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Data recovery of A06 and A07 WOCE cruises

N. M. Fajar, F. F. Pérez, A. Velo, and A. F. Ríos

Instituto de Investigaciones Marinas de Vigo (IIM-CSIC), C/Eduardo Cabello,
6. Vigo, Pontevedra, 36208, Spain

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Correspondence to: N. M. Fajar (nfajar@iim.csic.es)

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Abstract

The WOCE cruises were carried out during the 1990s and were included in GLODAP, which is an easily usable, available and fully calibrated global database. A_T and C_T data, together with the rest of carbon variables, were subjected to rigorous quality control and some adjustments were done assuming biases, in case of A_T and C_T, not greater than ±6 µmol kg^{-1} and ±4 µmol kg^{-1}, respectively. The A06 and A07 cruises were deleted from GLODAP database owing to A_T and C_T data were not suitable for analysis. However, these data are still available in CLIVAR and Carbon Hydrographic Data Office web site, demonstrated the unreliable quality of A_T and C_T, but contrarily, the more realistic profiles of pH data. The main goal of the present work is to recover A_T and C_T data of A06 and A07 using GLODAP database combining with CARINA database and the most contemporary cruise MOC^{2}Equatorial 2010. Thus, A_T data of A06 and A07 will be renewed using directly these data in a particular application of Multiple Linear Regression: the 3-D moving window MLR estimation method. Moreover, C_T data will be recalculated using the $\frac{C_T}{A_T}$ ratio together with the obtained results from the crossovers analysis method. In order to demonstrate the quality of the recovered A_T and C_T, the new pH has been calculated, showing the good agreement in terms of pH obtained between A06 and A07 related to MOC^2. To sum up, the entire carbon databases of A06 and A07 were checked and recovered.

1 Introduction

The World Ocean Circulation Experiment (WOCE) together with the Joint Global Ocean Flux Study (JGOFS), and the Ocean-Atmosphere Carbon Exchange Study (OACES) were carried out during the 1990s. The three programs covered different ocean regions, improving the combined global coverage. The collaborative efforts between scientists concluded in the known Global Ocean Data Analysis Project (GLODAP) (Sabine et al., 2005) as an easily usable and fully calibrated global database. Between the general goals of GLODAP, it is worth highlighting the distribution of the variables of

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carbon system in order to estimate their changes and the possibility of evaluate the inventory of natural and anthropogenic carbon (Key et al., 2004). Thus, the data were merged into a common format database divided by ocean, which is available in the GLODAP website hosted by the Carbon Dioxide Information Analysis Center (CDIAC) (http://cdiac.ornl.gov/oceans/glodap/index.html).

In the Atlantic Ocean, not only there are several cruises merged in GLODAP (Key et al., 2004) database but also in CARbon IN the Atlantic Ocean (CARINA) (Key et al., 2010). CARINA database was generated in order to create a merged calibrated database from open ocean measurements of biogeochemical investigations, in particular, studies involving the carbon system. The wide set of historical and recent hydrographic cruises include the entire Atlantic, the Artic and Southern Ocean giving one CARINA data product for each region. The CARINA products and a significant volume of supporting information are available in the CARINA web site also hosted by CDIAC (http://cdiac.ornl.gov/oceans/CARINA/). Despite the fact that the CARINA data products are compatible with the GLODAP data products, they are not identical, differing in column order, included parameters and number of data. Thus, in order to obtain a complete database, historical and recent cruises have been taken from both GLODAP and CARINA databases in the present work.

One key point in both GLODAP and CARINA databases is that an extensive calibration and quality control procedures have been designed to remove measurement bias and bad data in the carbonate system measurements sampled during the cruises involved in CARINA and GLODAP. The carbonate system in seawater describes the equilibrium between dissolved CO_2 and carbonate and is defined by four parameters, i.e. total inorganic carbon (C_T), total alkalinity (A_T), pH and fugacity of CO_2 (fCO_2). Knowing at least two of these parameters allows calculating the unknowns. Only A_T and C_T data, focused on the Equatorial Atlantic Ocean, will receive the whole attention hereinafter, being their biases, assumed by both GLODAP and CARINA databases, not greater than ±6 and ±4 μmol kg^{-1} for A_T and C_T, respectively (Key et al., 2004, 2010).

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The combined GLODAP + CARINA database contains bottle and carbon data from surface to deep ocean waters in the Atlantic Ocean from historical and recent cruises. In order to complete this combined database and to contribute with more modern data, the most contemporary cruise in the equatorial Atlantic Ocean is included in that study: MOC^2Equatorial (Meridional Overturning Circulation – Memoria Oceánica del Clima, http://www.icm.csic.es/oce/ca/content/moc2/), hereafter MOC^2. MOC^2 cruise was spanned along 7.5° N during April–May in 2010 on board of *BIO Hespérides*. Carbon system water samples, i.e. C_T, A_T and pH, have been sampled and analysed in the whole water column.

The A06 (Oudot, 1993a) and A07 WOCE (Oudot, 1993b) cruises were carried out on board of N/O *l'Atalante* as part of the French CITHER project. A07 took place in January 1993 along 4.5 ° S while A06 took place in February–March 1993 along 7.5° N. The A_T and C_T data of both cruises were deleted from GLODAP database because these data were not suitable for analysis (Wanninkhof et al., 2003). However, these data are still available in CLIVAR and Carbon Hydrographic Data Office (CCHDO) web site (http://cchdo.ucsd.edu/) inside the Atlantic Ocean data section. Thus, taking into account the combined GLODAP + CARINA + MOC^2 database, the complete database of A06 and A07 cruises can be objectively revised and corrected.

