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**pH data scale
unification and cruise
adjustments**

A. Velo et al.

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

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Abstract

Data on carbon and carbon-relevant hydrographic and hydrochemical parameters from previously non-publicly available cruise data sets in the Arctic Mediterranean Seas (AMS), 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 database 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; AMS, Atlantic and Southern Ocean. Out of a total of 188 cruise entries in the CARINA database, 59 reported pH measured values.

Here we present details of the secondary QC on pH for the CARINA database. Procedures of quality control, including crossover analysis between cruises and inversion analysis of all crossover data are briefly 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 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 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 and for model validation.

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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

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

Available at: http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/

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

10 Date/Time End: 2006-02-10

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
phsws25	phsws25f	PH_SWS	PH_SWS_FLAG_W	

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.

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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 is to produce a mutually consistent dataset of carbon-related parameters that can be used to assess and quantify carbon uptake, storage and inventories in these regions. Focus was placed not only on the collection of relevant data but also ensuring quality control within these datasets. The CARINA working group has performed both primary and secondary quality control (QC) on those datasets contributing to the CARINA database. This report is a summary of the pH data for the CARINA data set and describes the data consistency analysis (secondary QC) and scale conversions undertaken. For an overview of the CARINA data set see Key et al. (2009) 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 defines the carbonic 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 measurements and interpretation have been resolved through the development of rational pH scales (Dickson, 1993), photometric measurements methods (Clayton and Byrne, 1993) and reliable pH buffers standards of seawaters (Dickson, 1993; Millero et al., 1993). Seawater pH reflects the thermodynamics state of the acid-base systems in seawater, especially of the geochemically important carbonate system.

The term “carbonate buffer” is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean H^+ concentration, and thus pH. The carbonate buffer acts to stabilize the average pH of seawater because of the following two processes: (i) uptake of CO_2 from the atmosphere and (ii) interaction

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of seawater with oceanic sediments composed of CaCO_3 . Because CaCO_3 is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10 000 years. However, over historical timescales, significant changes in surface and near surface ocean pH can occur, closely by following the absorption of CO_2 from the atmosphere. In fact, it's estimated that the global oceanic pH trends have already acidified by 0.1 pH units relative to preindustrial times (Caldeira and Wickett, 2003; Olafsson et al., 2009).

1.2 Variability of pH

Surface oceans have an average pH globally of about 8.2. Nevertheless, pH can vary by ± 0.3 units due to local, regional and seasonal factors. The two primary factors governing the spatial distribution of ocean pH are (i) temperature of the surface oceans and (ii) upwelling of CO_2 -rich deep water into the surface waters. Lower surface water temperatures tend to increase the CO_2 uptake, whilst surface warming drives its release. In the deep oceans, the CO_2 concentration increases as sinking organic matter from biological production is decomposed, and these additions of CO_2 to the deep oceans cause its pH to decrease. Seasonal changes such as those in temperature and in bio-productivity, including variations in photosynthesis and respiration, contribute to fluctuations of the pH in the global surface ocean (Raven et al., 2005).

1.3 Different scales

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

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dilute solution, what is very useful in dilute natural waters such as rivers and lakes, but in contrast, this scale is not recommended for seawater because the large differences in ionic strength between the calibration buffer and the sample (Dickson, 1984; Millero et al., 1993).

5 In addition to NBS pH scale for aqueous solutions, three specific 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 (origin) for the existence of four simultaneous pH scales is primarily historical. They reflect the gradual refinement of the experimentally potentiometric determination of the acidity in seawater. Their
10 definitions are summarized in Table 1.

The free pH scale is conceptually the clearest being explicitly defined only by the H^+ concentration, which is however not directly measured. This operational inconvenience is resolved with the total and seawater scales. The total pH scale (Hansson, 1973) accounts for the reaction of dissociation HSO_4^- ion (including SO_4^{2-} in its calibration
15 solutions), avoiding the definition of the HSO_4^- dissociation constant which accurate value is difficult to obtain in seawater. The seawater scale (Dickson and Riley, 1979) includes beside the bisulphate, the dissociation reaction for the hydrogen fluoride. The differences between the total and the seawater scales arise from the fact whether the medium in which the scale is based includes fluoride or not. However, this difference
20 is numerically small (about ~ 0.01 pH units at salinity 35) because the concentration of HSO_4^- is much larger than HF in the seawater. Contrarily, the pH reported in the free scale is about 0.11 and 0.12 pH units higher than on the total and the seawater scale, respectively Zeebe and Wolf-Gladrow (2001). These differences are much larger than the present precision achieved in the pH measurements, which is in the order of
25 ± 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 acidity constant of the H_2CO_3 are defined for a specific pH scale; thus, if the appropriate inter-conversion between pH scales is ignored, serious errors

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in the $p\text{CO}_2$ calculation can occur that can reach the amount of $100 \mu\text{atm}$, specially whenever pH is a master variable of the carbonic system.

1.4 Methodology of pH measurements

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

Potentiometric method is based in 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). Their precision relies on the preparation of the calibration buffers, which is a common source of problems, and also, on the precision on the control of temperature. The reproducibility is no better than ± 0.02 pH units (Dickson, 1993).

Spectrophotometric methods are based on the absorbance of a pH indicator, and so, they have not the problems associated with buffers preparation and handling. Furthermore, the errors due to temperature can be also partially reduced, by using m-cresol (meta-cresol) as indicator, as they pK value is centered in the range of the oceanic expected pH. This indicator has a variation with temperature similar to the pH, and thus the uncertainties in temperature during the measurement, get reduced (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 Provenance and Structure

pH data included in the CARINA dataset comes from a recompilation of cruise data from a multitude of international research groups until 2005. There are data taken from both potentiometric and spectrophotometric methods, mainly due to the existence or

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availability of spectrophotometric methods at the time the cruise was performed, or the decisions taken by the group that did the measurements.

Totalizing, the CARINA database, has pH data from 59 cruises on 3761 stations, resulting in a total of 49915 pH measurement in the CARINA data set.

3 Conversions to pH SWS 25°C

Conversion on pH scales was done by using the CO2SYS Matlab routines maintained by Steven Van Heuven under the scope of the Carboocean project (van Heuven et al., 2009). The CO2SYS Matlab routines are the adaptation of the programs developed by E. Lewis and D. Wallace (1998) and D. Pierrot (2006) for MS-DOS and Excel respectively. This toolbox can be accessed at <http://cdiac.ornl.gov/oceans/co2rprt.html> and does all calculations needed to get the full solution of a carbonic system in seawater, providing the minimal parameters. This solution also includes the calculation of pH in all of the four scales used in seawater. The toolbox also allows the user to choose which set of constants he wants to use for carbon and sulfate.

This way, the CO2SYS routines were run with the pH values of all data of cruises not in pH_{SWS} and not at 25°C, along with the info on their pH original scale and temperature used as input. Sample pressure and salinity were also supplied, as they are needed for scale conversions. Silicate, phosphate, and alkalinity were also supplied. Constants used were the ones of choice in 2007 Carboocean meetings, i.e. Mehrbach refitted by Dickson and Millero (Dickson and Millero, 1987; Mehrbach et al., 1973) for carbon, and Dickson (Dickson, 1990) for sulphate. The matlab routines convert all pH values to total scale in first place, and then calculate all four scales from this total scale values. Equations used by the software are the summarized in the following table (Table 2), and they are based on the definitions of the Table 1 in previous paragraph:

Then, output in pH_{SWS} is calculated from pH_{TS} by reversing the first equation from

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Table 2, so:

$$\text{pH}_{\text{SWS}} = \text{pH}_{\text{TS}} + \log \left(\frac{1 + \frac{\text{TS}}{\text{KS}}}{1 + \frac{\text{TS}}{\text{KS}} + \frac{\text{TF}}{\text{KF}}} \right) \quad (1)$$

Where:

TS is the Total Sulfate, calculated with the equations from Morris and Riley (1966)

5 TF is the Total Fluorine, calculated with the equations from Riley (1965)

KS stands for the bisulfate ion dissociation constant, from Dickson (1990)

KF stands for the hydrogen fluoride dissociation constant, from Dickson (1979)

f_{H} stands for the activity coefficient of hydrogen ion in seawater (Pérez and Fraga, 1987), calculated according Takahashi et al. equations (Takahashi et al., 1982)

10 The next step taken by CO2SYS routines, is bringing all CO₂ system to the output temperature of 25°C. This is achieved by recalculating the constants, solving the system, and getting the pH again. Internally, the routines use Total Scale for pH, so the scale is converted again to SWS as explained above.

15 The following table (Table 3) shows the cruises identified to be in a scale different than SWS at 25°C. Original scale is noted on the second column, and reported temperature in the third.

4 Methods

20 The methods and techniques are described in detail in the methods paper of this issue (Tanhua et al., 2009). In summary, the procedure starts with a one to one comparisons between stations from different cruises that are either co-located or “near” each other. Only data that were flagged “good” during the primary QC procedure (Key et al., 2009) are considered. The data start point, is the Carina cruise database filtered by the first quality control. The application of various software packages (Tanhua et al., 2009) generates statistical and objective information about the differences between

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pairs of cruises, as well as the graphics needed to visually verify the computer generated differences. Each crossover analysis determines the difference in data between two cruises, calculated for samples deeper than 1500 m, the standard deviation of this difference, as well as the number of contributing stations and samples.

