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CARINA TCO_2 data in the Atlantic Ocean

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Abstract. Water column data of carbon and carbon-relevant hydrographic and hydrochemical parameters from 188 cruises in the Arctic Mediterranean Seas, Atlantic and Southern Ocean have been retrieved and merged in a new data base: the CARINA (CARbon IN the Atlantic) Project. These data have gone through rigorous quality control (QC) procedures so as to improve the quality and consistency of the data as much as possible. Secondary quality control, which involved objective study of data in order to quantify systematic differences in the reported values, was performed for the pertinent parameters in the CARINA data base. Systematic biases in the data have been tentatively corrected in the data products. The products are three merged data files with measured, adjusted and interpolated data of all cruises for each of the three CARINA regions (Arctic Mediterranean Seas, Atlantic and Southern Ocean). Ninety-eight cruises were conducted in the "Atlantic" defined as the region south of the Greenland-Iceland-Scotland Ridge and north of about 30° S. Here we report the details of the secondary QC which was done on the total dissolved inorganic carbon (TCO_2) data and the adjustments that were applied to yield the final data product in the Atlantic. Procedures of quality control – including crossover analysis between stations and inversion analysis of all crossover data – are briefly described. Adjustments were applied to TCO_2 measurements for 17 of the cruises in the Atlantic Ocean region. With these adjustments, the CARINA data base is consistent both internally as well as with GLODAP data, an oceanographic data set based on the WOCE Hydrographic Program in the 1990s, and is now suitable for accurate assessments of, for example, regional oceanic carbon inventories, uptake rates and model validation.

Data coverage and parameter measured

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

For a list of parameters, see Key et al. (2010).

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1 Introduction

CARINA is a database containing inorganic carbon, alkalinity and relevant associated data such as temperature, salinity inorganic nutrients and oxygen from hydrographic cruises in the Arctic Mediterranean Seas, Atlantic and Southern Oceans. The project started as an informal, unfunded project in Delmenhorst, Germany, in 1999 during the workshop on "CO_2 in the North Atlantic", with the main goal to create a uniformly formatted database of carbon and carbon relevant variables in the ocean to be used for accurate assessments of oceanic carbon inventories and uptake rates. The collection of data and the quality control of the data have been a main focus of the CARINA project. During the project, both primary and secondary quality control (QC) of the data have been performed. Primary QC is the process whereby the quality of the data is assessed to be reasonable, based on general knowledge of the data and known trends in the Atlantic. Secondary QC assesses the quality of the data based on more advanced knowledge of parameters affecting the data and usually requires further analysis. This report describes the consistency analysis of total dissolved inorganic carbon (TCO_2) for the Atlantic Ocean part of the CARINA database. A more comprehensive description of the complete CARINA database can be found in Key et al. (2010) as well as the other papers in this special issue. The CARINA database consists of two parts: the first part is the individual cruise files containing all the original data as reported by the measurement teams including, in many cases, the quality flags originally assigned to the data. These files are in the World Ocean Circulation Experiment (WOCE) Hydrographic Program Office (WHPO) exchange format where the first lines consist of the condensed metadata. There are no calculated or interpolated values in the individual cruise files, and no adjustments have been applied to any of these values.

The second part of CARINA is three merged data sets, one for each of the Atlantic Ocean (NA), Arctic Mediterranean Seas (AMS), and Southern Ocean (SO) regions. These files constitute the whole CARINA data set which has been modified from the original data set in the following ways: it includes interpolated values for nutrients, oxygen, and salinity when those data were missing and the criteria for interpolation described in Key et al. (2010) was met. It also includes calculated carbon parameters when possible (e.g. if pH was missing but TCO_2 and Total Alkalinity (TALK) were measured, pH was calculated). Calculations were made using the Matlab® version of the CO2SYS Program (van Heuven et al., 2009), using the sulfuric acid constant of Dickson (1990), the hydrofluoric acid constant of Dickson and Riley (1979) and the carbonate constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). Calculated and interpolated values have been given the quality flag "0" to distinguish them from measured data. Finally, most parameters in the merged data files have been adjusted according to the corrections described in Sect. 4. The parameters that were considered for adjustment in CARINA are salinity, TCO_2, TALK, pH, O_2, nutrients and CFCs. Other parameters, such as ^{14}C, ^{13}C and SF_6, which were present in the individual cruise files, have not been included in the secondary QC procedures and are included in the merged data files as is. This article reports on the adjustments determined for the TCO_2 data.

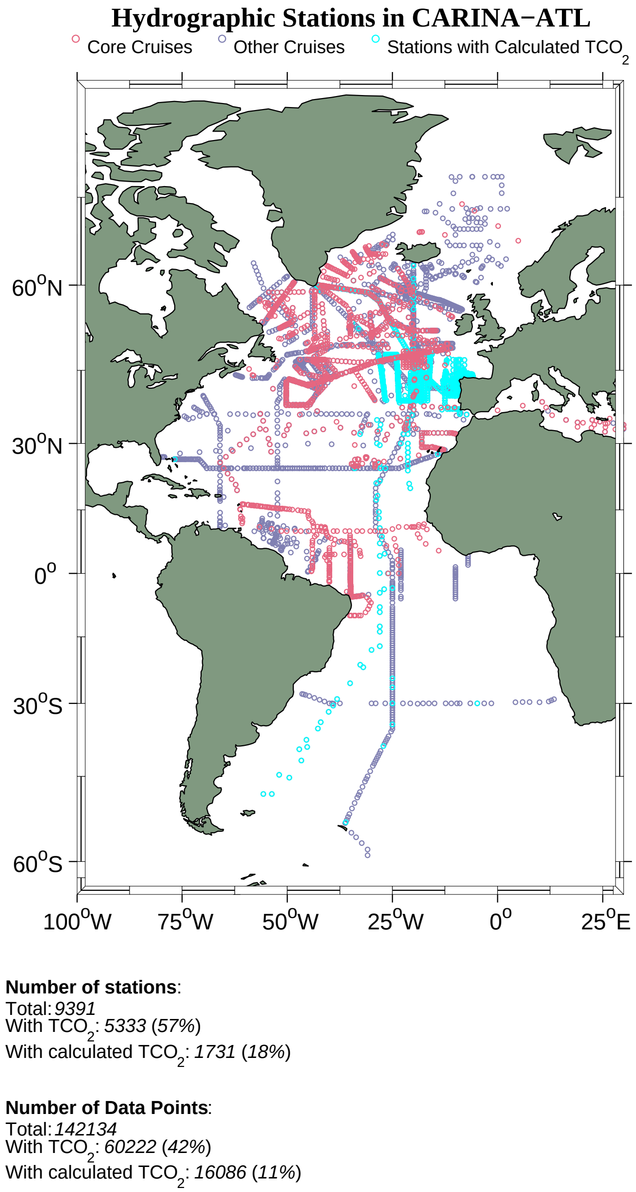


Figure 1. Plot of all the hydrographic stations in CARINA-Atlantic data set (CARINA-ATL). Only about half the stations (stations "with TCO_2") reported TCO_2 values (measured or calculated).