Despite the fact that the A_T and C_T values of A06 and A07 cruises are out of quality controls of CARINA and GLODAP, the calculated pH data, involving these A_T and C_T, seem to show realistic and reliable profiles, as it can be seen in Fig. 1. In this figure, the pH profiles of A06, A07 and MOC^2 cruises are shown, observing the coherence between A06 and A07 profiles related to MOC^2 pH profile. The relevance of this good agreement among cruises is that the combination of A_T and C_T, in spite of being unreliable data, produces suitable pH results, hence, the ratio $\frac{C_T}{A_T}$ is valid. Taking into account not only that there are many stations or even cruises driven close in time and location to A06 and A07 cruises (Fig. 2) but also the suitability of calculated pH data together with the validity of the $\frac{C_T}{A_T}$ ratio, the possibility of recovery the A_T and C_T data of A06 and a07 cruises, is planned as main aim of the present manuscript. Bear in mind that A_T is the parameter of the carbonic system with less variability, A_T data A06 and A07 will be used directly in a 3-DwMLR method (Velo et al., 2011). Moreover, C_T data will be checked and complete using the $\frac{C_T}{A_T}$ ratio and reassert the obtained A_T and C_T results using crossovers analysis (Tanhua, 2010). To sum up, the entire carbon databases of A06 and A07 will be tested and recovered.

2 Data

Data of GLODAP and CARINA databases were widely revised and involved in different quality control processes in order to assure the highest veracity and consistency to their included measurements. Thus, carbon data of cruises of the Atlantic Ocean merged in both databases were downloaded from their respective web sites (http://cdiac.ornl.gov/oceans/). Table 1 shows all the cruises selected in this work including A06 and A07 cruises, specifying cruise number, expocode, alias, database to which belong each cruise, year and, in the last column, if the defined cruise was carried out near A06, A07 or both of them. The geographical distribution of these cruises is showed in Fig. 2, where the entire Atlantic Ocean basin is represented.

Databases of A06 and A07 cruises are available in CCHDO web site (http://cchdo.ucsd.edu/). A06 and A07 cruises were carried out in the winter season along 7.5° N and 4.5° S, respectively, sampling and analysing some variables that defined the carbon system, i.e. pH and C_T. Measurements of C_T were made by gas chromatography according to the modified method as described in Oudot et al. (1995). pH measurements were based on the total hydrogen ion concentration scale (pH_{SWS}) using a Ross combination electrode calibrated in Tris buffer. Because of the unknown temperature and calibration data of pH data of A06 and A07 cruises (Wanninkhof, 2003), in the present work the pH data were calculated from A_T and C_T using the Excel CO_2sys program (Pierrot et al., 2006) (http://cdiac.ornl.gov/ftp/co2sys/CO2SYS_calc_XLS/) and the acid constants from Mehrbach et al. (1973) fitted by Dickson and Millero (1987) together with the boron to chlorinity ratio from Lee et al. (2010). The A_T data of cruises A06

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and A07 collected in the CCHDO were determined from C_T and pH measurements using the equation describing the terms of alkalinity contributions defined by UNESCO (Oudot et al., 1995).

MOC^2 cruise was carried out at spring season along 7.5° N in 2010 on board of *BIO Hespérides*. This 2010 cruise is very close repetition of the leg spanned along 7.5° N by the cruise A06 in 1993 (see geographical location of A06 in Fig. 2). A_T and pH samples have been analysed in the progression of the cruise, and the C_T samples data were analysed in the laboratory of IIM-CSIC (Vigo). Measurements of A_T were done by a one endpoint method using an automatic potentiometric titrator with a combined glass electrode (Mintrop et al., 2000), in which the potentiometric titration was carried out using the two pH endpoints method according to Pérez and Fraga (1987). Seawater pH measurements were made using the spectrophotometric method described in Clayton and Byrne (1993) adding m-cresol purple as indicator and controlling the temperature at 25 °C by a thermostatic bath. The pH scale fixed in MOC^2 was the total scale (pH_T), but, with the aim of normalized pH data, MOC^2 pH_T were rescaled to pH_{SWS} using the CO_2sys program. C_T data were calculated from A_T and pH using the CO_2sys program because there were not C_T measured in the whole levels of the water column. The coulometric C_T measured (Johnson et al., 1993, 1998) is relevant to check if the calculated C_T fits well with measured C_T, observing a good consistence between them. In order to estimate the accuracy of the A_T and C_T methods, calibrations were performed with certified reference material (CRM) of CO_2 provided by Andrew Dickson.

3 Methodology

As previously said, the A_T and C_T of A06 and A07 cruises were deleted from GLODAP because of being out of quality controls. However, the combination of A_T and C_T produces suitable pH results, being the $\frac{C_T}{A_T}$ ratio valid. Therefore, the main phases of the present work were outlined. (1) Due to the low A_T variability, the 3-D moving window

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Multiple Linear Regression method (3-DwMLR) developed by Velo et al. (2011) was applied to try to obtain the consistent A_T data of these cruises, defining successfully new A_T data ($A_{T\,MLR}$). In order to check if the adjustments of $A_{T\,MLR}$ are well done, the widely applied in CARINA secondary quality control (2nd QC) crossovers analysis (Tanhua, 2010; Tanhua et al., 2010a, b; Velo et al., 2010a) method was used. (2) Taking into account the $\frac{C_T}{A_T}$ ratio, the C_T data were calculated using the Eq. (1):

$$C_T = \frac{C_{T\,orig}}{A_{T\,orig}} \cdot A_{T\,MLR} \tag{1}$$

Where $C_{T\,orig}$ and $A_{T\,orig}$ are the C_T and A_T original data for the A06 and A07 cruises and $A_{T\,MLR}$ is the modified data set of A_T for the A06 and A07 cruises. Nonetheless, a little bias in pH profiles is slightly appreciated (Fig. 1). Therefore, the same little bias should be transfer to the $\frac{C_T}{A_T}$ ratio. In order to solve this deviation, the crossover analysis method was applied to the cruises listed in Table 1, calculating C_T data by Eq. (2):

$$C_T = \frac{C_{T\,orig}}{A_{T\,orig}} \cdot A_{T\,MLR} \cdot \mathrm{FACTOR} \tag{2}$$

Where the factor, one for each A06 and A07 cruises, is calculated as function of the value of crossover offset obtained from crossovers analysis and taking into account 2100 μmol kg^{-1} as the mean C_T value for deep water in the Atlantic Ocean.