5 In this work, manual, running-cluster and *cnaX* crossover procedures were run for all possible pairs of CARINA 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
10 cruise adjustment calculations. Good crossovers are the ones with enough sample data and that yields a reasonably uniform data over the entire zone of analysis. As additive offsets are being used for analysis, both cruise profiles have to go in parallel, so the offset can be determined. Standard Deviation for individual cruise data and difference profiles was also used to provide more information on crossover quality.

15 In Figs. 1 and 2, two examples of pH crossovers are shown. First one was made by Running Cluster routines, and second one was made by *cnaX* routines (Tanhua et al., 2009).

20 After this first iteration, automated procedures described in the methods paper weighted the crossover quality by statistical parameters for later adjustment calculations for all cruises. This process was followed for all available cruise crossovers. 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),
25 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., 2009). Also, pH calculated data from A_T and C_T was used in order to help to improve the confidence of adjustments been made for cruises without so many crosses with another cruises with pH. Totalizing 217 individual crossovers were obtained when using only measured pH data, and 311 when using also calculated pH from A_T and C_T .

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Figure 3 shows the pH differences between cruise pairs calculated from all individual crossovers (red dots), and the pH differences obtained after applying the full solution of inversion results to all cruises. As can be shown, after applying the corrections, the differences are lower, and most of them fit between the ± 0.005 pH units boundary.

Once the adjustments were determined for all analyzed parameters and then applied, a final quality control run 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. The aim was to verify if the adjustments had improved this consistency. 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. Adjustments were calculated and applied to these data, see below.

4.1 Overall accuracy

The offsets for the crossovers applied to the data product were used to estimate the overall accuracy of the pH data, Fig. 4. 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):

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

Based on this analysis we have estimated the internal accuracy of the CARINA pH data to 0.005

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5 Results

Results are summarized in Table 4. This table shows the results for cruises in this exercise with pH data in CARINA database for all areas and with at least two acceptable crossovers. The following data is presented in the table:

- Cruise ID: CARINA assigned identification number for the cruise.
- Cruise Expocode: String that identify the cruise. Is composed by 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 measurement method: Potentiometric (P) or Spectrophotometric (S)
- 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 0.005 pH units are applied.

6 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 indicated between the parentheses.

In the following paragraphs 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.

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- 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.

6.1 Cruise 74AB19910501 (160) (Fig. 5)

This cruise is the so called Vivaldi expedition, on board R/V Charles Darwin. It has 614 stations, from which only 34 are deep stations. The samples were taken with a 24 place rosette system. Original data were reported at NBS pH scale at 15°C. This cruise has 15 crossovers, with a fitted offset of $+0.022 \pm 0.001$. All residuals after full solution of offsets applied are very low and fit inside ± 0.005 . Very good fits also exist with 6 GLODAP cruises. Based on this evidence, an adjustment of $+0.022$ was applied to the pH data.

6.2 Cruise 29CS19930510 (52) (Fig. 6)

This cruise is called MORENA-I, on board R/V Cornide de Saavedra. It is a cruise along WOCE line AR16e. It has 92 stations taken with a 24 place rosette system. Original data were reported on NBS pH scale at 15°C. The cruise has 8 crossovers. The fitted offset of them is $+0.017 \pm 0.001$. All residuals are very low and fit inside ± 0.002 after the full solution of offsets is applied. Very good fits also exist with three

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core cruises. Based on this evidence, an adjustment of +0.017 was applied to the pH data.

6.3 Cruise 74DI19970807 (171) (Fig. 7)

This is the so called FOUREX cruise (IGY section Four Repeat Experiment), on board R/V Discovery, along the WOCE leg A25. It has 143 full depth stations. The cruise has 19 crossovers. The fitted offset of them is -0.005 ± 0.001 . Except one, all residuals are low and fits inside ± 0.005 after the full solution of offsets is applied. Very good fit also exist with 6 core cruises. Based on this evidence, an adjustment of -0.005 was applied to the pH data.

6.4 Cruise 74DI19980423 (172) (Fig. 8)

This is a cruise on a meridional section along 20° W from 20° N to 65° N, on board R/V Discovery. It has 44 full depth stations taken with a 24 place rosette system. The cruise has 22 crossovers. The fitted offset of them is $+0.018 \pm 0.001$. Except two, all residuals are low and fit inside ± 0.005 after the full solution of offsets is applied. Good fits also exist with 8 core cruises. Based on this evidence, an adjustment of $+0.018$ was applied to the pH data.

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

This is the so called GALICIA-V cruise, on board R/V Garcia del Cid on Atlantic area close to NW of Spain. It has 19 stations taken on an hydrocast with 5l Niskin bottles. The analysis of pH was done by potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 7 crossovers. The fitted offset of them is $+0.024 \pm 0.002$. Except one, all residuals are low and fit inside ± 0.005 after the full solution of offsets is applied. Good fits exits with 3 core cruises. Based on this evidence, an adjustment of $+0.024$ was applied to the pH data.

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

This is the so called GALICIA-VII cruise, on board R/V Garcia del Cid on Atlantic area close to NW of Spain. It has 33 stations taken on an hydrocast with 1.7l Niskin bottles. The analysis of pH was done by potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 8 crossovers. The fitted offset of them is $+0.023 \pm 0.001$. All residuals are low and fit inside ± 0.002 after the full solution of offsets is applied. Good fits exists with 3 core cruises. Based on this evidence, an adjustment of $+0.023$ was applied to the pH data.

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

This is the so called GALICIA-VIII cruise, on board R/V Garcia del Cid on Atlantic area close to NW of Spain. It has 118 stations taken on an hydrocast with 1.7l Niskin bottles. The analysis of pH was done by potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 8 crossovers. The fitted offset of them is -0.017 ± 0.002 . Except one, all residuals are low and fit inside ± 0.005 after the full solution of offsets is applied. Good fits also exist with 3 core cruises. Based on this evidence, an adjustment of -0.017 was applied to the pH data.

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

This is the so called GALICIA-IX cruise, on board R/V Garcia del Cid on Atlantic area close to NW of Spain. It has 50 stations taken on hydrocasts with 1.7L Niskin bottles. The analysis of pH was done by potentiometric method with a glass electrode. The claimed accuracy is 0.003. The cruise has 7 crossovers. The fitted offset of them is $+0.032 \pm 0.001$. All residuals are very low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with 3 core cruises. Based on this evidence, an adjustment of $+0.032$ was applied to the pH data.

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6.9 Cruise 35LU19890509 (94) (Fig. 13)

This is the so called BORDEST-3 cruise on board R/V 'Le Noroit', on a rectangular grid on the Atlantic area close to the west of Iberian Peninsula. It has 47 full depth stations taken with a rosette system. The cruise has 6 crossovers. The fitted offset of them is $+0.024 \pm 0.002$. Very good fits also exist with 4 core cruises. Based on this evidence, an adjustment of $+0.024$ was applied to the pH data.

6.10 Cruise 06MT19960910 (15) (Fig. 14)

This is the so called M36/5 cruise, on board R/V Meteor, on North Atlantic area. It has 62 stations taken with a 24 place rosette system. The cruise has 12 crossovers. The fitted offset of them is -0.007 ± 0.001 . Except one, all residuals are very low and fits inside ± 0.003 after the full solution of offsets is applied. Very good also exist fit with 5 core cruises. Based on this evidence, an adjustment of -0.007 was applied to the pH data.

6.11 Cruise 91AA19971204 (183) (Fig. 15)

This is the so called SWEDARP 1997 expedition, on board S.A Agulhas vessel on South Africa area, mostly on 6° E. It has 40 stations. The analysis of pH was done by spectrophotometric method. Original data were reported at TS pH scale (Total Scale) at 15°C . The cruise has only 2 crossovers. The fitted offset of them is $+0.021 \pm 0.005$. All residuals fit inside ± 0.010 after the full solution of offsets is applied. Based on this evidence, an adjustment of $+0.021$ was applied to the pH data.

6.12 Cruise 29HE20010305 (61) (Fig. 16)

This is the so called FICARAM II cruise, on board R/V Hesperides along WOCE section A17 on Western South Atlantic area. It has 29 full depth stations taken with a 24 place rosette system. The analysis of pH were done by spectrophotometric method. CRM

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batch 41 and 51 were used, with an uncertainty of 0.002. Original data were reported at TS pH scale (Total Scale) at 25°C. The cruise has 9 crossovers. The fitted offset of them is $+0.005 \pm 0.001$. Except one, all residuals are low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with 5 core cruises. Based on this evidence, an adjustment of $+0.005$ was applied to the pH data.

6.13 Cruise 323019940104 (Fig. 17)

This is the so called CITHER 2 cruise on board R/V Maurice Ewing, along WOCE section A17 on Western South Atlantic area. It has 235 stations taken with a 32 place rosette system. The analysis of pH was done by potentiometric method with an overall precision of ± 0.003 . Original data were reported at NBS scale at 15°C. The cruise has 10 crossovers. The fitted offset of them is -0.009 ± 0.001 . All residuals are low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with 3 GLODAP cruises. Based on this evidence, an adjustment of -0.009 was applied to the pH data.

6.14 Cruise 90MS19811009 (Fig. 18)

This is the so called Weddell Polynya Expedition 81 (WEPOLEX 81) cruise on board R/V Mikhail Somov on Wedell sea. It has 24 stations taken with a 12 place rosette system. The analysis of pH were done by potentiometric method. The cruise has only 2 crossovers. The fitted offset of them is -0.034 ± 0.001 . All residuals are very low and fit inside ± 0.002 after the full solution of offsets is applied. Based on this evidence, an adjustment of -0.034 was applied to the pH data.

