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Consistency of cruise data of the CARINA database in the Atlantic sector of the Southern Ocean

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Abstract. Initially a North Atlantic project, the CARINA carbon synthesis was extended to include the Southern Ocean. Carbon and relevant hydrographic and geochemical ancillary data from cruises all across the Arctic Mediterranean Seas, Atlantic and Southern Ocean were released to the public and merged into a new database as part of the CARINA synthesis effort. Of a total of 188 cruises, 37 cruises are part of the Southern Ocean, including 11 from the Atlantic sector. The variables from all Southern Ocean cruises, including dissolved inorganic carbon (TCO₂), total alkalinity, oxygen, nitrate, phosphate and silicate, were examined for cruise-to-cruise consistency in one collective effort. Seawater pH and chlorofluorocarbons (CFCs) are also part of the database, but the pH quality control (QC) is described in another Earth System Science Data publication, while the complexity of the Southern Ocean physics and biogeochemistry prevented a proper QC analysis of the CFCs. The area-specific procedures of quality control, including crossover analysis between stations and inversion analysis of all crossover data (i.e. secondary QC), are briefly described here for the Atlantic sector of the Southern Ocean. Data from an existing, quality controlled database (GLODAP) were used as a reference for our computations – however, the reference data were included into the analysis without applying the recommended GLODAP adjustments so the corrections could be independently verified. The outcome of this effort is an internally consistent, high-quality carbon data set for all cruises, including the reference cruises. The suggested corrections by the inversion analysis were allowed to vary within a fixed envelope, thus accounting for natural variability. The percentage of cruises adjusted ranged from 31% (for nitrate) to 54% (for phosphate) depending on the variable.



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Data Product Parameter Name	Data Product Flag Name	Exchange File Parameter Name	Exchange File Flag Name	Units
station		STANBR		
day		DATE		
month		DATE		
year		DATE		
latitude		LATITUDE		decimal degree
longitude		LONGITUDE		decimal degree
cruiseno				
depth				meter
temperature		CTDTMP		°C
salinity	sf	SALNTY	SALNTY_FLAG_W	
pressure		CTDPRS		decibar
oxygen	of	OXYGEN	OXYGEN_FLAG_W	$\mu\text{mol kg}^{-1}$
nitrate	no3f	NITRAT	NITRAT_FLAG_W	$\mu\text{mol kg}^{-1}$
silicate	sif	SILCAT	SILCAT_FLAG_W	$\mu\text{mol kg}^{-1}$
phosphate	po4f	PHSPHT	PHSPHT_FLAG_W	$\mu\text{mol kg}^{-1}$
tco2	tco2f	TCARBN	TCARBN_FLAG_W	$\mu\text{mol kg}^{-1}$
alk	alkf	ALKALI	ALKALI_FLAG_W	$\mu\text{mol kg}^{-1}$

For a list of all properties in the CARINA database: 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.

Data coverage and parameter measured

Repository-Reference:

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

Available at:

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

CARINA project main website:

http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html

Coverage: 30° S–75° S; 70° W–30° E

Location Name: Atlantic sector of the Southern Ocean

Date/Time Start: February 1989

Date/Time End: February 2005

1 Introduction

The development of the CARINA database with carbon-relevant cruise data from the Atlantic Ocean was initiated in 1999 as an essentially unfunded project by Ludger Mintrop and Doug Wallace following a workshop in Delmenhorst, Germany. It resulted in a large collection of previously unavailable data (about 30 cruises). The focus of the project was not only to retrieve data, but also quality control. In 2006, at a meeting in Laugarvatn, Iceland, this slumbering effort was refurbished, facilitated by the EU CARBOOCEAN integrated project and the International Ocean Carbon Co-ordination Project (IOCCP). It was decided that the CARINA data synthesis should be extended to include the Arctic and Southern Oceans. Because of the strong zonal structure of the Southern Ocean, it was deemed most appropriate to include the entire circumpolar ocean (instead of only the Atlantic sector) in the new synthesis effort. In Iceland a Southern Ocean Carbon Synthesis (SOCS) group was formed, which met three times since then in Kiel, Germany

(March 2007), Delmenhorst, Germany (December 2007) and Paris, France (June 2008) to tune the methodology and evaluate the emerging results. Close contact with the Atlantic and Arctic Mediterranean Seas working groups was maintained throughout the process, both at the four meetings and via additional visits and contacts. These interactions ensured that consistent data processing and evaluation were maintained among the groups.