3.1 The 3-D moving window MLR estimation (3-DwMLR)

A_T is the parameter that can be computed most accurately with less uncertainty due to its low variability in the ocean. Moreover, A_T can be well correlated with salinity, silicate, and even temperature (Wallace, 1995; Millero, 1995; Lee et al., 2006). Due to that, A_T data can be directly used for MLR computations (Velo et al., 2011). The objective is to improve the results of a MLR by using a 3-D moving window around the node where A_T is being calculated. An algorithm extracts a pool of data from a box around each

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A_T data to perform the calculation. That box is the central node of the moving window, and each A06 and A07 A_T data have assigned their specific data window. Each data window has a particular width and depth, which have been selected according to the experience taking in Velo et al. (2010b and 2011). Thus, the unreliable quality A_T data of A06 and A07 has been replaced by the 3-DwMLR method, giving back the successfully fitted $A_{T\,MLR}$ data for A06 and A07.

3.2 2nd QC: crossovers analysis

Crossovers analysis is an objective comparison of deep water data from one cruise with data from other cruises in the same area, available as a MATLAB tool-box in CDIAC web site (http://cdiac.ornl.gov/oceans/2nd_QC_Tool/) (Tanhua, 2010). The result of a crossover analysis is an *offset* ± *standard deviation*, which is defined as the difference between two cruises, A (cruise will be analysed) and B (cruise as reference), derived from the analysis. This tool interpolates vertical profiles of stations from A and B cruises in the nearest area and calculates the "difference profile". This procedure is repeated in each pair of stations and the result is a crossover offset media for each crossover pair. For C_T, A_T and salinity, these offsets are quantified as an additive adjustment, while, in case of O_2 and nutrient data are quantified as a lineal correction factor.

Here, the crossovers analysis has two main goals, (1) to confirm that the $A_{T\,MLR}$ data obtained using 3-DwMLR agree with GLODAP/CARINA quality criteria, i.e. biases not greater than ±6 µmol kg^{-1} and (2) to recover C_T data (Eq. 2), to obtain a valid offset to minimize the deviation of $\frac{C_{T\,orig}}{A_{T\,orig}}$ ratio giving a new coherent ratio.

4 Results and discussion

4.1 Recovery of A_T data

In order to check and complete the A_T data of both A06 and A07 cruises along the Equatorial Atlantic Ocean, the 3-DwMLR method was used in this dataset. The evident improvements reached by using this method is observed in Fig. 3, where the A_T original

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(Fig. 3a and b) and $A_{T\,MLR}$ profiles (Fig. 3c and d) of A06 and A07 cruises are shown. The Fig. 3a and b show the A_T original data calculated from pH and C_T, while the $A_{T\,MLR}$ profiles (Fig. 3c and d) show more reliable profiles for both 7.5° N and 4.5° S legs, respectively from A06 and A07 cruises. Even though the $A_{T\,orig}$ profiles show a columnar distribution proceeding from the poor quality of $C_{T\,orig}$ measurements, there are common patterns in both $A_{T\,orig}$ and $A_{T\,MLR}$ profiles. For instance, the distribution of the upper waters is roughly similar reaching in both profiles the highest A_T values and the influence of the bottom waters are also shared in these profiles. Moreover, the intermediate waters are also lightly correlated with the water masses present in the Equatorial Atlantic Ocean. However, more realistic and clearer profiles are shown by $A_{T\,MLR}$ profiles for A06 and A07 cruises (Fig. 3c and d), accordingly with the horizontal and vertical distribution of the water masses in this area. Importantly the minimum of A_T associated to the Antarctic intermediate waters is clearly shown in $A_{T\,MLR}$ in both A06 and A07 profiles (Fig. 3c and d).

In order to confirm the good quality of $A_{T\,MLR}$ data recovered, the cruises listed in Table 1 have been used to the crossover analysis of A06 and A07. However, not all listed cruises have given an offset. The valid $A_{T\,MLR}$ offsets are summed up in the Table 2 together with the standard deviation and the mean offset value. The graphical representation of A06 and A07 A_T crossovers is shown in upper panels of Fig. 4 (Fig. 4a and b). Each point in these graphs is the offset ± standard deviation value of cruise A (cruise crossover ID listed in Table 2) taking as reference cruise B, A06 and A07, respectively, in Fig. 4a and b. In general terms, the offset value of both A06 and A07 crossover analysis are not greater than $\pm 6\,\mu mol\,kg^{-1}$, which is the value of A_T data bias accepted by CARINA and GLODAP databases. The mean crossovers offset values (black bold line in Fig. 4a and b and the last column of A_T in Table 2) obtained for $A_{T\,MLR}$ A06 and A07 were $-2.1 \pm 3.7\,\mu mol\,kg^{-1}$ and $-1.0 \pm 3.6\,\mu mol\,kg^{-1}$, respectively. These mean offset values are also in the quality control of GLODAP and CARINA. Therefore, $A_{T\,MLR}$ biases are not necessary to apply. From now on, $A_{T\,MLR}$ data can be used as A_T data corrected and recovered from A06 and A07 cruises.

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4.2 Recovery of C_T data

The C_T measurements of A06 and A07 cruises are not very reliable data, as it is shown in the Fig. 5a and b, where the distribution of C_T lacks of continuity, even though the known patterns in surface, intermediate and bottom waters are lightly distinguished. As previously said, the pH_{orig}, calculated with $A_{T\,orig}$ and $C_{T\,orig}$, are realistic data (Fig. 1), which is an indicator of the validity of the $\frac{C_{T\,orig}}{A_{T\,orig}}$ ratio. In order to check how valid the $\frac{C_T}{A_T}$ ratio is, the mean $\frac{C_T}{A_T}$ profiles of both A06 and A07 cruises have been made. The mean profile is the mean value of the defined layers of depth. The layers from surface to 1000 m are calculated each 200 m, while from 1000 m to bottom (~5000 m) each 500 m. The resultant mean $\frac{C_T}{A_T}$ profiles of A06 (continuous grey light line), A07 (continuous grey dark line) and MOC^2 (black line) are shown in Fig. 6a. Bear in mind these both A06 and A07 profiles, a slight deviation of these profiles related to the MOC^2 $\frac{C_T}{A_T}$ profile is observed overall from 1000 m to bottom. Taking into account the recovered A_T data ($A_{T\,MLR}$) and the reliability of the $\frac{C_T}{A_T}$ ratio, C_T was recalculated using Eq. (1), and therefore, the newest C_T profiles would better fit than the $C_{T\,orig}$ profiles. However, the deviation of the $\frac{C_T}{A_T}$ ratio has more influence than the corrected $A_{T\,MLR}$, giving the same deviated behaviour that the mean $\frac{C_T}{A_T}$ profiles. Therefore, in order to minimize that deviation a crossover analysis of $C_{T\,orig}$ is proposed.