6.15 Cruise 35LU19950909 (95) (Fig. 19)

This is the so called ETAMBOT1 cruise, on board R/V “Le Noroit” along WOCE section AR04g, on west equatorial Atlantic area, near Brazil. It has 85 full depth stations taken with a 24 place rosette system. The analyses of pH were done by potentiometric

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method with standard deviation of replicates of 0.002. Original data were reported at TS pH scale (Total Scale) at in-situ conditions for temperature and pressure. Data were measured at 25°C. The cruise has 3 crossovers. The fitted offset of them is -0.028 ± 0.003 . All residuals are very low and fit inside ± 0.005 after the full solution of offsets is applied. Based on this evidence, an adjustment of -0.028 was applied to the pH data.

6.16 Cruise 316N19970717 (Fig. 20)

This is a cruise on board R/V Knorr along WOCE section A20 on North Atlantic area. It has 95 stations taken with a 36 place rosette system. The analysis of pH was done by potentiometric method. CRM batch 33, 36 and 37 were used. The cruise has 6 crossovers. The fitted offset of them is -0.009 ± 0.003 . Except two, all residuals are very low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with two GLODAP cruises. Based on this evidence, an adjustment of -0.009 was applied to the pH data.

6.17 Cruise 316N19970815 (Fig. 21)

This is a cruise on board R/V Knorr along WOCE section A22 on North Atlantic area. It has 7 stations taken with a 36 place rosette system. The analysis of pH was done by potentiometric method. CRM batch 33, 36 and 37 were used. The cruise has 3 crossovers. The fitted offset of them is -0.010 ± 0.001 . Very good fits also exist with two core cruises and one GLODAP cruise. Based on this evidence, an adjustment of -0.010 was applied to the pH data.

6.18 Cruise 33LK19960415 (84) (Fig. 22)

This is the so called ETAMBOT2 cruise, on board R/V Edwin Link along WOCE section AR04h, on west equatorial Atlantic area, near Brazil. It has 94 stations taken with a 24 place rosette system. The analysis of pH was done by potentiometric method with

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standard deviation of replicates of 0.003. Original data were reported at TS pH scale (Total Scale) at in-situ conditions of temperature and pressure. Data were measured at 25°C. The cruise has 3 crossovers. The fitted offset of them is -0.018 ± 0.003 . All residuals are very low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with one GLODAP cruise. Based on this evidence, an adjustment of -0.018 was applied to the pH data.

6.19 Cruise 35TH19990712 (106) (Fig. 23)

This is the so called EQUALANT99 cruise, on board R/V “Thalassa” on Equatorial Atlantic area. It has 102 stations taken with a 24 place rosette system. The analysis of pH was done by potentiometric method with standard deviation of replicates of 0.003. Original data were reported at TS pH scale at in-situ conditions of temperature and pressure. Data were measured at 25°C. The cruise has 5 crossovers. The fitted offset of them is -0.008 ± 0.004 . All residuals are very low and fit inside ± 0.003 after the full solution of offsets is applied. Very good fits also exist with three GLODAP cruise. Based on this evidence, an adjustment of -0.008 was applied to the pH data.

6.20 Cruise 06MT20010717 (25) (Fig. 24)

This is the experiment called SFB400, on board R/V Meteor on North Atlantic area under Iceland, including reoccupation. It has 139 stations taken with a 22 place rosette system. The analysis of pH was done by 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 at TS pH scale (Total Scale) at 21°C. The cruise has 16 crossovers. The fitted offset of them is -0.005 ± 0.001 . Except for two crossovers, all residuals are very low and fit inside ± 0.003 after the full solution of offsets is applied. Very good fits exist with four core cruises and two GLODAP cruises. Based on this evidence, an adjustment of -0.005 was applied to the pH data.

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6.21 Cruise 06MT20010507 (23) (Fig. 25)

This is the experiment called SFB460, on board R/V Meteor on Subpolar North Atlantic at South West of Iceland area. It has 53 stations taken with a 24 place rosette system. The analysis of pH was done by spectrophotometric method with precision of ± 0.002 .

- 5 Original data were reported at TS pH scale (Total Scale) at 21°C . The cruise has 7 crossovers. The fitted offset of them is -0.008 ± 0.005 . Except for two crossovers, all residuals are very low and fit inside ± 0.005 after the full solution of offsets is applied. Very good fits also exist with two core cruises. Based on this evidence, an adjustment of -0.008 was applied to the pH data.

10 6.22 Cruise 58JH19970414 (141)

This is the so called 58JH9704 cruise, on board R/V “Johan Hjort” in the Nordic Seas. It has 135 stations taken with a 12 place rosette system. The analysis of pH was done by spectrophotometric method. Original data were reported at TS pH scale (Total 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 TALK and TCO_2 support this adjustment, as do the MLR analysis (see below) Based on this evidences, an adjustment of 0.025 was applied to the pH data.

6.23 Cruise 58JH19980801 (142)

- 20 This is the so called 58JH9808 cruise, on board R/V “Johan Hjort” in the Nordic Seas. It has 49 stations taken with a 12 place rosette system. The analysis of pH was done by spectrophotometric method, with a reported precision of about ~ 0.005 pH units. Original data were reported at TS pH scale (Total 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
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with pH calculated from adjusted TALK and TCO₂ support this adjustment, as do the MLR analysis (see below). Based on this evidences, an adjustment of 0.020 was applied to the pH data

6.24 Cruise 58AA19950217 (119)

5 This is the so called 58AA9502 cruise on board R/V Haakon Mosby in the Nordic Seas. It has 34 stations taken with a 12 place rosette system. The analysis of pH was done by 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,
10 and not include them in the data product.

7 Data quality evaluation

In order to make an overall evaluation of pH 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
15 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 second layer ($32.25 \leq \sigma_1 < 32.39 \text{ kg m}^{-3}$). Depth waters between 2000 to 3000 meters approximately was defined by and $32.39 \leq \sigma_1 < 32.53 \text{ kg m}^{-3}$, which corresponds to North Atlantic Deep Waters (NADW). And finally, fourth layer attends for depths to bottom
20 waters, where the presence of Antarctic Bottom Waters (AABW) dominates. This last layer is set by $\sigma_1 > 32.53 \text{ kg m}^{-3}$. The surface layer with depths $< 200 \text{ m}$ was removed for this evaluation.

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

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

$$\text{pH}_{\text{residuals}} = \text{pH}_{\text{measured}} - \text{pH}_{\text{MLR}} \quad (3)$$

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

The pH residuals in each density layers are showed in the Fig. 26. The figure shows a box plot of pH residuals cruise data for each cruise. Width of boxes attends for the number of samples for that cruise.

The best fit ($R^2=0.98$) is obtained for the shallower waters, with a mean standard deviation of 0.015. The next two layers have a slightly lower mean standard deviation (0.012 and 0.012 for layer 2 and 3 respectively) and the deepest layer has a standard deviation of 0.016. In terms of mean deviation of each cruise, the mean standard deviation 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 joined pH residuals of the four density layers.

As can be shown, 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 that increase the variability of the pH residuals: the MLR being not able to explain all the real variability of pH; and the own measurement errors of the predictor parameters.

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Table 1. pH scales used on seawater measurements, definitions, and relationships.

Scale	pH definition
NBS	$\text{pH}_{\text{NBS}} = -\log a_{\text{H}}$
Free	$\text{pH}_{\text{F}} = -\log [\text{H}^+]_{\text{F}}$
Total	$\text{pH}_{\text{T}} = -\log ([\text{H}^+]_{\text{F}} + [\text{HSO}_4^-]) = -\log [\text{H}^+]_{\text{T}}$
Seawater	$\text{pH}_{\text{SWS}} = -\log ([\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}]) = -\log [\text{H}^+]_{\text{SWS}}$

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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

$$pH_{TS} = pH_{SWS} - \log\left(\frac{1+TS/KS}{1+TS/KS+TF/KF}\right)$$

$$pH_{TS} = pH_{free} - \log(1+TS/KS)$$

$$pH_{TS} = pH_{NBS} - (\log(1+TS/KS) + \log(f_H))$$

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

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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
160	74AB19910501		P	0.022
52	29CS19930510		P	0.017
171	74DI19970807	Y	S	-0.005
172	74DI19980423	Y	S	0.018
53	29GD19821110		P	0.024
55	29GD19840218		P	0.023
56	29GD19840711		P	-0.017
57	29GD19860904		P	0.032
94	35LU19890509		P	0.024
15	06MT19960910		P	-0.007
183	91AA19971204		S	0.021
61	29HE20010305		S	0.005
-	323019940104	Y	P	-0.009
-	90MS19811009		P	-0.034
95	35LU19950909		P	-0.028
-	316N19970717	Y	P	-0.009
-	316N19970815	Y	P	-0.010
84	33LK19960415		P	-0.018
106	35TH19990712		P	-0.008
25	06MT20010717		S	-0.005
23	06MT20010507		S	-0.008
141	58JH19970414		S	0.025
142	58JH19980801		S	0.020
119	58AA19950217		S	Flagged 3