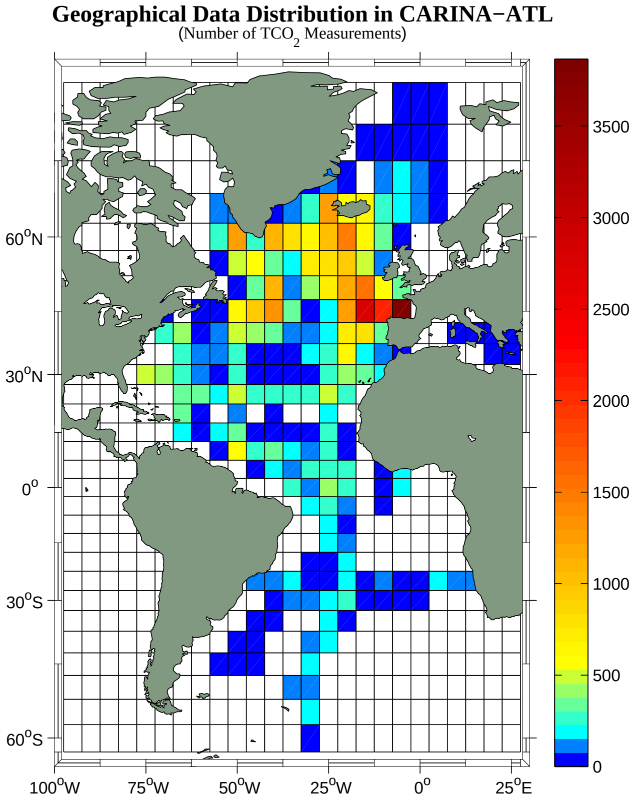


Figure 2. Geographical TCO_2 data distribution in the CARINA Atlantic data set. Each square is a $5^\circ \times 5^\circ$ bin and its color represents the number of TCO_2 measurements made in that bin. Bins with no TCO_2 measurements are blanked.

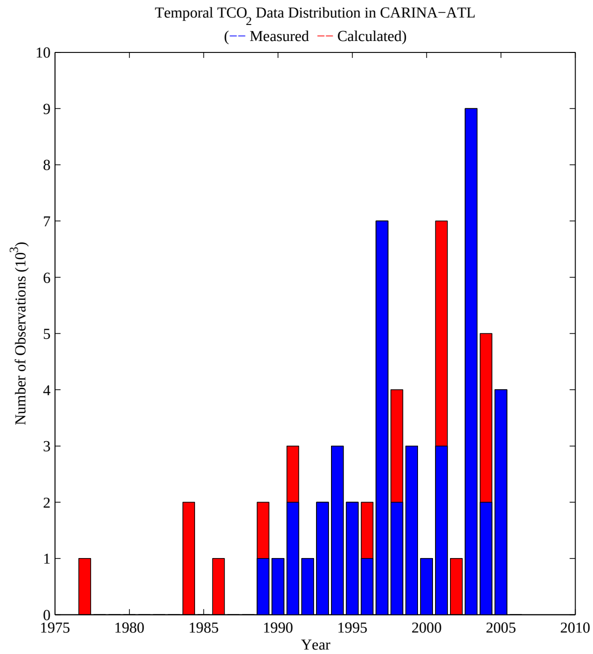


Figure 3. Temporal TCO_2 data distribution (measured in blue and calculated in red) in the CARINA Atlantic data set.

2 Data provenance and structure

The CARINA database includes data and metadata from 188 oceanographic cruises/campaigns, of which 5 entries consist of multiple cruises. The Atlantic Ocean subset of the CARINA data set (CARINA-ATL) consists of 98 cruises/entries, of which one is a time series, and two are collections of multiple cruises over several years within the framework of a common project. Five of these cruises are in common with the Southern Ocean (SO) region, and five are in common with the Arctic Mediterranean Seas (AMS) region. These overlapping cruises ensure consistency between the three regions of the CARINA data set. Additionally, six reference cruises are included in the secondary QC for CARINA-ATL to ensure consistency between CARINA and historical data bases, i.e. the Global Ocean Data Project (GLODAP). The cruises included in the CARINA data products generally exclude those that were included in GLODAP. This was done primarily to facilitate later merging of these two data products. There are, however, 3 exceptions: 06MT19941012, 06MT19941115 and 74DI19970807 (Cruise Numbers 12, 13 and 171 respectively). These cruises were added to CARINA because additional parameters critical to the CARINA goals became available after GLODAP was published.

The Atlantic Ocean region of CARINA is loosely defined as the area between the Greenland-Iceland-Scotland Ridge and 30° S (Key et al., 2010), but several cruises overlap with the surrounding regions, thus extending the spatial area covered. Figure 1 shows the position of all hydrographic stations in CARINA-ATL. Figure 2 shows the geographical distribution of the TCO_2 measurements whereas Fig. 3 represents the distribution of the TCO_2 measurements over the years. As can be seen from Figs. 1 and 2, most of the data are from the Subpolar North Atlantic. Large data gaps exist for the Tropical and South-Eastern part of the Atlantic Ocean. Figure 3 shows that although the CARINA-ATL database spans almost three decades from 1978 to 2006, the majority (71%) of the TCO_2 measurements were made from the mid 1990's to the mid 2000's. Overall, TCO_2 is measured at 57% the stations occupied on the cruises, about the same as TALK compared to about 80% for salinity, oxygen and nutrients. Of note is that chloro-fluoro carbon (CFC) data are particularly abundant for some regions.

The individual cruises/campaigns are uniquely identified by a string of 12 characters called an EXPOCODE. The first 2 characters represent a 2-digit number identifying the country code of the research vessel. They are followed by a two-character platform code uniquely assigned by the National Oceanographic Data Center (NODC, see www.nodc.noaa.gov). The final eight characters denote the date of departure from port in the format YYYYMMDD. For instance, the EXPOCODE 06MT20040311 refers to a cruise conducted on the German (06) ship Meteor (MT) which departed on 11 March 2004. The expocodes of the cruises used in CARINA-ATL are listed in Table 1. The table shows that a large number of nations and research ships were involved in the collection of the data over the years. Table 2 in Tanhua et al. (2010b) provides listing of ships and nations involved in the cruises. Several of these cruises were part of multi-cruise and multi-year, nationally and internationally funded projects. Table 1 contains the values of the adjustments which were agreed upon by the participants of the North Atlantic group of the CARINA project and which were applied to the original data to obtain the merged data product. This report presents the motivation for the TCO_2 adjustments.