The crossover analysis of $C_{T\,orig}$ from A06 and A07 cruises is applied including the cruises listed in Table 1. However, idem that happened in A_T crossover analysis, not all the cruises have given an offset. The obtained C_T offsets with their corresponding standard deviation for each cruises involved in the analysis are summed up in the Table 2, and their graphical representation is shown in the Fig. 4c and d for A06 and A07 cruises, respectively. The whole offset values obtained for C_T A06 and A07 are out of the quality controls assumed by GLODAP and CARINA (±4 $\mu mol\,kg^{-1}$). The

C_T offset values for A06 crossover analysis vary from −8 to −14 µmol kg^{-1} , giving a mean offset of −11.5 ± 2.0 µmol kg^{-1} , while, in case of A07 crossover analysis, the offset values vary from −4 to −20 µmol kg^{-1} and their corresponding mean value is −9.2 ± 4.3 µmol kg^{-1}. Taking into account the mean offset value obtained for A06 and A07 crossover analysis, two factors are calculated assuming that the mean C_T value in the Atlantic Ocean is 2100 µmol kg^{-1}. These factors are 1.0055 and 1.0045 for A06 and A07 C_T data, respectively. Using Eq. (2), the new C_T data ($C_{T\,MLR}$) for A06 and A07 cruises are calculated, as it is shown in lower panels of Fig. 5 (Fig. 5c and d). In these figures, the reliable profiles of $C_{T\,MLR}$ are observed, showing a distribution of the waters from surface to depth more homogenous than the $C_{T\,orig}$. For example in A07 profile (Fig. 5d), the highest values of C_T influenced by the Antarctic bottom waters are more outlined in $C_{T\,MLR}$ than $C_{T\,orig}$, as well as the minimum values of intermediate water around 2000 m in A06 profile (Fig. 5c).

In order to check if these corrected $C_{T\,MLR}$ values are really reliable, the mean $\frac{C_T}{A_T}$ profiles of both A06 and A07 are calculated. In Fig. 6a, the suitability between A06 and A07 $\frac{C_T}{A_T}$ profiles related to MOC^2 profile is shown across the grey (light and dark) dashed lines, where is clearly identified the good agreement among cruises.

4.3 pH data

The pH_{orig} data available of A06 and A07 data are not very reliable due to the unknown temperature and calibration data. Then, the pH_{orig} was recalculated with $A_{T\,orig}$ and $C_{T\,orig}$ original using the CO_2sys program showing reliable profiles (Fig. 1). In order to check if pH_{orig} data A06 and A07 are in agreement with their mate cruise in location, MOC^2, the mean pH profiles of these cruises have been made (Fig. 6b). The mean pH profiles of MOC^2 , A06 and A07 are shown in Fig. 6b. In this Fig. 6b, the grey continuous lines (light and dark) represent A06 and A07 pH_{orig}, respectively, while the black line represents MOC^2 pH. Following the same pattern than mean $\frac{C_T}{A_T}$ profiles,

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the deviation of these A06 and A07 profiles is clearly shown related to the MOC^2 pH profile.

In order to assert the good quality of the recovered carbon variables, i.e. $A_{T\,MLR}$ and $C_{T\,MLR}$, to A06 and A07 cruises, the pH_{MLR} has been calculated. In the same way than mean pH_{orig} profiles, the mean pH_{MLR} profiles have been estimated, obtaining the expected coherence among A06, A07 and MOC^2 mean pH profiles, in the same way that it happens in mean $\frac{C_T}{A_T}$ profiles. In Fig. 6b, the clear concordance between A06 and A07 (light and dark grey dashed lines, respectively) and MOC^2 mean pH profiles (black continuous line) is demonstrated. Therefore, the whole carbon database was recovered from A06 and A07 cruises.

5 Conclusions

The recovery of A_T and C_T data of A06 and A07 cruises suggests new branches of study about the carbon distribution in the equatorial Atlantic Ocean. Taking into account the transport and the exchanges of mass, the carbon transport in that area could be estimated together with the storage of anthropogenic CO_2 in 1990s. Giving a regional estimate of the accumulative oceanic sink for anthropogenic CO_2 could also be done. Moreover, bear in mind the MOC^2 cruise, the possibility of study the changes in anthropogenic carbon storage, calcite/aragonite horizon and pH from 1990s to present times are planned as future work.

Taking into account this recovery of carbon data in the Atlantic Ocean, the increment in global carbon databases should be noted. The recovery and analysis of these A_T and C_T data from A06 and A07 cruises allows to future works having old references in the equatorial Atlantic Ocean because this area has never again been sampled since the 1990s WOCE cruises.

The innovative 3-DwMLR method applied in this work to recover A_T in the Equatorial Atlantic Ocean could be applied to other carbon variables, and of course, in other areas

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of the Global Ocean being a useful tool to check and calculate data. On the other hand, the widely applied crossovers analysis is an easily and usable tool to check the quality of own data. Therefore, combining both 3-DwMLR and crossovers analysis methods could be used, as in the present work, to improve, for example, sampled and analysed data from a particular cruise and to recover data from rejected cruises.

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References

Clayton, T. and Byrne, R. H.: Spectrophotometric seawater pH measurements: Total hydrogen ion concentration scale concentration scale calibration of m-cresol purple and at-sea results, Deep-Sea Res. Pt. I, 40, 2115–2129, 1993.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res. Pt. I, 34, 1733–1743, 1987.

Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., and Wong, C. S.: Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector, Mar. Chem., 17, 1–21, 1993.