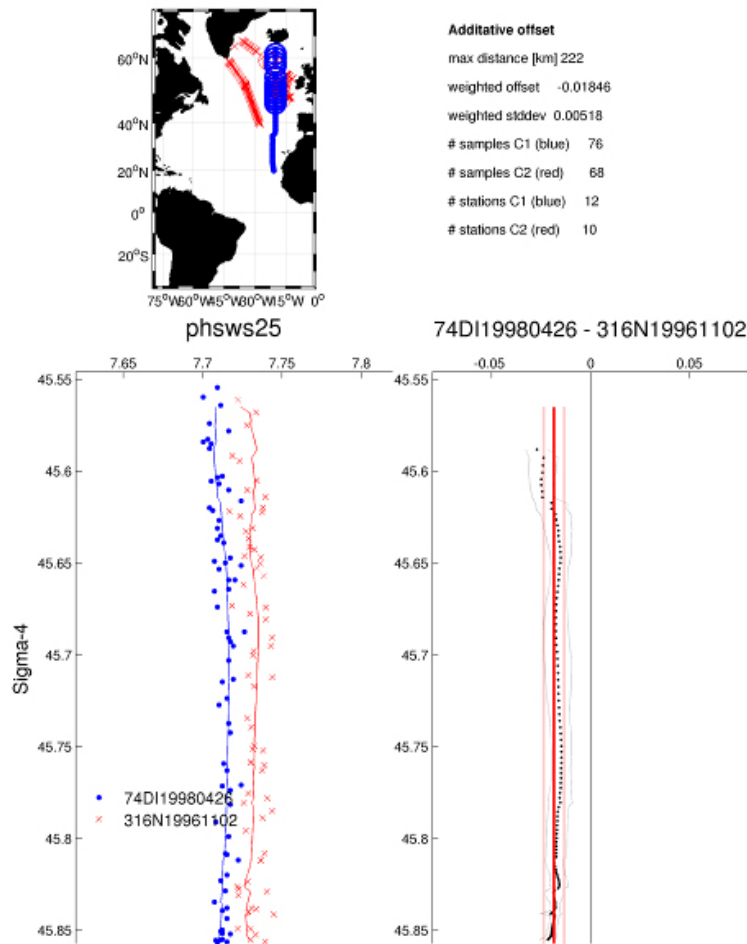


Fig. 1. Crossover made with Running Cluster Routines.

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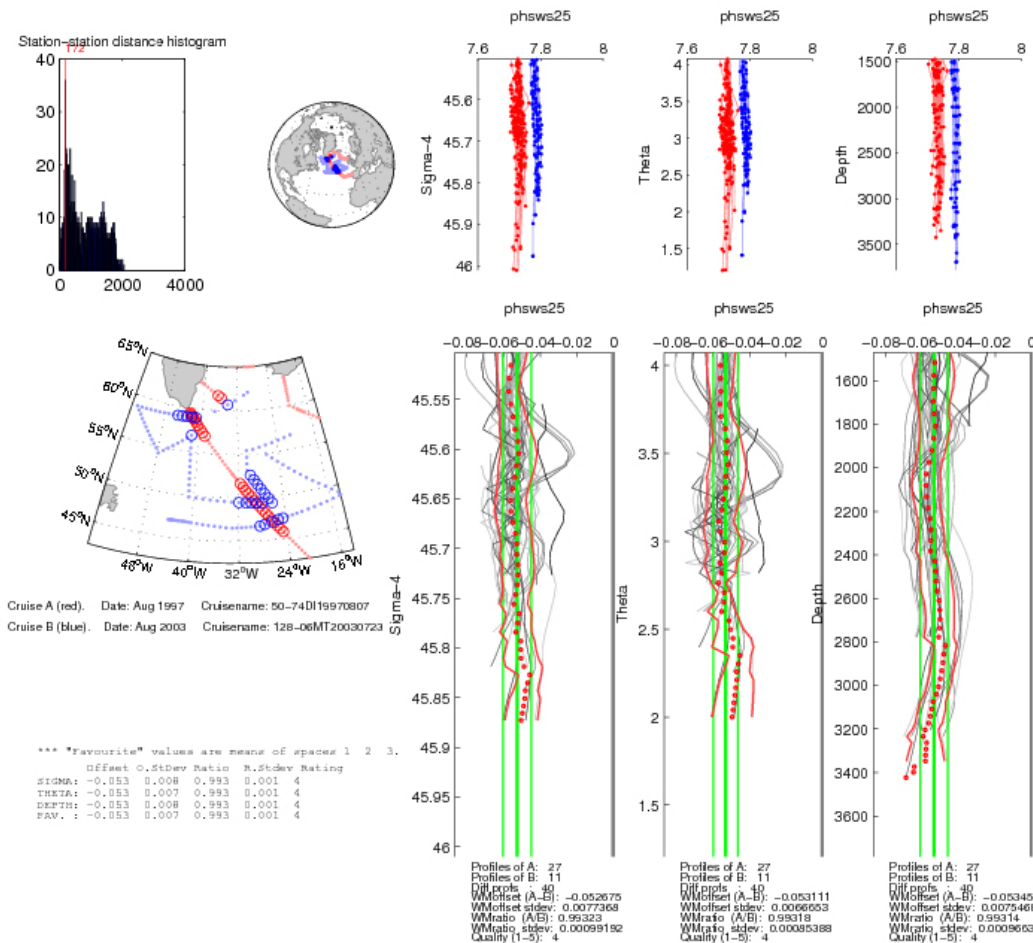


Fig. 2. Crossover made with cnaX routines.

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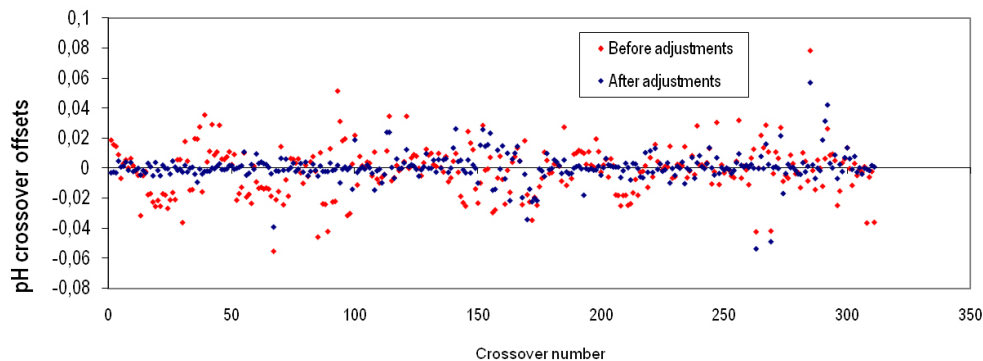


Fig. 3. Crossover pH offsets obtained with original database and after adjustments were applied.

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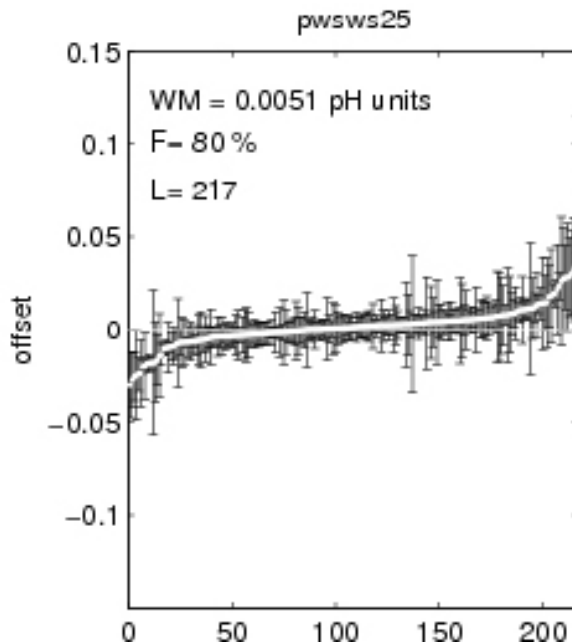


Fig. 4. Sorted offsets calculated for the crossovers in the CARINA data after adjustments have been applied. WL: the weighted mean of the offsets (see text); F: the percentage of offsets indistinguishable from 1 within their uncertainty; L: the number of crossovers.

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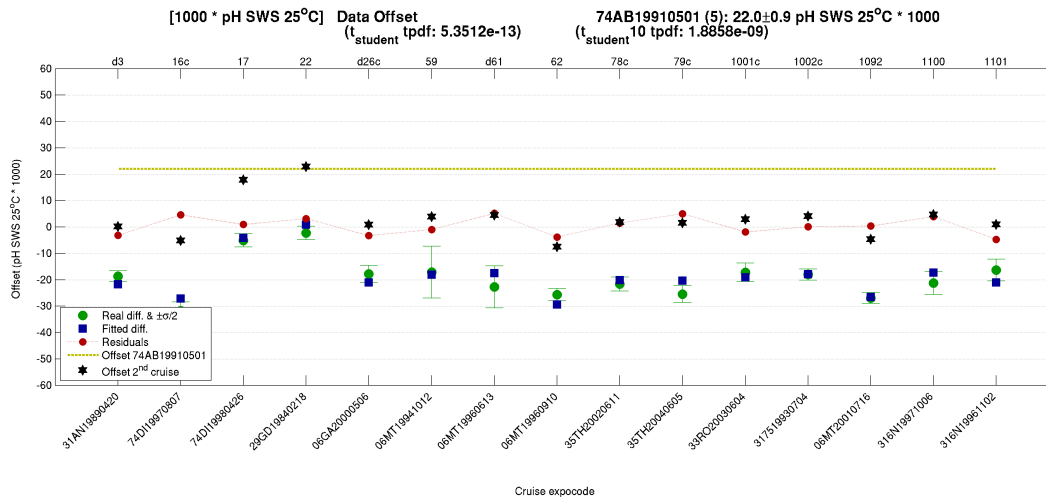


Fig. 5. Cruise crossover information plot for 74AB19910501.