Analyses

The TCO_2 measurements are a key parameter in the CARINA effort such that we provide a short description of analysis methodologies. Prior to the mid-1980s, TCO_2 was determined by potentiometric titration with acid as part of alkalinity titrations. The TCO_2 was determined from the amount of acid needed to go from the first to the second inflection point in the titration curve (Bradshaw et al., 1981). Electrodes give stable results but require careful calibrations, which is impractical for at-sea work so while the method is precise, the accuracy is poor (±10 µmol kg^{-1}). The second approach was to acidify a small aliquot of sample and measure to evolved CO_2 by a gas chromatograph (Takahashi, 1983) or infrared analyzer. This accuracy of this approach was limited by the accuracy of the delivery of the small sample (~0.5 ml). Adaptations of these methods are currently employed in underway and autonomous systems (Wang et al., 2007).

The accuracy of TCO_2 measurements greatly improved at the start of the WOCE Hydrographic Program (WHP) because of several major developments. An integrative analysis method was perfected based on coulometry and these analytical systems were commercially produced (UIC, Inc.). An accurate inlet and dispensing system was developed, called a Single Operator Multi-parameter Metabolic Analyzer (SOMMA) with a high degree of automation facilitating relatively rapid sample throughput of a sample every 15 to 20 minutes (Johnson et al., 1993). These systems were provided to all investigators of the CO_2 program of WHP funded by the US Department of Energy (DOE). This meant rapid and uniform adaptation to this technology. As part of the DOE effort a handbook of best practices was developed providing guidance on proper sampling, analysis, and data reduction techniques for inorganic carbon system analyses (DOE, 1994). Finally, the accuracy of the measurements was greatly improved by production of Certified Reference Materials, CRMs (Dickson et al., 2003) that were provided to all investigators making measurements on the WHP cruises free of charge or at nominal costs. With adaptation of the protocols and use of the new instrumentation, the accuracy of the measurements increased by 5 to 10-fold and reported accuracies of 1–2 µmol kg^{-1} are now common.

The CARINA data set for TCO_2 has a large number of cruises that benefited from these improvements. When the information is available, Table 1 indicates which cruises had analyses that were referenced to CRM values and which cruises used a coulometer, listed as Coul, for analyses, or a SOMMA for extraction of CO_2 from the sample. In the latter case, a coulometer was always used for analyses. Of the 26 cruises which are known to have used CRMs and have enough data, only 5 needed adjustments to reach consistency with the other cruises.

3 Computational analysis approach

The main goal of the CARINA project was to gather all available hydrographic cruise data for the Atlantic, Arctic Mediterranean Seas and Southern Ocean and using secondary quality control (QC) procedures, determine a set of corrections, or *adjustments*, per parameter. These adjustments are applied to the cruises to generate a self-consistent data set.

A first level of QC (primary QC) was applied as part of collating all cruises into the Atlantic, Arctic Mediterranean Seas and Southern Ocean data set. This involved correcting for obvious reporting errors and outliers (Tanhua et al., 2010a). The second level of QC (secondary QC), which involves determining the adjustments to make the TCO_2 values consistent for the data set, was highly automated using custom designed software and is described in detail in Tanhua et al. (2010a). The basic criteria if TCO_2 values need to be adjusted is based on comparison of stations of different cruises where they overlap or cross each other in space. This is called the crossover analyses. An inverse least squares routine was applied to all Atlantic crossover data and the deviation of the data from the least squares solution was determined. To assign adjustments, it was a priori assumed that the cruises would respectively be biased with a constant offset. That is, the methods do not lend themselves to determining trend in biases with depth, for instance, or with time along a cruise track.

Only data which were collected below ~1500 m and in the same oceanographic region (Atlantic) were compared to each other in order to minimize the effect of natural variability in the studied parameter. In the crossover approach, two cruises are compared if they have at least 3 stations with enough data below 1500 m within a radius of 222 km (i.e. 2° of latitude). For each crossover identified, an *offset* and its standard deviation were calculated. Thus each cruise had a set of offsets where it "crossed-over" other cruises.

Since each cruise can only have one potential *correction* applied to its data, a least-square method of determining the appropriate correction by matrix inversion (Wunsch, 1996) was applied to our data sets as described in

Table 1. List of the cruises considered in CARINA-ATL and the associated information regarding their TCO_2 data. A question mark refers to information unavailable at the time this article was published. The last columns give the results in μmol kg^{-1} of the different inversions (WLSQ and WDLSQ) performed as described in the text and the final adjustments (μmol kg^{-1}) which were applied to the data to produce the final self-consistent CARINA-ATL data set.