Johnson, K. M., Dickson, A. G., Eischeid, G., Goyet C., Guenther, P., Key, R. M., Millero, F. J., Purkerson, D., Sabine, C. L., Schottle, R. G., Wallace, D. W. R., Wilke, R. J., and Winn, C. D.: Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of

total inorganic carbon measurements made during the US Indian Ocean CO Survey 1994–1996, Mar. Chem., 63, 21–37, 1998.
Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J., Feely, R. A., Millero, F., Mordy, C. and Peng, T. H.: A global ocean carbon climatology: Results from GLODAP, Global Biogeochem. Cy., 18, GB4031, doi:10.1029/2004GB002247, 2004.
Key, R. M., Tanhua, T., Olsen, A., Hoppema, M., Jutterström, S., Schirnick, C., van Heuven, S., Kozyr, A., Lin, X., Velo, A., Wallace, D. W. R., and Mintrop, L.: The CARINA data synthesis project: introduction and overview, Earth Syst. Sci. Data, 2, 105–121, doi:10.5194/essd-2-105-2010, 2010.
Lee, K., Tong, L. T., Millero, F. J., Sabine, C. L., Dickson, A. G., Goyet, C., Park, G. H., Wanninkhof, R., Feely, R. A., and Key, R. M.: Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, Geophys. Res. Lett., 33, L19605, doi:10.1029/2006GL027207, 2006.
Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., and Liu, Y.-M.: The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim. Cosmochim. Ac., 74, 1801–1811, 2010.
Mehrbach, C., Culberson C. H., Hawley J. E., and Pytkowicz R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr. 18, 897–907, 1973.
Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Ac., 59, 661–677, 1995.
Mintrop, L., Pérez, F. F., González-Davila, M., Santana-Casiano, M. J., and Kortzinger, A.: Alkalinity determination by potentiometry: Intercalibration using three different methods, Cienc. Mar., 26, 23–37, 2000.
Oudot, C.: Total CO_2 and total alkalinity data obtained during the R/V L'Atalante cruise in the Atlantic Ocean, (WOCE Section A06, 2 January–10 February 1993) http://cdiac.ornl.gov/ftp/oceans/a06woce/, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.WOCE_A06_1993, 1993a.
Oudot, C.: Carbon Data Obtained during the R/V L'Atalante cruise in the Atlantic Ocean (WOCE Section A07, 13 February–19 March 1993) http://cdiac.ornl.gov/ftp/oceans/a07woce/, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.WOCE_A07_1993, 1993b.

Oudot C., Ternon, J. F. and Lecomte, J.: Measurements of atmospheric and oceanic CO_2 in the tropical Atlantic: 10 years fater 1982–1984 FOCAL cruises, Tellus, 47B, 70–85, 1995.

Pérez, F. F. and Fraga, F.: A precise and rapid analytical procedure for alkalinity determination, Mar. Chem., 21, 169–182, 1987.

Pierrot, D., Lewis, E., and Wallace, D. W. R.: MS Excel Program Developed for CO2 System Calculations. ORNL/CDIAC-105a, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 2006.

Sabine, C. L., Key, R. M., Kozyr, A., Feely, R. A., Wanninkhof, R., Millero, F. J., Peng, T.-H., Bullister, J. L., and Lee, K.: Global Ocean Data Analysis Project: Results and Data. ORNL/CDIAC- 145, NDP-083, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 110 pp., doi:10.3334/CDIAC/otg.ndp083, 2005.

Tanhua, T.: Matlab Toolbox to Perform Secondary Quality Control (2nd QC) on Hydrographic Data. ORNL/CDIAC-158, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.CDIAC_158, 2010.

Tanhua, T., Steinfeldt, R., Key, R. M., Brown, P., Gruber, N., Wanninkhof, R., Perez, F., Körtzinger, A., Velo, A., Schuster, U., van Heuven, S., Bullister, J. L., Stendardo, I., Hoppema, M., Olsen, A., Kozyr, A., Pierrot, D., Schirnick, C., and Wallace, D. W. R.: Atlantic Ocean CARINA data: overview and salinity adjustments, Earth Syst. Sci. Data, 2, 17–34, doi:10.5194/essd-2-17-2010, 2010a.

Tanhua, T., van Heuven, S., Key, R. M., Velo, A., Olsen, A., and Schirnick, C.: Quality control procedures and methods of the CARINA database, Earth Syst. Sci. Data, 2, 35–49, doi:10.5194/essd-2-35-2010, 2010b.

Velo, A., Pérez, F. F., Lin, X., Key, R. M., Tanhua, T., de la Paz, M., Olsen, A., van Heuven, S., Jutterström, S., and Ríos, A. F.: CARINA data synthesis project: pH data scale unification and cruise adjustments, Earth Syst. Sci. Data, 2, 133–155, doi:10.5194/essd-2-133-2010, 2010a.

Velo, A., Vázquez-Rodríguez, M., Padín, X. A., Gilcoto, M., Ríos, A. F., and Pérez, F. F.: A multiparametric method of interpolation using WOA05 applied to anthropogenic CO_2 in the Atlantic, Sci. Mar., 74, 21–32, 2010b.

Velo, A., Pérez, F. F., Tanhua, T., Gilcoto, M., Ríos, A. F., and Key, R. M.: Total alkalinity estimation using MLR and neural network techniques, J. Marine Syst., submitted, 2011.

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4, 99–122, 2011

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Wallace, D. W. R.: Monitoring global ocean carbon inventories, Ocean Observing System Development Panel, Texas A&M University, College Station, TX, 54 pp., 1995.
Wanninkhof, R., Peng, T.-H., Huss, B., Sabine, C. L., and Lee, K.: Comparison of inorganic carbon system parameters measured in the Atlantic Ocean from 1990 to 1998 and recommended adjustments, ORNL/CDIAC-140, 43 pp., 2003.