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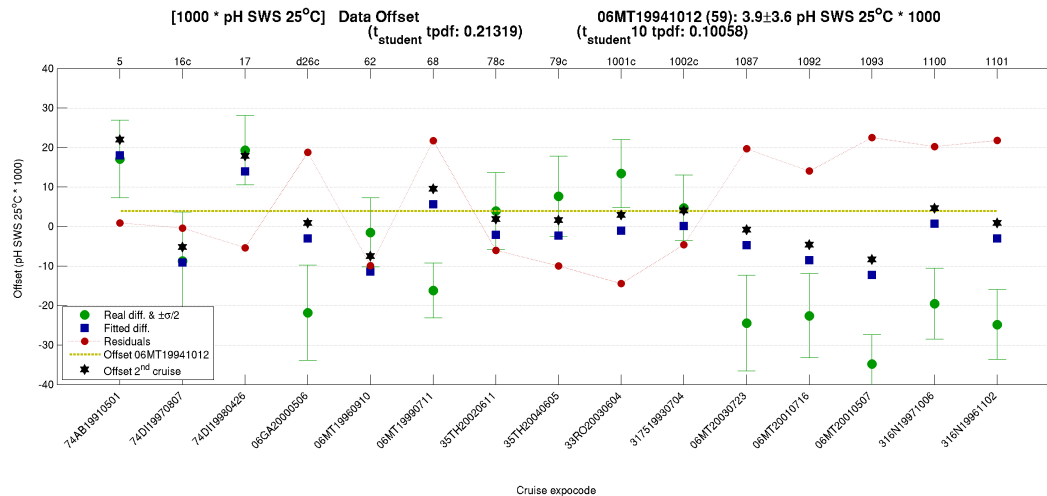


Fig. 6. Cruise crossover information plot for 29CS19930510.

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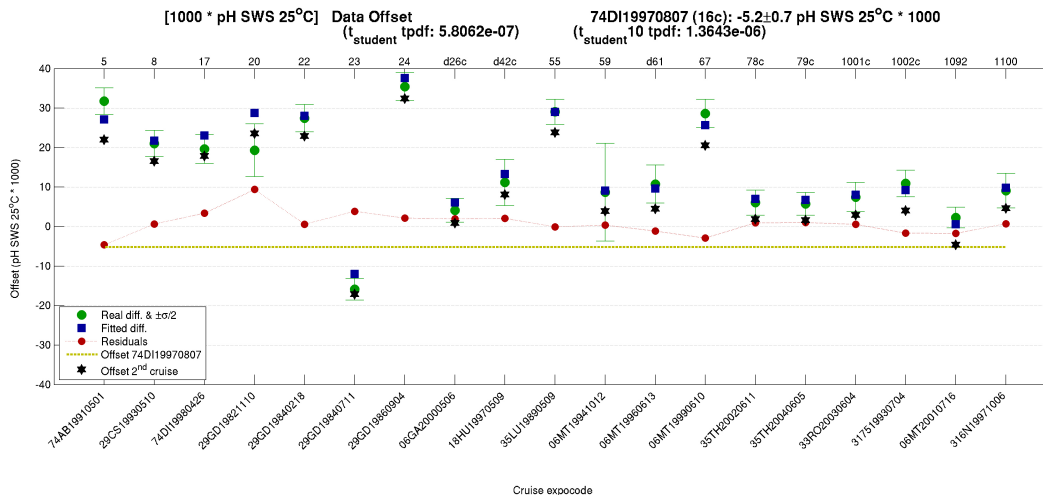


Fig. 7. Cruise crossover information plot for 74DI19970807.

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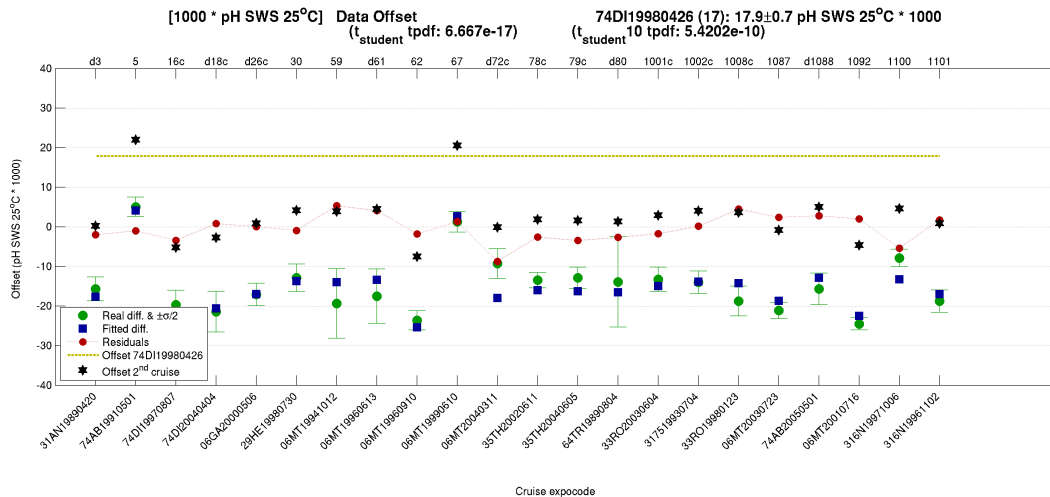


Fig. 8. Cruise crossover information plot for 74DI19980423.

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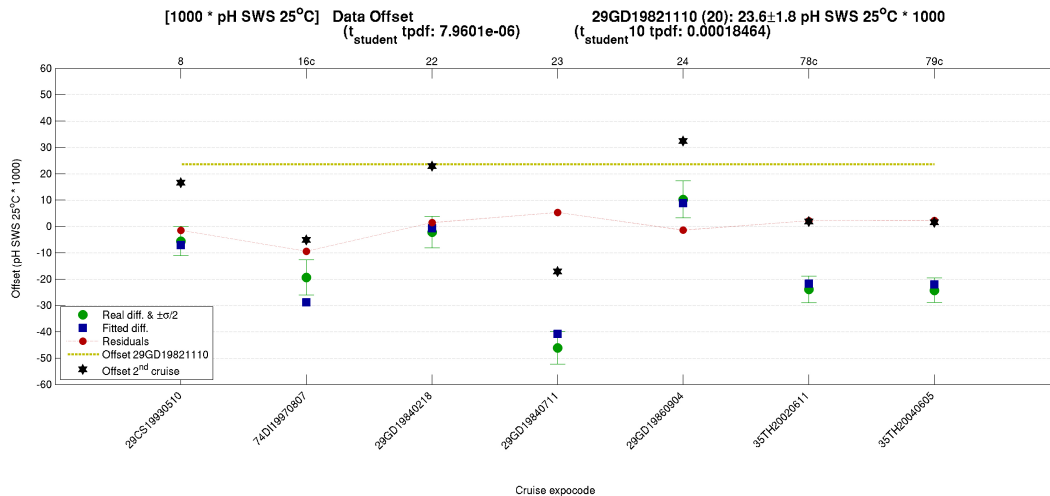


Fig. 9. Cruise crossover information plot for 29GD19821110.

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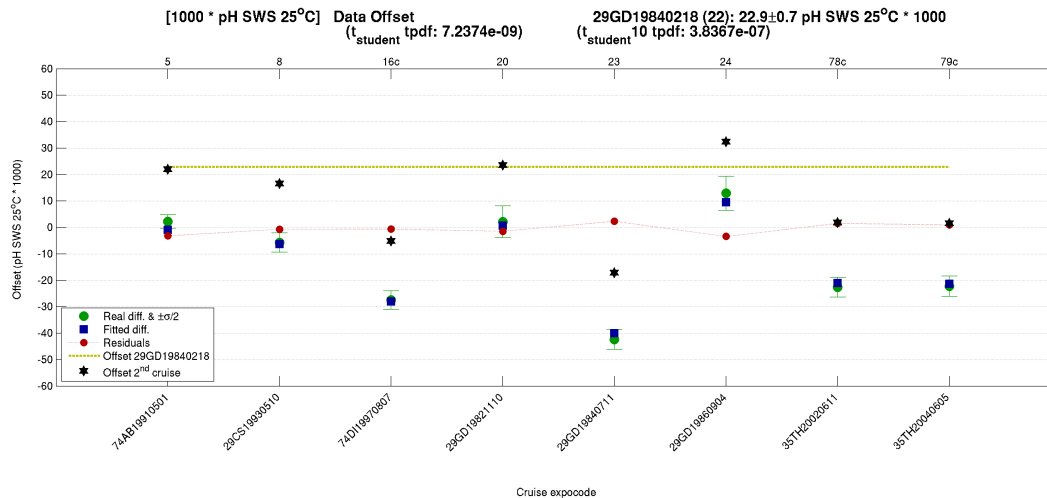


Fig. 10. Cruise crossover information plot for 29GD19840218.

