19950909		P	-0.028
106	35TH19990712		P	-0.008
119	58AA19950217		S	Flagged 3
141	58JH19970414		S	0.025
142	58JH19980801		S	0.02
160	74AB19910501		P	0.022
171	74DI19970807	Y	S	-0.005
172	74DI19980423	Y	S	0.018
183	91AA19971204		S	0.021
-	323019940104	Y	P	-0.009
-	90MS19811009		P	-0.034
-	316N19970717	Y	P	-0.009
-	316N19970815	Y	P	-0.01

6 Results

Results are summarized in Table 4. This table shows the cruises in the three CARINA datasets (ATL, AMS and SO) for which pH adjustments have been applied. The following data is presented in the table:

- Cruise ID: CARINA assigned identification number for the cruise.
- Cruise Expocode: String that identifies the cruise. It is composed of a country code (two numbers), vessel code (two characters or numbers) and the departure date in year, month, day format (YYYYMMDD)
- Indicator for cruises used as “Core Cruises” in the crossover analysis.
- pH analysis method: Potentiometric (P) or Spectrophotometric (S)
- Adjustment: Adjustments applied for the cruises in the data products. All adjustments are fully supported by the CARINA group and no adjustments smaller than 0.005 pH units were applied.

7 Data quality evaluation

7.1 Overall level of internal consistency

A new crossover analysis was performed for the final adjusted CARINA data product, and the resulted offsets were used to estimate the internal consistency of the pH data, Fig. 26. The weighted mean (WM) was calculated for pH by using the absolute value of the offset (D) of the L crossovers with the uncertainty (σ):

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

Based on this analysis we have estimated the overall level of internal consistency of the CARINA pH data to 0.005.

7.2 Overall evaluation

To make an overall evaluation of the dataset quality, 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 pH, but rather a way of getting residuals with natural variability removed to a large extent (adjusted R-square for MLR with full pH adjusted dataset of 0.96), so that they can be used to test the data quality. This analysis

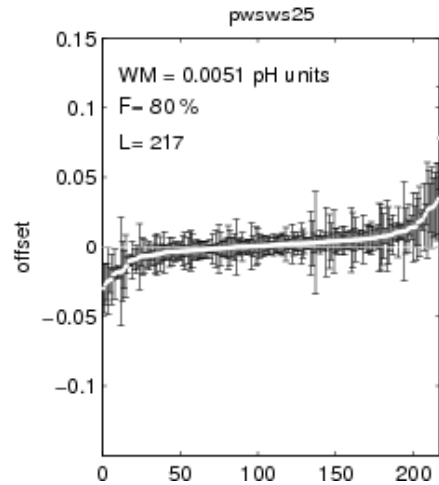


Figure 26. Sorted offsets calculated for the crossovers in the CARINA data after adjustments have been applied. WL: the weighted mean of the offsets (see text); F : the percentage of offsets indistinguishable from 0 within their uncertainty; L : the number of crossovers.

method facilitates a better assessment of scatter and biases in the pH dataset, and even to test the applied adjustments. A fact that has to be born in mind is that the MLR procedure can transmit the measurement error of the explanatory variables to the pH residuals, so this result has to be analyzed knowing its limitation.

In order to improve 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 $\sigma_1 < 32.25 \text{ kg m}^{-3}$. Intermediate waters (depths from about 1000 to 2000 m) were defined by $32.25 \leq \sigma_1 < 32.39 \text{ kg m}^{-3}$. Waters between approximately 2000 to 3000 m were defined by $32.39 \leq \sigma_1 < 32.53 \text{ kg m}^{-3}$, which corresponds to North Atlantic Deep Waters (NADW). And finally, a fourth layer that applies for depths close to the bottom, where the presence of Antarctic Bottom Waters (AABW) dominates. This last layer was defined by $\sigma_1 > 32.53 \text{ kg m}^{-3}$. The surface layer with depths $< 200 \text{ m}$ was not used in this evaluation.

Using the MLR analysis, pH residuals were calculated by the following equation:

$$\text{pH}_{\text{MLR}} = \sum_{i=1}^8 a_i \cdot X_i \quad (3)$$

$$\text{pH}_{\text{residuals}} = \text{pH}_{\text{measured}} - \text{pH}_{\text{MLR}}$$

where X_i stand for Theta, Salinity, Latitude, AOU, Nitrate, Phosphate, Silicate, and a constant term. This procedure was done with CARINA corrected database, and also for the database without pH adjustments applied.