ESSDD
4, 99–122, 2011

Table 1. Information about the cruises selected from combined GLODAP and CARINA database including A06 and A07 cruises. The cruise number is the number assigned by GLODAP or CARINA databases, Expocode is the international name for the cruise, Alias is a little name for each cruise, Year is the year when the cruise was carried out, Database is the open access database to which belong each cruise, and, in the last column, Crossovers means if the defined cruise was selected to use in crossover analysis of A06, A07 or both of them.

Cruise number	Expocode	Alias	Year	Database	Crossovers
19	35A3CITHER3_2	A13	1995	GLODAP	A07
20	35A3CITHER3_1	A14	1995	GLODAP	A07
21	316N142_3	A15	1994	GLODAP	A06 & A07
22	OACES91_1-2	A16Sa	1991	GLODAP	A07
23	OACES93	A16Na	1993	GLODAP	A06 & A07
24	3230CITHER2_1-2	A17	1994	GLODAP	A06 & A07
35	316N83_a,c	A12/A13	1983	GLODAP	A06 & A07
43	GEOSECS_1-9	GEOSECS	1972	GLODAP	A06 & A07
46	TTOTAS_1-3	TTO-TAS	1982	GLODAP	A06 & A07
48	318MSAVE_1-5_HYDROS4	SAVE	1987	GLODAP	A06 & A07
61	29HE20010305	(FICARAM II; HE073; WOCE A17 repeat)	2001	CARINA	A06 & A07
62	29HE20020304	(FICARAM IV; HE081; WOCE A17 repeat)	2002	CARINA	A06 & A07
84	33LK19960415	(33LKETAMBOT2_1; WOCE AR04h/AR15)	1996	CARINA	A06 & A07
86	33RO20030604	(CLIVAR A16N_2003)	2003	CARINA	A06 & A07
87	33RO20050111	(CLIVAR A16S_2005)	2005	CARINA	A07
95	35LU19950909	(35LLETAMBOT1_1; WOCE AR04g)	1995	CARINA	A06 & A07
106	35TH19990712	(35TH9907; Equalant99)	1999	CARINA	A06 & A07
10	35A3CITHER1_2	A06	1993	–	
11	35A3CITHER1_1	A07	1993	–	

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Table 2. Results from crossover analysis applied to $A_{T\,MLR}$ and $C_{T\,orig}$ of A06 and A07 cruises. Cruise number is the number assigned by GLODAP or CARINA databases. Cruise Crossover ID is the identity given to each cruise in the crossover analysis. Offset and Uncertainty are the offset ± standard deviation obtained from crossover analysis, while the mean offset is the mean value of all offsets including in each A_T or C_T analysis.

	$A_{T\,MLR}$					$C_{T\,orig}$			
	Cruise number	Cruise Crossover ID	Offset	Uncertainty	Mean offset A_T	Cruise Crossover ID	Offset	Uncertainty	Mean offset C_T
A06	84	1	−0.7	4.6	−2.1	1	−8.2	5.6	−11.5
	86	2	0.2	1.8		2	−12.6	1.9	
	95	3	−3.2	2.6		3	−9.8	3.3	
	106	4	−8.7	3.3		–	–	–	
	23	5	−0.4	2.2		4	−13.2	2.0	
	24	6	−5.7	2.0		5	−11.9	2.5	
	46	7	−1.1	4.4		6	−13.1	4.3	
	48	8	3.1	7.6		–	–	–	
A07	84	1	−0.7	8.1	−1.0	1	−8.2	6.7	−9.2
	86	2	−1.4	1.6		2	−5.2	2.8	
	87	3	0.4	2.5		3	−8.9	3.7	
	106	4	0.4	7.0		4	−9.2	9.1	
	19	–	–	–		5	−20.7	4.9	
	20	5	−7.3	3.2		6	−8.0	3.4	
	21	6	3.1	3.3		7	−7.2	2.6	
	22	7	2.5	3.3		8	−12.2	1.5	
	23	–	–	–		9	−4.7	1.8	
	24	8	−5.1	2.0		10	−7.7	1.9	
	48	–	–	–		11	−9.8	10.9	

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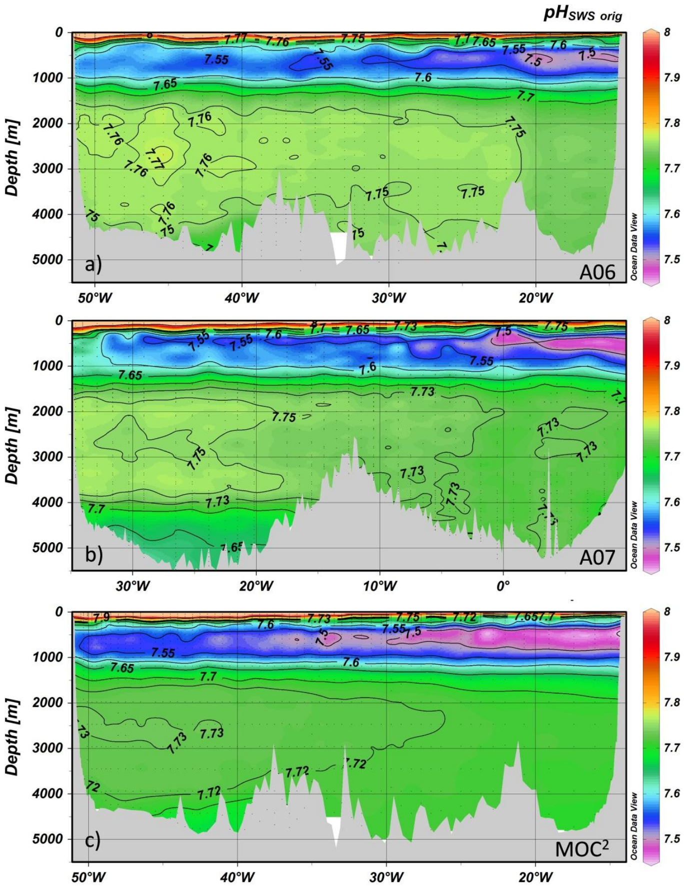

Fig. 1. pH profiles of **(a)** A06, **(b)** A07 and **(c)** MOC^2 cruises. $pH_{SWS\,orig}$ values from A06 and A07 cruises were calculated from $A_{T\,orig}$ and $C_{T\,orig}$ data using the CO_2sys, while $pH_{SWS\,orig}$ values from MOC^2 were measured values.