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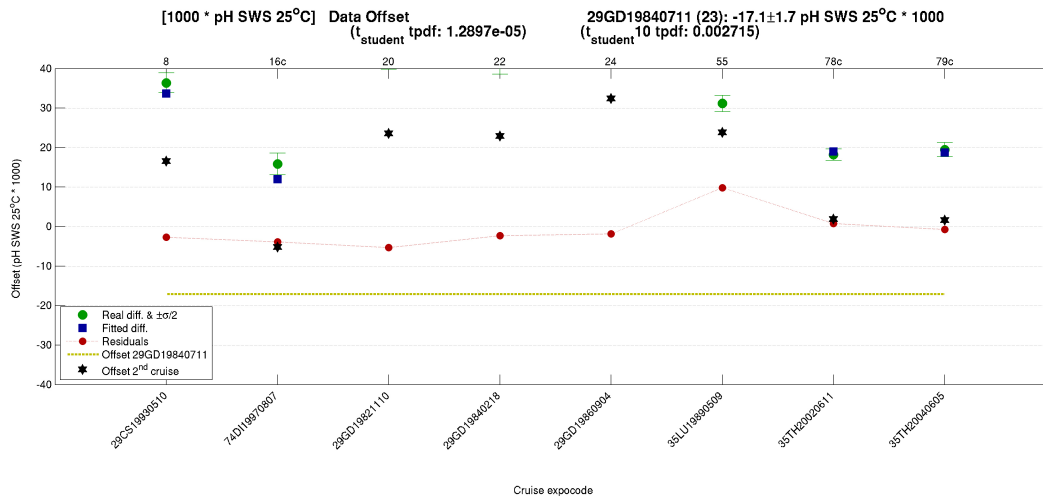


Fig. 11. Cruise crossover information plot for 29GD19840711.

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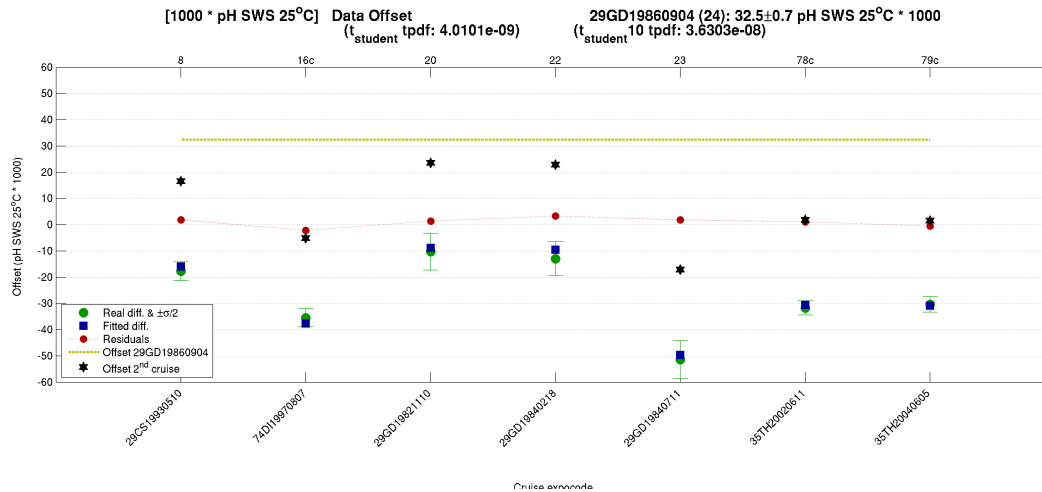


Fig. 12. Cruise crossover information plot for 29GD19860904.

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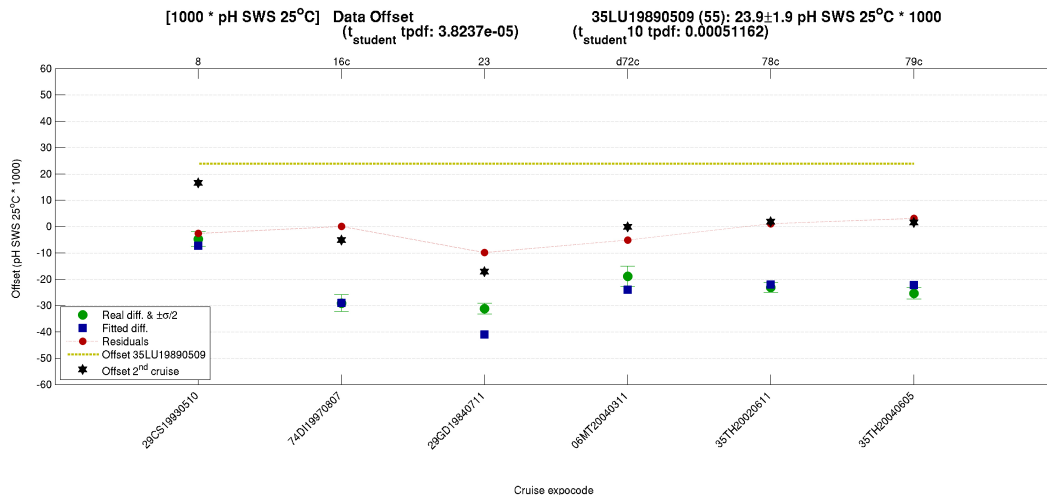


Fig. 13. Cruise crossover information plot for 35LU19890509.

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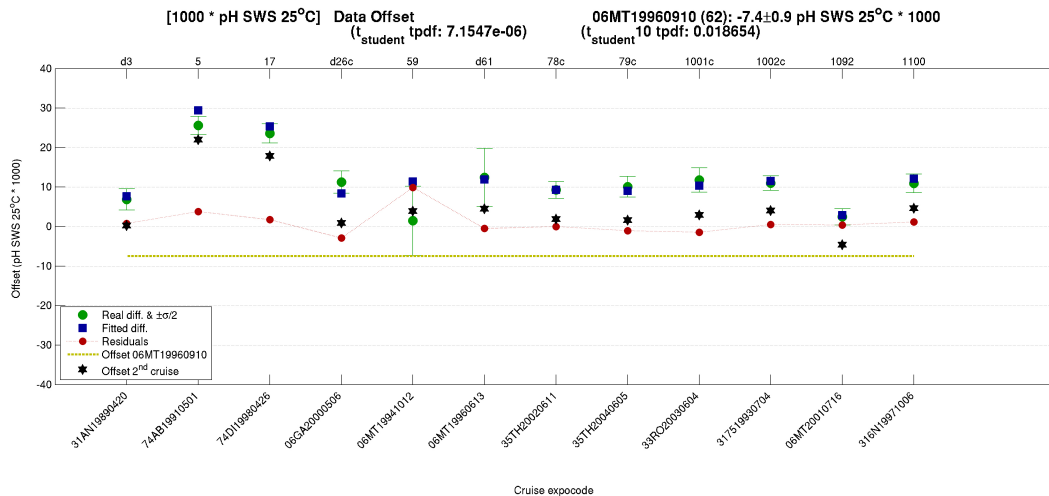


Fig. 14. Cruise crossover information plot for 06MT19960910.

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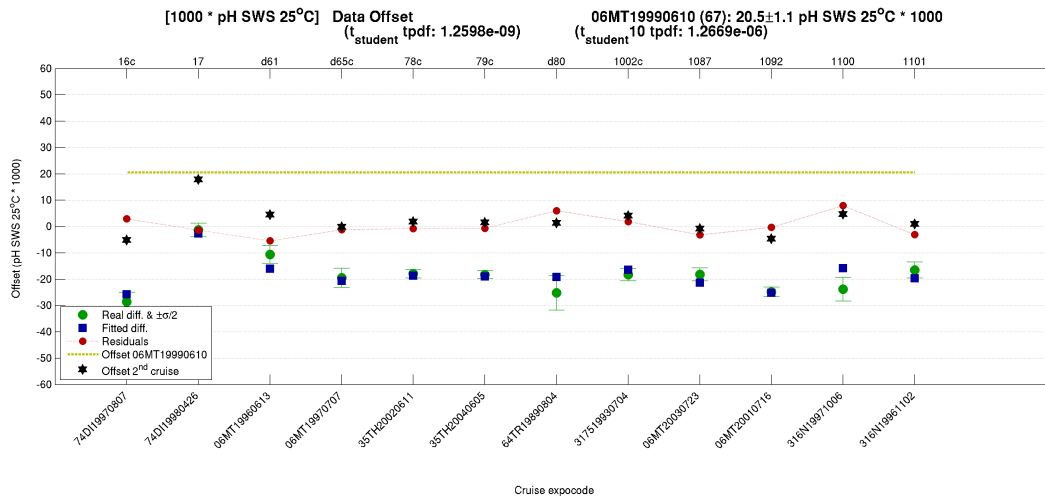


Fig. 15. Cruise crossover information plot for 91AA19971204

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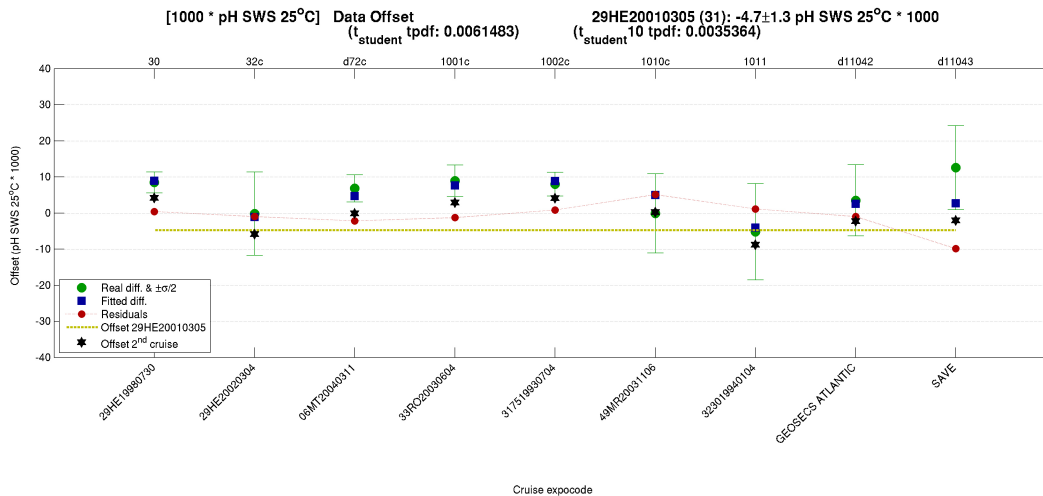


Fig. 16. Cruise crossover information plot for 29HE20010305.