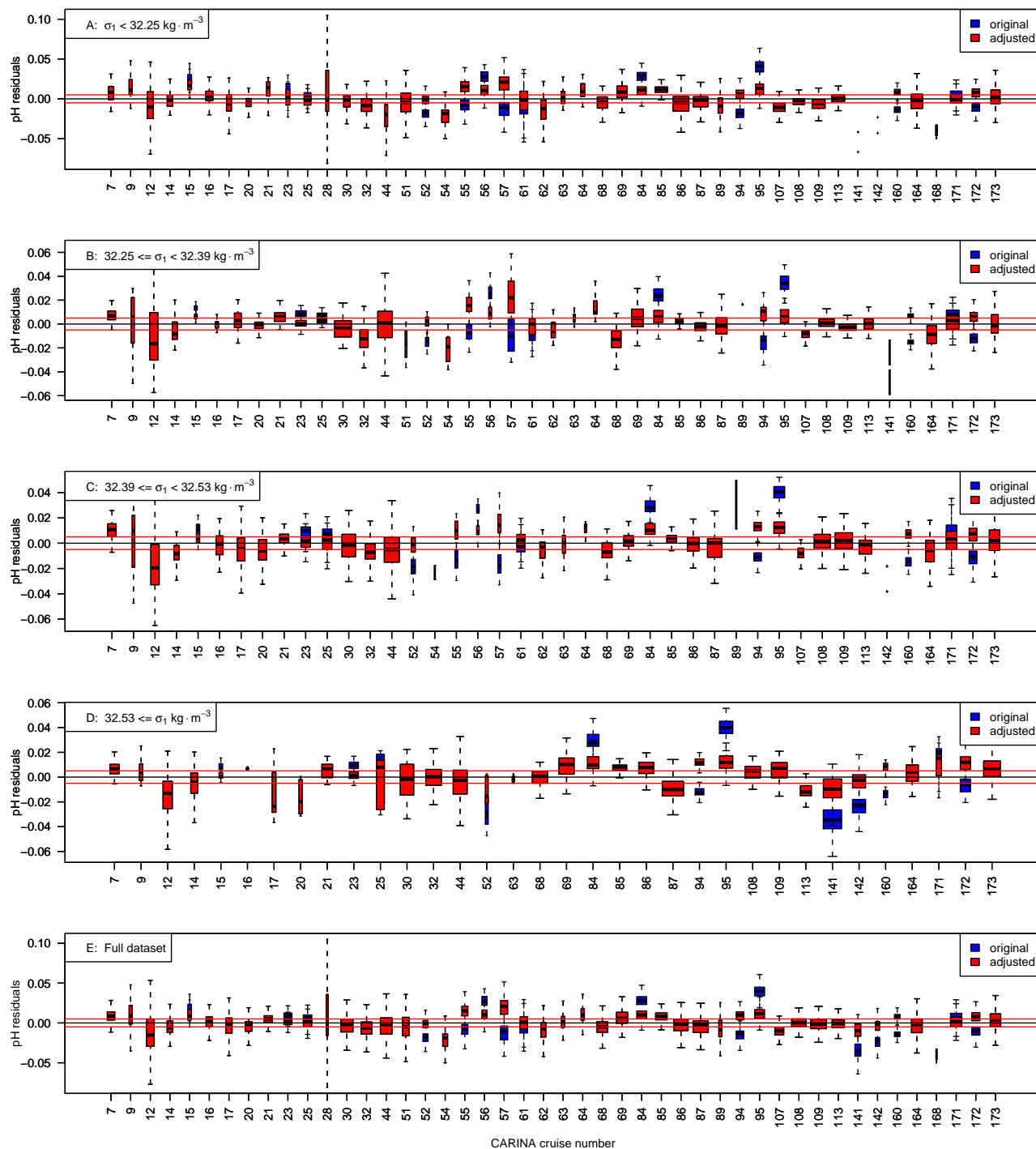


Figure 27. pH residuals obtained from the CARINA dataset by applying an MLR for pH data against Theta, Salinity, Latitude, AOU, Nitrate, Phosphate and Silicate. (A) to (D) are CARINA subsets for the indicated σ_1 intervals, and (E) is the combined residual for the full dataset. Blue values are residuals with the original unadjusted pH values, and red values are the final adjusted pH values. Red lines are the ± 0.005 pH units used as lower limit for adjustments in the secondary QC.

The pH residuals in each density layers are shown in the Fig. 27. The figure shows a box plot of pH residuals 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 3.

The best MLR fit ($R^2 = 0.98$) is obtained for the shallower waters, with a mean residual standard error of 0.015. The next two layers have a slightly lower mean residual standard error (0.012 for layer 2 and 3 with a R^2 of 0.87 and 0.69 respectively) and the deepest layer has a residual standard error of 0.016 (R^2 of 0.77). In terms of mean deviation of each cruise, the mean standard error of the medians of all cruises is 0.009 pH units for each of three deepest density layers. The lower panel in the figure stands for the combined pH residuals of the four density layers.

The pH residuals are lower when using the corrected database, in comparison with the uncorrected original ones. Most of the cruises have the pH residuals median inside of the ± 0.005 boundary. In addition to the pH measurement errors, there are two other sources for the pH residuals: the MLR being not able to explain all the real variability of pH; and the measurement errors of the predictor parameters.

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