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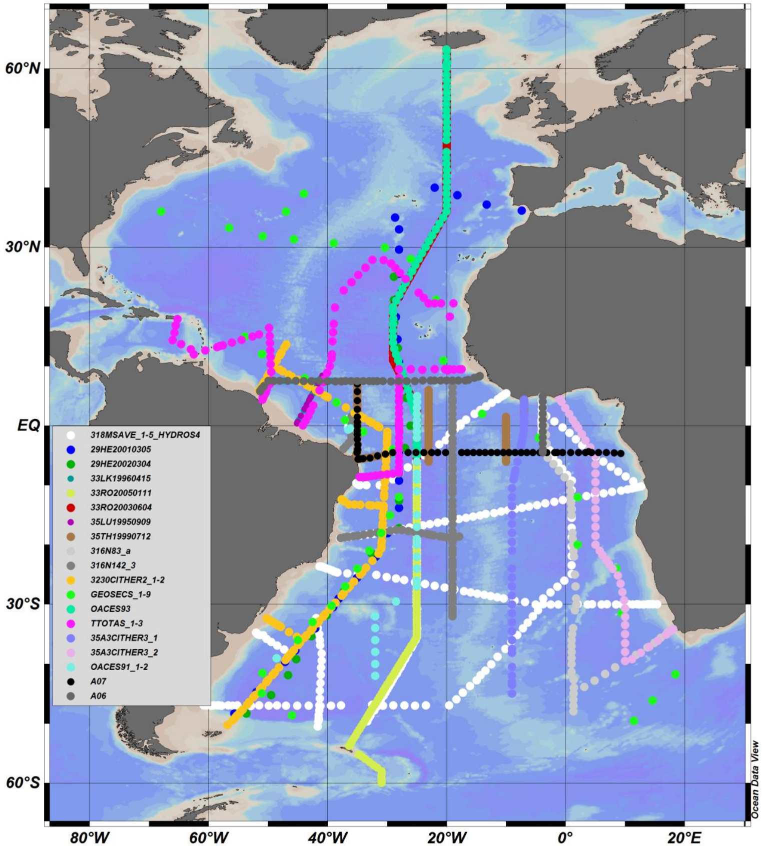

Fig. 2. Geographical distribution of selected cruises of the combined GLODAP and CARINA database carried out near A06 and A07 cruises. These both A06 and A07 cruise are also shown while MOC^2 cruise, which is not show, is a repetition of A06 stations.

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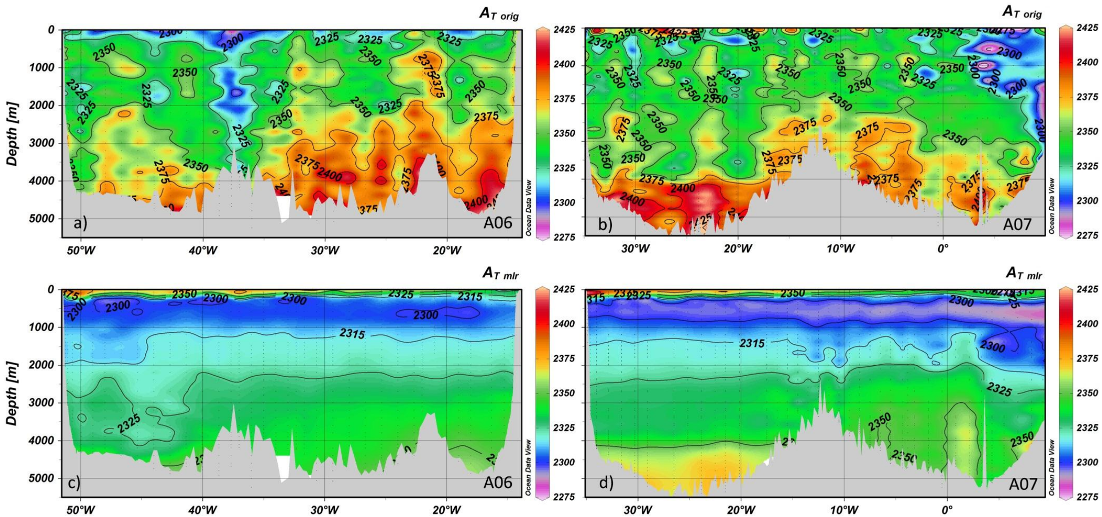

Fig. 3. A_T data. The upper panels show the unreliable $A_{T\,\mathrm{orig}}$ profiles of A06 and A07 cruises (**a** and **b**, respectively) while the lower panels, **(c)** and **(d)**, show the recovered $A_{T\,\mathrm{MLR}}$ profiles of A06 and A07, respectively.

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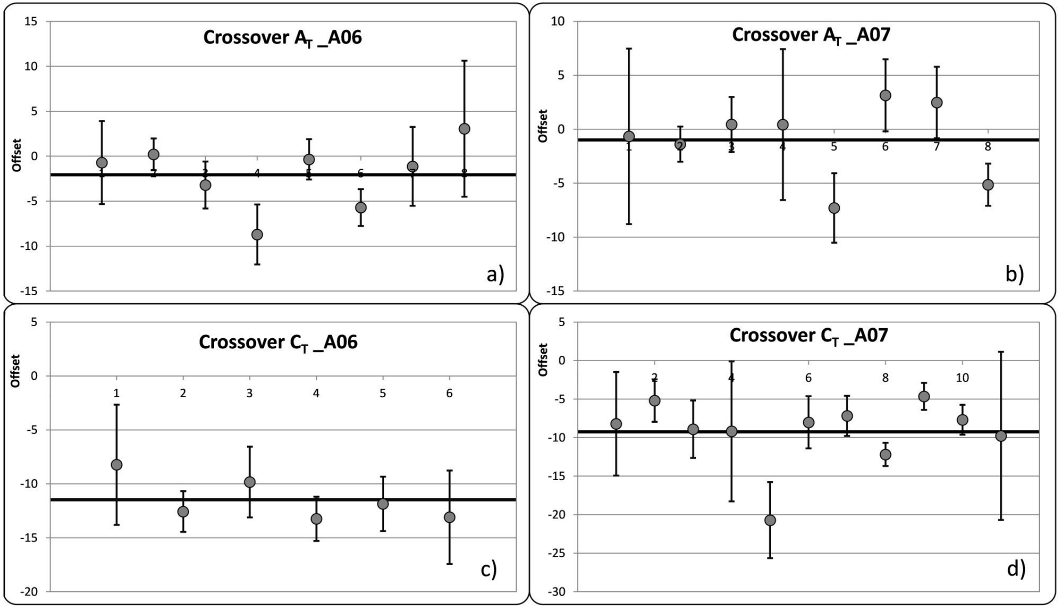