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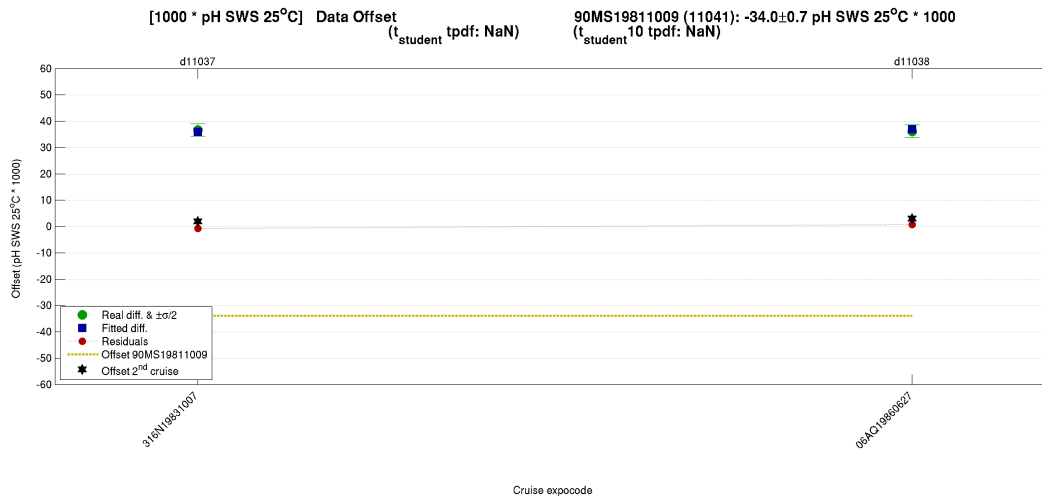


Fig. 17. Cruise crossover information plot for 323019940104.

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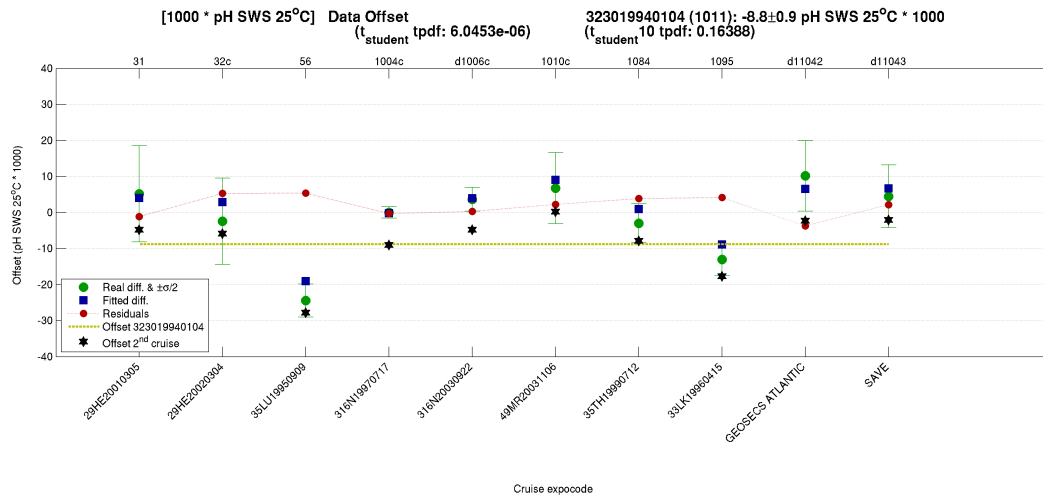


Fig. 18. Cruise crossover information plot for 90MS19811009.

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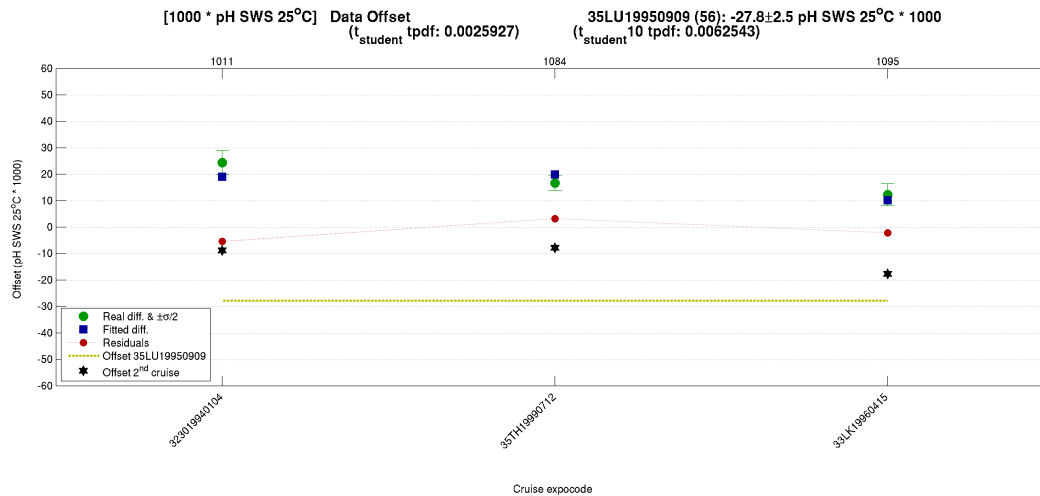


Fig. 19. Cruise crossover information plot for 35LU19950909.

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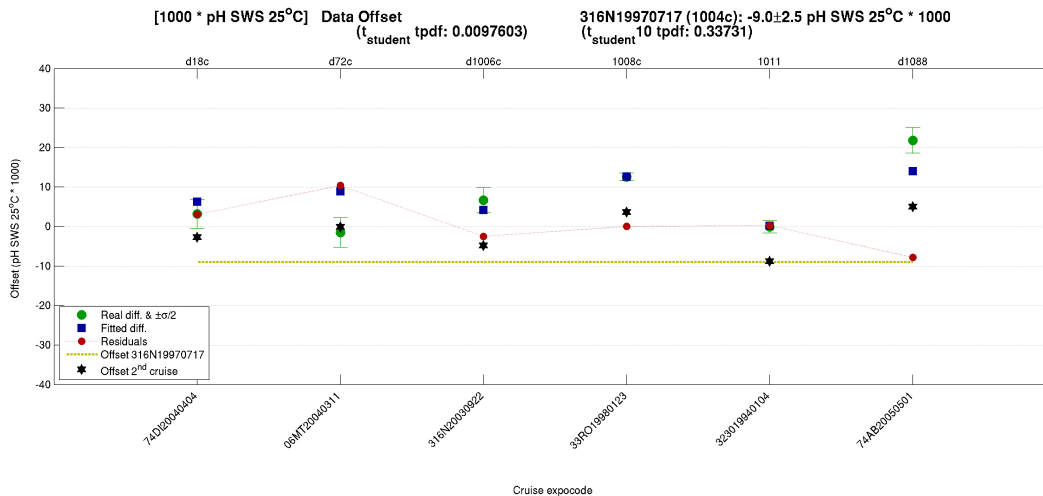


Fig. 20. Cruise crossover information plot for 316N19970717.

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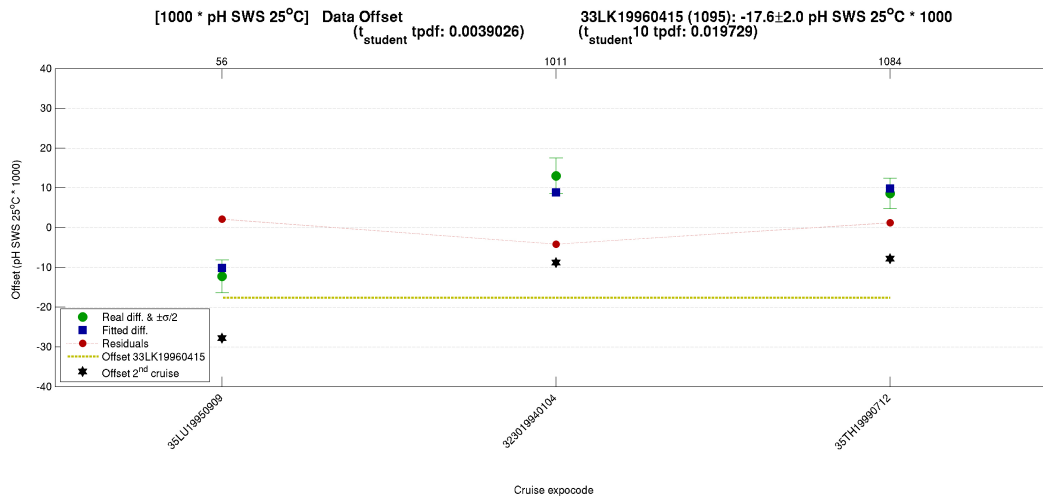


Fig. 21. Cruise crossover information plot for 316N19970815.