Cruise No.	Expocode	Area[a]	Number of Stations[b]	TCO_2^c	CRM	Method	Core Cruise	WLSQ method	WDLSQ method	WLSQ(adj) method[d]	WDLSQ(adj) method[d]	Adjustment	Adjustment Flag	Article Section[e]
6	06GA19960613	1	125	122	?	?		−2.13 (±1.2)	−1.71 (±1.39)	−1.68 (±1.2)	−1.46 (±1.39)	0	2	4.4
7	06GA20000506	1	75	59	?	?	Yes	−2.31 (±0.48)	−1.86 (±0.83)	−1.73 (±0.48)	−1.48 (±0.85)	0	2	4.4
8	06MT19920316	1	140	59	?	Coul		NA	NA	NA	NA	NC	3	4.2
9	06MT19920509	1	59	58	?	?		−2.54 (±0.75)	−2.11 (±1.02)	−1.46 (±0.67)	−1.22 (±0.98)	0	2	4.4
10	06MT19920701	5	88	88	?	Coul		2.23 (±0.89)	2.66 (±1.13)	3.28 (±0.84)	3.51 (±1.1)	0	3	4.2
12	06MT19941012	1	53	29	yes	Somma		−0.04 (±0.37)	0.4 (±0.78)	1.49 (±0.37)	1.72 (±0.8)	0	2	4.4
13	06MT19941115	1	62	44	yes	?	Yes	0.21 (±0.87)	0.6 (±1.08)	0.86 (±0.87)	1.05 (±1.09)	0	2	4.4
14	06MT19960613	1	16	15	?	?		8.87 (±0.55)	9.3 (±0.88)	4.54 (±0.56)	4.77 (±0.9)	5	2	4.6
15	06MT19960910	1	62	C				−5.98 (±0.98)	−5.52 (±1.2)	−0.09 (±1.01)	0.15 (±1.24)	NA	NA	4.1
16	06MT19970107	1	45	20(C)	yes	Somma		2.26 (±2.23)	2.75 (±2.32)	−2.49 (±2.25)	−2.1 (±2.34)	NC	2	4.3
17	06MT19970515	1	67	30	yes	Somma	Yes	−1.84 (±0.57)	−1.41 (±0.88)	−1.02 (±0.57)	−0.78 (±0.9)	0	2	4.4
18	06MT19970707	1	98	46	?	?	Yes	−0.4 (±0.58)	0 (±0.89)	0.46 (±0.58)	0.67 (±0.9)	0	2	4.4
19	06MT19970815	1	110	78	?	?	Yes	2.63 (±0.65)	2.96 (±0.94)	3.43 (±0.65)	3.58 (±0.95)	0	2	4.4
20	06MT19990610	1	53	29	yes	Somma		2.23 (±0.48)	2.65 (±0.84)	3.31 (±0.48)	3.54 (±0.85)	0	2	4.4
21	06MT19990711	1	100	37	yes	Somma		0.41 (±0.76)	0.81 (±1.03)	1.08 (±0.76)	1.27 (±1.04)	0	2	4.4
23	06MT20010507	1	53	26(C)	yes	Somma		−1.05 (±0.67)	−0.63 (±0.97)	−0.43 (±0.59)	−0.2 (±0.92)	0	2	4.4
25	06MT20010717	1	139	114(C)	yes	?		−1.51 (±0.32)	−1.07 (±0.76)	0.16 (±0.33)	0.39 (±0.78)	0	2	4.4
26	06MT20011018	1	41	14	yes	Coul		NA	NA	NA	NA	NC	NA	4.2
28	06MT20021013	1	51	6	yes	Coul		NA	NA	NA	NA	NC	NA	4.2
30	06MT20030723	1	138	75(C)	yes	Coul	Yes	−2.87 (±0.46)	−2.45 (±0.83)	−2.32 (±0.44)	−2.08 (±0.83)	0	2	4.4
32	06MT20040311	1	46	46	yes	Coul	Yes	−1.77 (±0.66)	−1.23 (±0.93)	−1.66 (±0.71)	−1.34 (±0.96)	0	2	4.4
37	18HU19920527	1	46	27	?	?		−5.43 (±0.79)	−5 (±1.05)	3.77 (±0.81)	3.96 (±1.07)	−9	2	4.6
38	18HU19930405	1	59	15	?	Coul		NA	NA	NA	NA	NC	NA	4.2
39	18HU19930617	1	26	20	?	?	Yes	1.32 (±0.96)	1.65 (±1.15)	2.04 (±0.96)	2.14 (±1.16)	0	2	4.4
40	18HU19931105	1	104	88	?	?		−0.26 (±0.96)	0.22 (±1.18)	0.12 (±1.02)	0.37 (±1.24)	0	2	4.4
41	18HU19940524	1	40	19	?	?		1.72 (±1.98)	2.09 (±2.11)	2.4 (±1.98)	2.56 (±2.11)	0	2	4.4
42	18HU19941012	1	97	80	no	Coul		1.92 (±0.91)	2.28 (±1.12)	2.31 (±0.94)	2.43 (±1.15)	0	2	4.4
43	18HU19950419	1	107	74	no	?		−1.42 (±0.77)	−0.99 (±1.03)	−1.29 (±0.79)	−1.08 (±1.06)	0	2	4.4
44	18HU19970509	1	130	95	yes	?	Yes	−0.86 (±0.79)	−0.45 (±1.05)	0.13 (±0.79)	0.34 (±1.06)	0	2	4.4
51	29CS19771007	1	88	C				NA	NA	NA	NA	NA	NA	4.1
52	29CS19930510	1	92	C				NA	NA	NA	NA	NA	NA	4.1
53	29GD19821110	1	19	C				−7.97 (±2.23)	−7.33 (±2.34)	−1.27 (±2.24)	−0.99 (±2.35)	NA	NA	4.1
54	29GD19831201	1	24	C				NA	NA	NA	NA	NA	NA	4.1
55	29GD19840218	1	33	C				−5.76 (±1.01)	−5.27 (±1.24)	0.2 (±1.02)	0.45 (±1.26)	NA	NA	4.1
56	29GD19840711	1	118	C				8.45 (±1.04)	8.89 (±1.27)	−0.65 (±1.05)	−0.4 (±1.28)	NA	NA	4.1
57	29GD19860904	1	50	C				−11.6 (±1.1)	−11.07 (±1.32)	0.15 (±1.11)	0.4 (±1.34)	NA	NA	4.1
60	29HE19980730	1	44	24(C)	yes	Somma		0.08 (±1.01)	0.54 (±1.23)	0.17 (±1.09)	0.43 (±1.31)	0	2	4.4
61	29HE20010305	3	29	C				−6.72 (±1.65)	−6.17 (±1.79)	−0.67 (±1.65)	−0.36 (±1.8)	NA	NA	4.1
62	29HE20020304	3	29	C			Yes	−0.95 (±2.89)	−0.33 (±2.41)	−0.92 (±2.88)	−0.42 (±2.41)	NA	NA	4.1
63	29HE20030408	1	7	7(C)	yes	Somma		NA	NA	NA	NA	−NC	NA	4.2
64	31AN19890420	1	51	48	no	?		1.58 (±0.79)	2 (±1.05)	2.59 (±0.79)	2.82 (±1.06)	0	2	4.4
65	316N19971005	1	162	44	?	?		−0.96 (±0.54)	−0.53 (±0.87)	−0.32 (±0.52)	−0.07 (±0.88)	0	2	4.4
66	316N20010627	1	29	29	yes	Somma		NA	NA	NA	NA	NC	NA	4.2
68	316N20030922	1	88	88	yes	Somma	Yes	−2.12 (±0.65)	−1.56 (±0.91)	−1.21 (±0.78)	−0.86 (±0.99)	0	2	4.4
69	316N20031023	1	82	82	yes	Somma	Yes	0.62 (±0.72)	1.18 (±0.95)	−0.99 (±0.79)	−0.64 (±1)	0	2	4.4
81	32OC19950529	1	51	6	?	?		NA	NA	NA	NA	NC	NA	4.2
84	33LK19960415	1	94	85	yes	?		6.43 (±5.34)	5.97 (±4.99)	1.32 (±4.02)	1.7 (±3.85)	5	2	4.6
85	33RO19980123	1	130	126(C)	yes	Somma	Yes	−1.52 (±0.6)	−0.97 (±0.87)	−1.28 (±0.68)	−0.93 (±0.92)	0	2	4.4
86	33RO20030604	1	150	149(C)	yes	Somma	Yes	−0.66 (±0.4)	−0.22 (±0.79)	−1.27 (±0.42)	−1 (±0.81)	0	2	4.4
87	33RO20050111	3	121	119(C)	yes	Somma	Yes	−1.98 (±1.24)	−1.45 (±1.33)	−2.12 (±1.24)	−1.66 (±1.34)	0	2	4.4
89	33SW20010102	1	34	34	yes	Somma		NA	NA	NA	NA	NC	NA	4.2
90	33SW20030418	1	27	27	yes	Somma		NA	NA	NA	NA	NC	NA	4.2
92	35A320010203	1	79	C				−1.19 (±0.93)	−0.75 (±1.16)	−0.36 (±0.93)	−0.12 (±1.17)	NA	NA	4.1
93	35A320010322	1	48	C				NA	NA	NA	NA	NA	NA	4.1
94	35LU19890509	1	47	C				−5.47 (±0.87)	−4.95 (±1.13)	0.83 (±0.94)	1.09 (±1.19)	NA	NA	4.1
95	35LU19950909	1	85	47	yes	?		7.32 (±6.96)	6.26 (±6.32)	−1.69 (±6.86)	−1.04 (±6.28)	9	2	4.6
106	35TH19990712	1	99	91(C)	yes	?		5.05 (±2.1)	5.35 (±2.13)	−0.87 (±1.99)	−0.44 (±1.99)	6	2	4.6
107	35TH20010823	1	83	C				NA	NA	NA	NA	NA	NA	4.1
108	35TH20020611	1	90	C			Yes	−5.14 (±0.32)	−4.7 (±0.76)	−3.54 (±0.33)	−3.3 (±0.78)	NA	NA	4.1
109	35TH20040604	1	114	C			Yes	−0.93 (±0.32)	−0.49 (±0.76)	0.67 (±0.33)	0.91 (±0.78)	NA	NA	4.1
113	49NZ20031106	3	111	54(C)	yes	Coul	Yes	−0.34 (±2.18)	0.08 (±1.94)	−0.61 (±2.05)	−0.13 (±1.85)	0	2	4.4
125	58AA20010527	5	129	92	yes	?		NA	NA	NA	NA	0	2	4.4
130	58JH19920712	5	31	24	yes	Coul		−4.74 (±1.4)	−4.34 (±1.57)	−3.94 (±1.4)	−3.7 (±1.58)	NA	2	4.3
135	58JH19940723	5	74	78	yes	Coul		−5.62 (±0.72)	−5.2 (±1)	−4.83 (±0.72)	−4.59 (±1.01)	NC	2	4.3
152	64PE20000926	1	39	39	yes	f		8.63 (±1.19)	8.97 (±1.39)	0.37 (±1.08)	0.6 (±1.3)	9	2	4.5
153	64TR19890731	1	73	34	yes	Coul		3.86 (±0.77)	4.27 (±1.04)	5.04 (±0.77)	5.26 (±1.05)	0	2	4.4
154	64TR19900417	1	23	15	?	?		8.34 (±0.33)	8.78 (±0.77)	NA	NA	NC	3	4.2
155	64TR19900701	1	33	14	?	Coul	Yes	6.71 (±0.64)	6.98 (±0.93)	0.11 (±0.64)	0.34 (±0.94)	7	2	4.5
156	64TR19900714	1	74	34	?	Coul		0.82 (±1)	1.22 (±1.22)	1.63 (±1)	1.86 (±1.23)	0	2	4.4
157	64TR19910408	1	141	138	?	Coul	Yes	5.53 (±0.89)	5.67 (±1.1)	0.35 (±0.89)	0.55 (±1.11)	6	2	4.5
158	67SL19881117	1	20	C				NA	NA	NA	NA	NA	NA	4.1
159	74AB19900528	1	71	1	?	?		NA	NA	NA	NA	NC	NA	4.2
160	74AB19910501	1	614	C				0.91 (±0.74)	1.34 (±1.01)	1.77 (±0.74)	2.01 (±1.03)	NA	NA	4.1
161	74AB19910614	1	143	17	?	?		NA	NA	NA	NA	NC	NA	4.2
164	74AB20050501	1	144	70	yes	Coul		−1.37 (±0.67)	−0.85 (±0.94)	NA	NA	0	2	4.4
165	74DI19890511	1	990	786	?	?		NA	NA	NA	NA	NC	NA	4.2
166	74DI19890612	1	87	4	?	?		NA	NA	NA	NA	NC	NA	4.2
168	74DI19900425	1	17	14	?	?		NA	NA	NA	NA	NC	NA	4.2
169	74DI19900515	1	43	7	?	?		NA	NA	NA	NA	NC	NA	4.2