Fig. 4. Offsets obtained from crossover analysis method applied to $A_{T\,orig}$ (**a** and **b** for A06 and A07, respectively) and $C_{T\,orig}$ data (**c** and **d** for A06 and A07, respectively). For each individual graph, the "y-axis" represents the offset value in µmol kg^{-1} and the "x-axis" the *crossover ID* given to each cruises. Each point is the obtained offset with their associated uncertainty.

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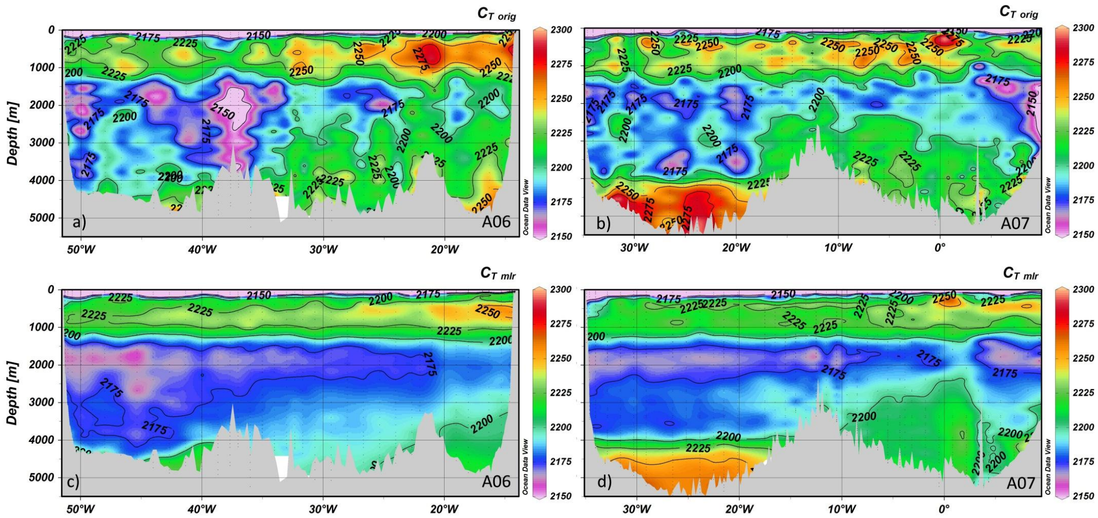

Fig. 5. C_T data. The **(a)** and **(b)** panels show the unsuitable $C_{T\,orig}$ profiles of A06 and A07 cruises, respectively, while the **(c)** and **(d)** panels show the recovered $C_{T\,MLR}$ profiles of A06 and A07, respectively.

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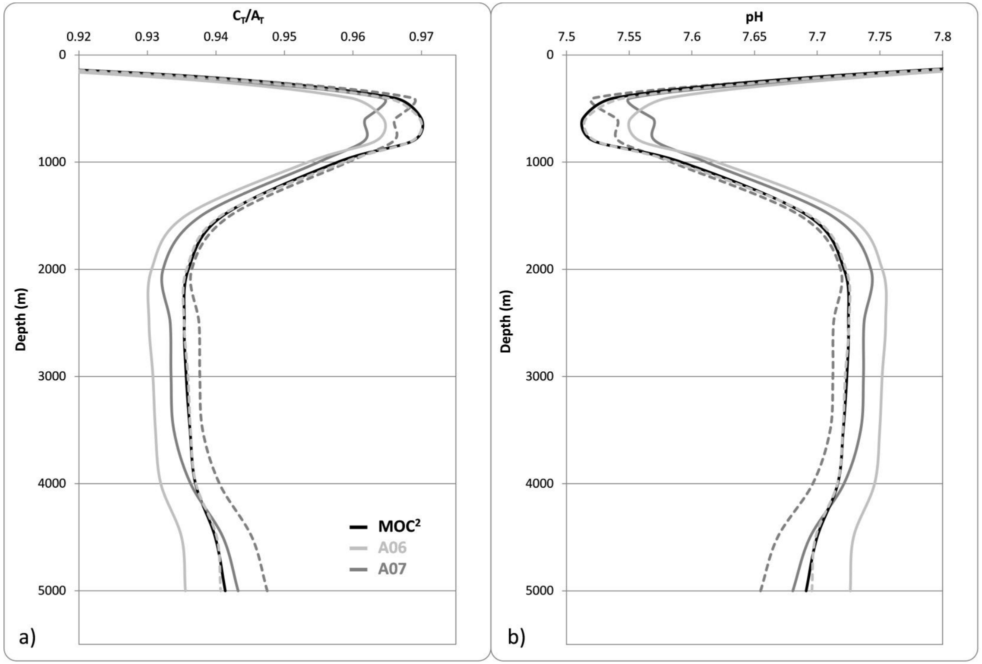

Fig. 6. Mean profiles of **(a)** $\frac{C_T}{A_T}$ ratio and **(b)** pH for A06 (light grey lines), A07 (dark grey lines) and MOC^2 (black lines). The A06 and A07 continuous lines display the original data, $\frac{C_T\,\mathrm{orig}}{A_T\,\mathrm{orig}}$ ratio and pH_{orig}, while the dashed lines are the recovered data, $\frac{C_T\,\mathrm{MLR}}{A_T\,\mathrm{MLR}}$ ratio and pH_{MLR}.