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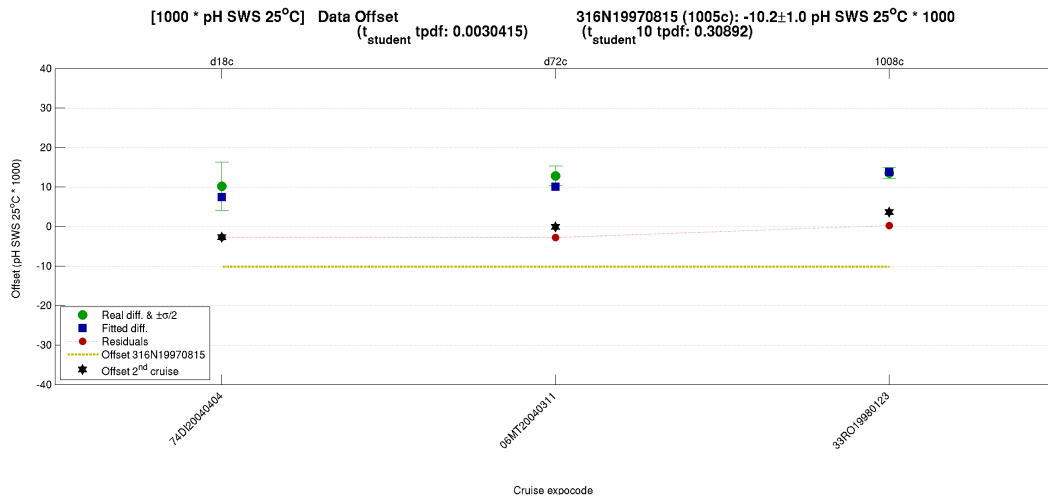


Fig. 22. Cruise crossover information plot for 33LK19960415.

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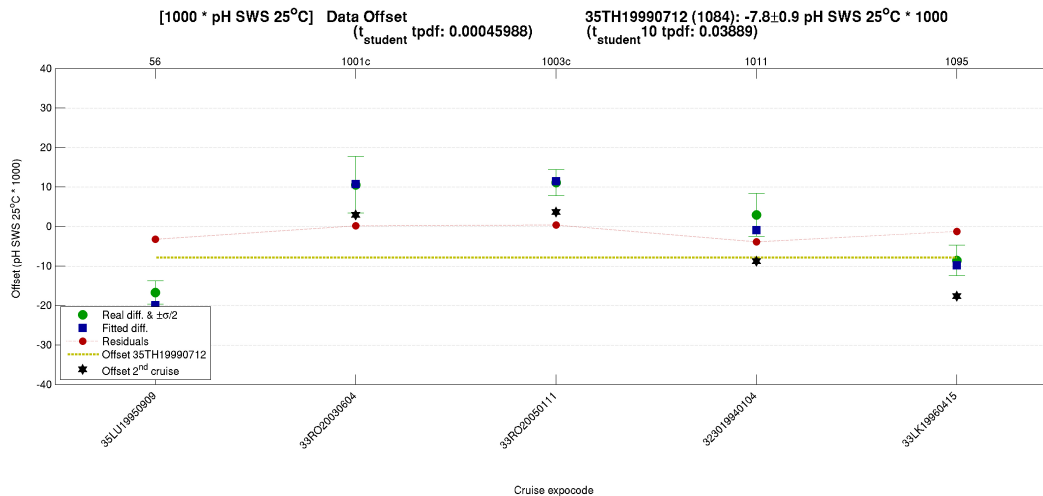


Fig. 23. Cruise crossover information plot for 35TH19990712.

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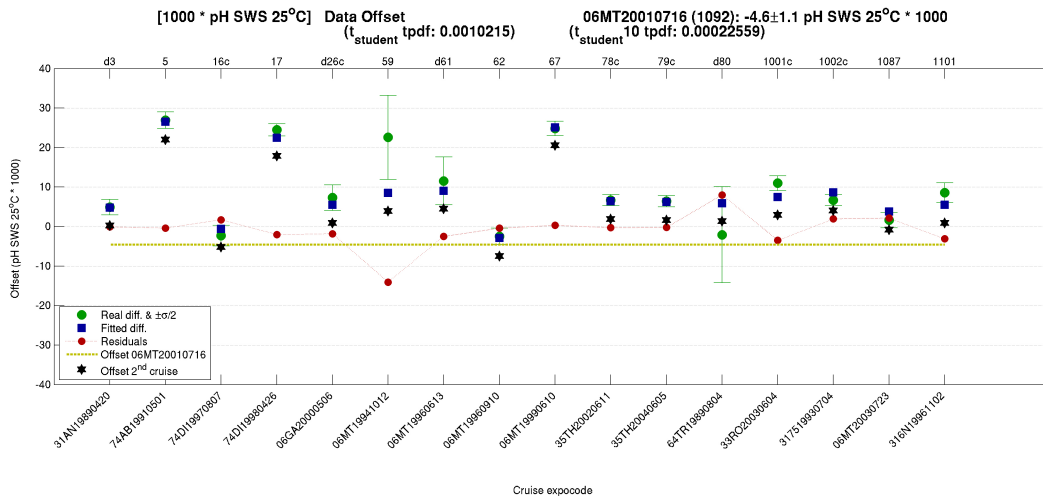


Fig. 24. Cruise crossover information plot for 06MT20010716.

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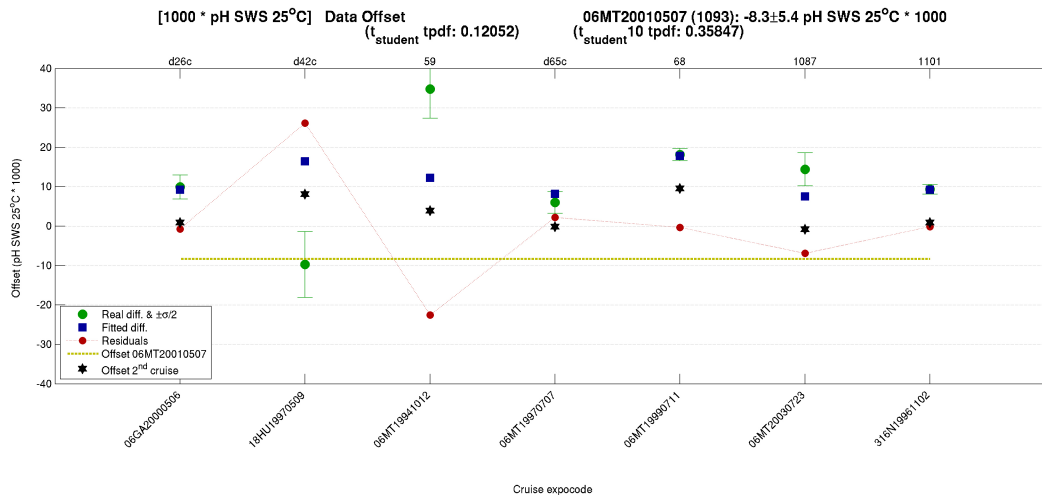


Fig. 25. Cruise crossover information plot for 06MT20010507.

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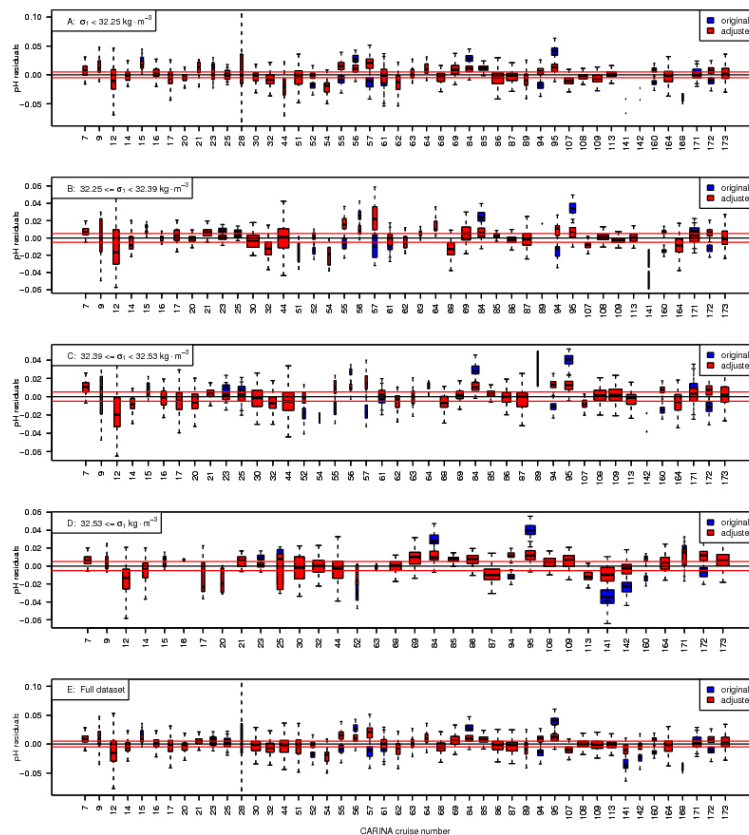


Fig. 26. pH residuals obtained from CARINA dataset by applying an MLR for pH data against Theta, Salinity, Latitude, AOU, Nitrate, Phosphate and Silicate. **(A) to (D)** are CARINA subsets for the indicated σ_1 interval, and **(E)** is the join for the full dataset. Blue values are residuals with the original unadjusted pH values, and Red values are the final adjusted pH values. Red lines are the ± 0.005 pH units of pH used as lower limit for adjustments in the crossover exercise.

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