Table 1. Continued.

Cruise No.	Expocode	Area[a]	Number of Stations[b]	TCO_2^c	CRM	Method	Core Cruise	WLSQ method		WDLSQ method		WLSQ(adj) method[d]		WDLSQ(adj) method[d]		Adjustment	Adjustment Flag	Article Section[e]
170	74DI19900612	1	20	11(C)	?	?		−9.96	(±0.32)	−9.52	(±0.76)	−1.36	(±0.32)	−1.12	(±0.78)	−7	2	4.6
171	74DI19970807	1	143	90(C)			Yes	−1.11	(±0.65)	−0.66	(±0.94)	−1.21	(±0.67)	−0.95	(±0.97)	0	2	4.4
172	74DI19980423	1	44	C			Yes	0.53	(±0.82)	0.9	(±1.05)	1.3	(±0.84)	1.47	(±1.07)	NA	NA	4.1
173	74DI20040404	1	123	69	yes	Coul	Yes	−0.92	(±0.84)	−0.41	(±1.05)	−0.86	(±0.85)	−0.54	(±1.06)	0	2	4.4
185	IrmingerSea	1	2	1	yes	Coul		NA		NA		NA		NA		NC	NA	4.2
Ref[g]	29HE19920714	1					Yes	−5.92	(±0.73)	−5.28	(±0.96)	NA		NA		0	3	4.6
Ref[g]	316N19961102	1					Yes	−1.18	(±0.51)	−0.75	(±0.85)	−0.23	(±0.46)	0	(±0.84)	0	2	4.4
Ref[g]	316N19970717	1					Yes	−1.02	(±0.71)	−0.47	(±0.95)	−0.22	(±0.89)	0.1	(±1.08)	0	2	4.4
Ref[g]	316N19970815	1					Yes	−0.5	(±0.87)	0.05	(±1.06)	−0.47	(±0.97)	−0.13	(±1.14)	0	2	4.4
Ref[g]	317519930704	1					Yes	−0.69	(±0.39)	−0.25	(±0.78)	−0.11	(±0.4)	0.14	(±0.8)	0	2	4.4
Ref[g]	323019940104	3					Yes	−0.66	(±2.49)	−0.36	(±2.13)	−0.68	(±2.15)	−0.2	(±1.91)	0	2	4.4

[a] Synthesis Regions: 1 = Atlantic Ocean, 2 = Southern Ocean, 3 = Atlantic & Southern Ocean, 4 = Arctic Mediterranean Seas, 5 = Atlantic Ocean & Arctic Mediterranean Seas
[b] See CARINA online table for additional information (http://cdiac.esd.ornl.gov/oceans/CARINA/Carina_table.html).
[c] "C" indicates calculated from pH and alkalinity. See CARINA online table for additional information (http://cdiac.esd.ornl.gov/oceans/CARINA/Carina_table.html).
[d] Inversion results after data have been adjusted.
[e] Refers to the section of this article describing the category under which this cruise falls.
[f] Technicon Traacs 800 rapid flow auto-analyzer.
[g] Reference Cruise – see text for explanation.

Johnson et al. (2001). Of the three least-square methods described in Johnson et al. (2001), only two were used here: the Weighted Least-Square (WLSQ) where weights are assigned to cruises in the inversion process, and the Weighted Dampened Least-Square (WDLSQ) in which, in addition to the weights assigned in the WLSQ method, limits are also set for the corrections calculated by the procedure. More details about the methods used are provided in Tanhua et al. (2010a). A set of 29 cruises was selected as *core cruises* because of the expected higher quality of their data, due to the use of CRMs and SOMMAs, as well as their geographical coverage. These core cruises were assigned a higher weight than the others in the inversion procedure to insure that the final CARINA-ATL data set be consistent with the data of highest quality.

An additional 6 cruises, designated as *reference cruises*, were taken from the GLODAP data set (Key et al., 2004), a similar project based on the WHP of the 1990s. These 6 reference cruises were incorporated in the CARINA-ATL database as core cruises to insure consistency with GLODAP but were removed from the final data product. Core cruises are indicated in column 8 of Table 1. Reference cruises do not have an associated cruise number but are listed at the end of Table 1.

The result of the inversion procedure yields a set of *corrections* which, when applied to the individual cruises, are called *adjustments* and reduce the offsets of the crossovers by minimizing the weighed sum of their squares. In the case of TCO_2, additive, rather than multiplicative, corrections were calculated. Since offsets between cruises would most likely be due to offsets in calibration standards, a constant offset was deemed more appropriate. Each correction was thoroughly reviewed by the participants of the project, taking into account the quality of the crossovers, the quality of the data and other factors such as possible temporal or geographical variability to determine whether a correction was reasonable or not. It was agreed that, in general, corrections smaller than 4 μmol kg^{-1} would be within the uncertainty of the offsets and therefore not significant. In these cases, no adjustment was applied and the adjustment was listed as 0 in Table 1. Corrections greater than 4 μmol kg^{-1} which were deemed reasonable were rounded to the nearest integer. When it could not be determined whether the offset was real or not, the adjustment was reported as N/C in Table 1 (i.e. "not considered).

The accepted corrections, referred to as *adjustments*, were then applied to the data set and a new inversion was performed. The inversion results on the "adjusted" data set were used to help determine the final set of adjustments.

4 Results

All results and analyses made by the group for the crossovers and inversions, including figures for each individual crossover can be found on the CARINA website at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html.

Table 1 lists the adjustments and their respective standard deviation in parentheses based on both WLSQ and WDLSQ methods (see Tanhua et al., 2010a). Figure 4 is a plot of these values as a function of cruise number. As can be seen on the figure, both the WLSQ and WDLSQ methods produced very similar results. In most cases, the adjustments significantly lowered the differences between the cruises. Figure 5 shows the values of the offsets from the crossover analysis before and after applying the adjustments. As expected, the vast majority of the offsets were reduced, indicating that the new data set is more self-consistent. The few offsets, which became larger after adjustment are most likely related to the different weight assigned to some cruises. The columns labeled as WLSQ(adj) and WDLSQ(adj) in Table 1 show that the inversion procedure, when applied on the "adjusted" data set, suggests lower corrections.

Out of the collection of cruises considered in CARINA-ATL, 19 did not have any deep DIC data and their adjustment

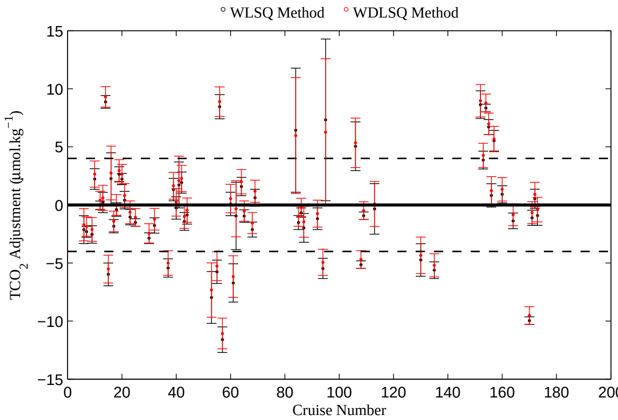


Figure 4. Adjustment values (dots) and their respective standard deviation (vertical bars) obtained from the two inversion methods used as a function of cruise number (see Table 1). Black dots were obtained with the WLSQ method; red dots were obtained with the WDLSQ method. An explanation of the difference between the two methods is provided in the text.

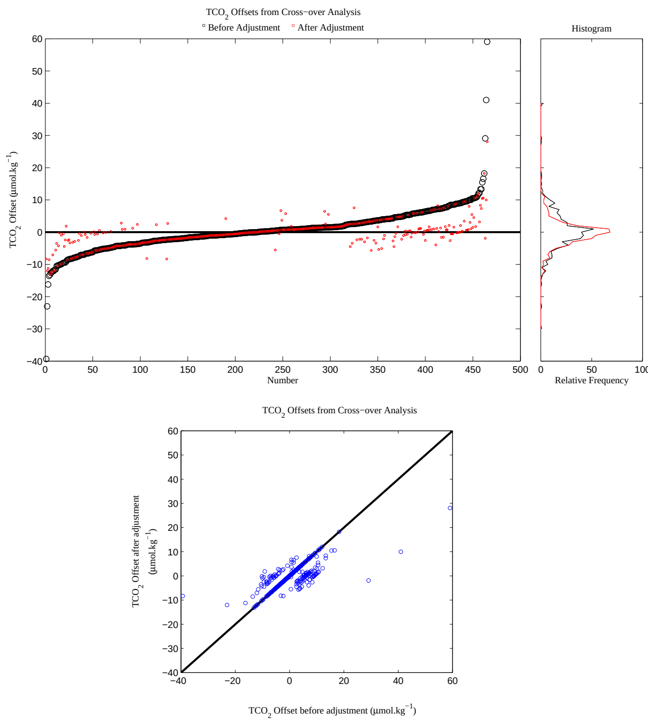


Figure 5. Top graph: Plot of the offsets in TCO_2 for all crossovers before adjustments (black symbols) in ascending order (Number) from left to right. The red symbols are the offsets after adjustments were made. Bottom graph: Scatter plot of the offsets after adjustments versus the same offsets before adjustments. Offsets for cruises which have not been adjusted fall on the 1:1 line (black line).

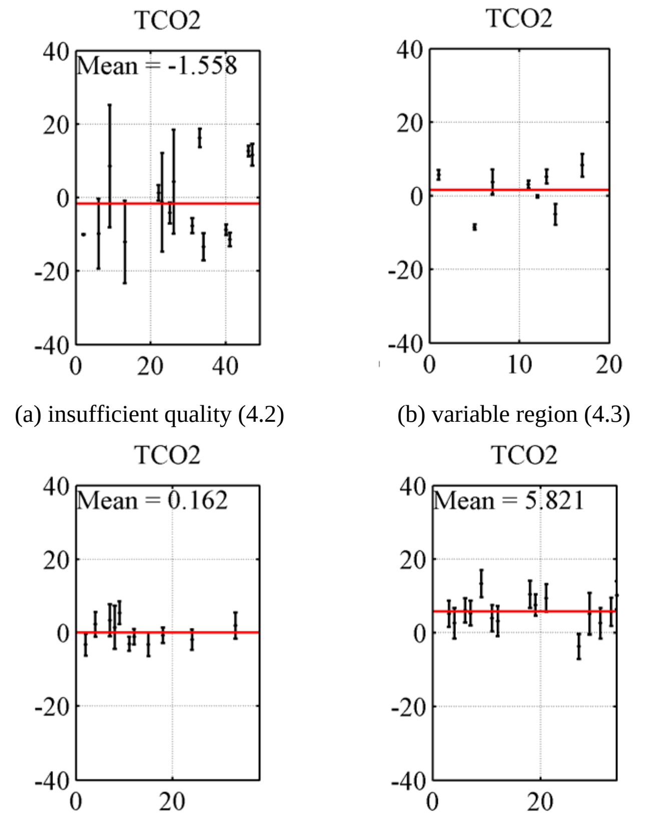
was set to N/A (i.e. "not available"); 20 had data that, for reasons given in Sect. 4.7, did not allow us to assign a meaningful adjustment value which was therefore set to N/C (i.e. not considered); 36, whose suggested correction was less than 4 µmol kg^{-1}, excluding the reference cruises, were not adjusted and their adjustment value is therefore 0. The TCO_2 values for 9 cruises showed consistent offsets with the different approaches and were assigned a non-zero adjustment.

The value of the adjustments, whether it be 0 or not, were vetted by the group taking several factors into consideration. Some adjustments were quite obvious, as when a particular cruise showed a similar offset with all the cruises with which it crossed. In these cases, the results of the inversions agreed with the crossover results from, not only the core cruises but the other ones as well. Other adjustments were not as simple and the results from the inversions, although taken as a starting point, were either accepted, rejected or modified based on all information available. This ranged from the quantity and quality of the data used for each crossover to a knowledge of the region considered. The results are presented below and are categorized as a function of the type of analysis it required. The sections below explain the values of the adjustments listed in the table, as well as the adjustment flags. The adjustment flags usually refer to the quality of the data used to make the adjustment. A value of 2 means that the quality is good and a value of 3 means that the quality is questionable, resulting in the data not being included in the merged data product. A flag set to N/A indicates that there was insufficient data to make a meaningful suggestion. A plot of all the offset values for each cruise is a diagnostic tool that was very useful and widely used in the determination of the corrections. Typical examples of such plots are shown in Fig. 6, each illustrating one of the different situations the cruise data could present and which are discussed below. Cruises which only contained calculated TCO_2 data were obviously not adjusted in the final data product and therefore do not have an adjustment value (N/A) reported in Table 1. However, for some of them, adjustment values are reported in the CARINA online table (http://cdiac.esd.ornl.gov/oceans/CARINA/Carina_table.html) as they were included in the crossover and inversion analyses. In the sections below, we present six different categories of cruises with respect to the consistency of their TCO_2 measurements.

We used the offsets of the crossovers calculated for the adjusted data product to estimate the level of internal consistency of the TCO_2 data (Fig. 7). We calculated the weighted mean (WM) using the absolute value of the offset (D) of L crossovers with the uncertainty (σ):

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

Based on this analysis, we estimate the internal consistency of the CARINA-ATL TCO_2 data to 2.1 µmol kg^{-1}.



(a) insufficient quality (4.2) (b) variable region (4.3)

(c) no offset (4.4) (d) clear offset (4.5)

Figure 6. Example of plots of all offsets for one cruise and their standard deviation as a vertical bar versus cruise number. The standard deviation is the deviation of the mean of all points below 1500 m used for the particular crossover comparison. Each plot is representative of a type of cross-over analysis result described in Sect. 4: **(a)** data is of insufficient quality or from variable regions, based on the large standard deviation, to estimate an adjustment, **(b)** the geographical region where the cruise took place is known to experience too much variability to suggest an adjustment, **(c)** The cross-over offset was well below the 4 μmol kg^{-1} cutoff and no adjustment is recommended and **(d)** the cross-over analysis showed a large and consistent offset with other cruises and an adjustment was applied.

4.1 Cruises with no data to suggest an adjustment (N/A)

Cruises with no TCO_2 data were assigned N/A in the adjustment column. In most cases, TCO_2 was not measured on these cruises. These cruises were removed from Table 1 but can be found on the CARINA data repository web site (http://carina.ifm-geomar.de). This category also includes cruises, which only had calculated TCO_2 data, i.e. an adjustment to TCO_2 is not possible but an offset suggest that either alkalinity or pH is in need of an adjustment.

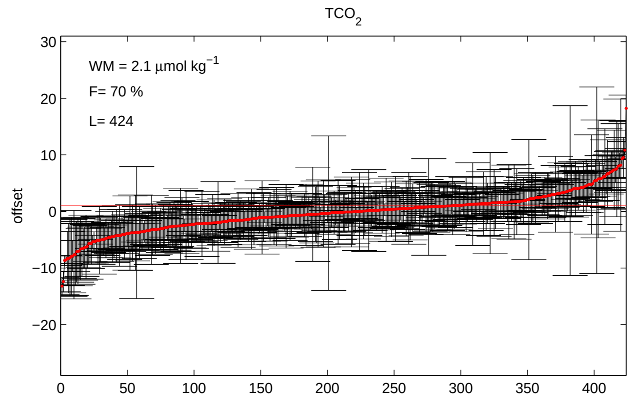


Figure 7. Offsets in TCO_2 (μmol kg^{-1}) in ascending order (Number) from left to right calculated for the crossovers in the CARINA-ATL data after adjustments have been applied. WL: the weighted mean of the offsets (see text); *F*: the percentage of offsets indistinguishable from 1 within their uncertainty; *L*: the number of crossovers.

4.2 Cruises with insufficient data or insufficient quality data to suggest an adjustment (N/C)

Cruises with insufficient data or insufficient quality data could not be adjusted and N/C was entered in the adjustment table to indicate that. Since a successful crossover analysis between two cruises requires each cruise to have at least 3 stations meeting the requirements of a crossover (Tanhua et al., 2010a), cruises with sparse data fell under that category. In most cases, they were shallow cruises and had no data below 1500 m, which was the only data considered to do the analysis, or they were either short cruises or in remote geographical area and therefore did not have any stations which could be considered as a crossover. When data were insufficient, it was obviously not possible to assign an adjustment flag so its value was set to N/A. Two cruises had enough data but their quality was deemed too low to suggest an adjustment. These cruises were assigned N/C for the adjustment but the adjustment flag was set to 3 to indicate the reason.

4.3 Cruises in regions too variable to suggest an adjustment (N/C)

Cruises in regions too variable to suggest an adjustment were not given any adjustment, and N/C was used in the table to indicate that. The adjustment flags have been given a value of 2 to indicate that the precision of the data is good but the geographical region of the cruise is naturally variable and the offsets observed between the cruises could be real. Therefore, the values generated by the WLSQ and WDLSQ methods are not applied and no adjustment is assigned (see Fig. 6b). There are three cruises in the CARINA-ATL data set for which it is the case: *58JH19920712* and *58JH19940723 (cruises #130* & *135)* both occurred in the highly variable Greenland-Iceland-Scotland ridge area, whereas *06MT19970107* was located in the Mediterranean outflow region.

4.4 Cruises which clearly show no offset with other cruises (0)

These cruises usually occurred in stable region and produced high quality TCO_2 data which compared well with other cruises in the same area, including the core cruises (see Fig. 6c). All offsets from the crossover analysis where below the 4 µmol kg^{-1} limit and therefore, no adjustment was warranted. An exception is *58AA20010527*, which did not have enough station in the Atlantic to determine an adjustment. The adjustment value of 0 has been determined from the stations in the AMS region (Olsen, 2009).

4.5 Cruises which clearly show an offset with other cruises

Crossover analysis for these cruises showed a consistent offset, indicating that the TCO_2 data in question was clearly either too high or too low (see Fig. 6d). The inversion results also confirmed that assessment. From the offsets determined by the different methods, an adjustment was proposed and agreed upon by the group. For these cases, the adjustments were rounded to the nearest integer.

4.6 Cruises with a different adjustment than the one suggested by inversions

Cruises with a different adjustment than the one suggested by inversions usually occurred in regions where some variability is expected. As a result, some crossovers showed fairly large offsets which skewed the inversion results. In general, the average offset with the core cruises was a good indicator as to whether the adjustment was reasonable or not. An example of this is *18HU19920527 (cruise #37)*, a cruise that happened in the variable Labrador Sea. In most of the cases, though, the crossovers with the core cruises simply helped decide whether the inversion result was going to be rounded up or down.

4.7 Details on the non-zero adjustments

4.7.1 06MT19960613, Cruise #14

The inversion suggested a correction of ~9 µmol kg^{-1}. However, the average offset of all crossovers was about −5 µmol kg^{-1}. Likewise, the crossovers with the core cruises agreed with each other and also suggested an upward adjustment of ~5 µmol kg^{-1}. Additionally, when adjusted by 5 µmol kg^{-1}, the original data for that cruise also compared favorably with the 1993 Ocean-Atmosphere Carbon Exchange Study (OACES) data. That evidence strongly suggested that an upward adjustment of ~5 µmol kg^{-1} was warranted.

4.7.2 18HU19920527, Cruise #37

The average of all crossover offsets agree with the crossovers with the core cruises to within the 4 µmol kg^{-1}limit. The inversion calculation showed the TCO_2 measurements to be too high by about 5 µmol kg^{-1} but the offsets with the core cruises were consistently around 9 µmol kg^{1}. So most crossovers showed a higher offset than the adjustment suggested by the inversion. Based on these results, the adjustment value was taken closer to the average of the crossovers and thus an adjustment of −9 is assigned.

4.7.3 33LK19960415, Cruise #84

The estimate of an adjustment was made difficult by the large scatter of the data. However, the few crossover results were all consistent with each other so that the slightly lower adjustment than the inversion result (5 µmol kg^{-1}) was warranted.

4.7.4 35LU19950909, Cruise #95

There were few crossovers to base a decision on but they were consistent with each other. The applied adjustment (9 µmol kg^{-1}) is higher than the suggested inversion value due to the crossover results with core cruises.

4.7.5 35TH19990712, Cruise #106

All crossovers agreed that the TCO_2 data were too low. The final adjustment of 6 µmol kg^{-1} is slightly higher than the one suggested by the inversion based on the crossovers with core cruises.

4.7.6 64PE20000926, Cruise #152

All crossovers agreed that the TCO_2 data were too low by about 8.5 to 9 µmol kg^{-1}. Crossovers with only core cruises confirmed the value.

4.7.7 64TR19900701, Cruise #155

The TCO_2 data had a good precision and consistently showed an offset of about −7 µmol kg^{-1} with all other cruises. Comparison with the core cruises confirmed it so that an adjustment of 7 µmol kg^{-1} was applied.

4.7.8 64TR19910408, Cruise #157

Despite the variability of the crossovers' region, offsets consistently show that the TCO_2 data were low. The value for the average offset with the core cruises (−6.23 µmol kg^{-1}) is in agreement with the inversion result, which justifies the applied adjustment value of 6 µmol kg^{-1}.

4.7.9 74DI19900612, Cruise #170

Although the data used in the crossover analysis were not abundant, they were consistently high by about 7 µmol kg^{-1}. Crossover analysis with core cruises showed a slightly higher offset (~8 µmol kg^{-1}) but not as high as the inversion suggested (9.50–10 µmol kg^{-1}). In view of the scarcity of the data and the crossovers' results, the lower range of the offsets was cautiously retained for the adjustment value of −7 µmol kg^{-1}.

4.7.10 29HE19920714 (reference cruise)

The inversion suggested a high correction of ~ −6 µmol kg^{-1} but the offsets with the core cruises were consistently below the 4 µmol kg^{-1} limit. In this case, the high correction value was driven by two crossovers involving the same stations from this cruise. This evidence suggested that the stations involved could be bad and therefore were disregarded and no adjustment was applied.

5 Data access

The whole CARINA database set is published at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html. It contains 188 individual cruise files in comma-separated, WHPO exchange format. Condensed metadata is contained in the header of each data file. In addition, the CARINA database contains three merged, comma separated, data files with the data products. These files are divided into the three geographical regions of CARINA, the Arctic Mediterranean Seas, Atlantic, and Southern Ocean files. No special software is needed to access the data, but software for Matlab® users is offered to facilitate reading of the data.

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