The need for consistent data in a large public database has been recognized after decades of measurement campaigns, particularly as scientists are trying to address large-scale issues, not only from an observational point of view, but also as a validation for large-scale modeling efforts. Moreover, the usefulness of accurate older data for time series was recognized as critical for documenting temporal changes. A major previous ocean carbon synthesis effort is GLODAP (Global Ocean Data Analysis Project) (Key et al., 2004; Sabine et al., 2005), which evaluated mainly data from the large international WOCE and JGOFS projects in the 1990s. At about the same time, a very large database of hydrographic, nutrient and oxygen measurements collected during WOCE cruises, combined with pre-WOCE historical data was constructed and quality controlled by Gouretski and Jancke (2001), so that their proposed adjustments could also be applied in GLODAP. This coherent data set of carbon and related variables has been widely used and many major results originated from it, e.g., the high-profile estimation of the oceanic sink of anthropogenic CO₂ (Sabine et al., 2004). It is evident that the experience gleaned from such an effort was invaluable for the success of the CARINA project and therefore we gladly made use of it in the form of reports and publications, but more importantly by involving key people from GLODAP in CARINA.

Reliable carbon-related data in the Southern Ocean were first collected during the world-wide GEOSECS program in the 1970s (Bainbridge, 1981). New data have been collected in the Southern Ocean since then, but the data density has been much lower than in other oceanic regions. Moreover, there is a strong bias towards austral summer cruises. Since data is still sparse in the Southern Ocean, every new cruise significantly improves the data coverage. We want to make a contribution by complementing the database that was initiated by the GLODAP project with recent, but also older (before 2000) cruises that were missed or not yet available at the time. Because of the relative sparseness of new data, the data coverage was extended as much as possible in order to obtain sufficient crossover points for reliable evaluation of as many new cruises as possible. This has been achieved by incorporating the Southern Ocean cruise data from GLODAP as reference for the new CARINA data (i.e., all processing and computations were done with these data as well). It was considered most efficient to divide the work into three specific Southern Ocean regions, the Atlantic, Indian and Pacific sectors, rather than divide it by variables; this paper presents the results of the analyses performed with the CARINA and GLODAP data for the Atlantic sector.

2 Data provenance

Compared to other regions within the CARINA data set, the Southern Ocean database consists of relatively few data. While the entire CARINA database contains 188 cruises (Key et al., 2009), there are only 37 CARINA cruises in the Southern Ocean, of which 11 are situated in the Atlantic sector. A composite of all stations in the Southern Ocean (Fig. 1) reveals a bias towards the north. Along the entire northern border of the Southern Ocean the nearly synoptic circum-global occupation at 30–32° S conducted by the Japanese ship “Mirai” is found. This expedition known under the designation BEAGLE 2003 (Blue Earth Global Expedition; Uchida and Fukasawa, 2005) has excellent data quality (see below). In the western South Atlantic reaching into the Sub-Antarctic Zone, the Spanish FICARAM cruises with RV “Hesperides” are shown. Near the Antarctic continent, the data density is low. Data from the process-oriented Spanish FRUELA cruises (Álvarez et al., 2002) were collected near the Antarctic Peninsula. In the Weddell Sea, data include the SWEDARP 88/89 campaign (Anderson et al., 1991), Polarstern cruises ANT X/6 in 1992 (Bakker et al., 1997) and ANT XV/4 from 1998 (Hoppema et al., 2002) and SWEDARP 1997/98 (Fransson et al., 2004). North of this the GoodHope cruise contributes a useful data set (Gladyshev et al., 2008). Most of these data are found at or near the Prime Meridian (Fig. 1), where also many historical data were collected (e.g., AJAX and several Polarstern cruises from 1992 onwards). Finally, the South Atlantic cruise by NOAA/NSF

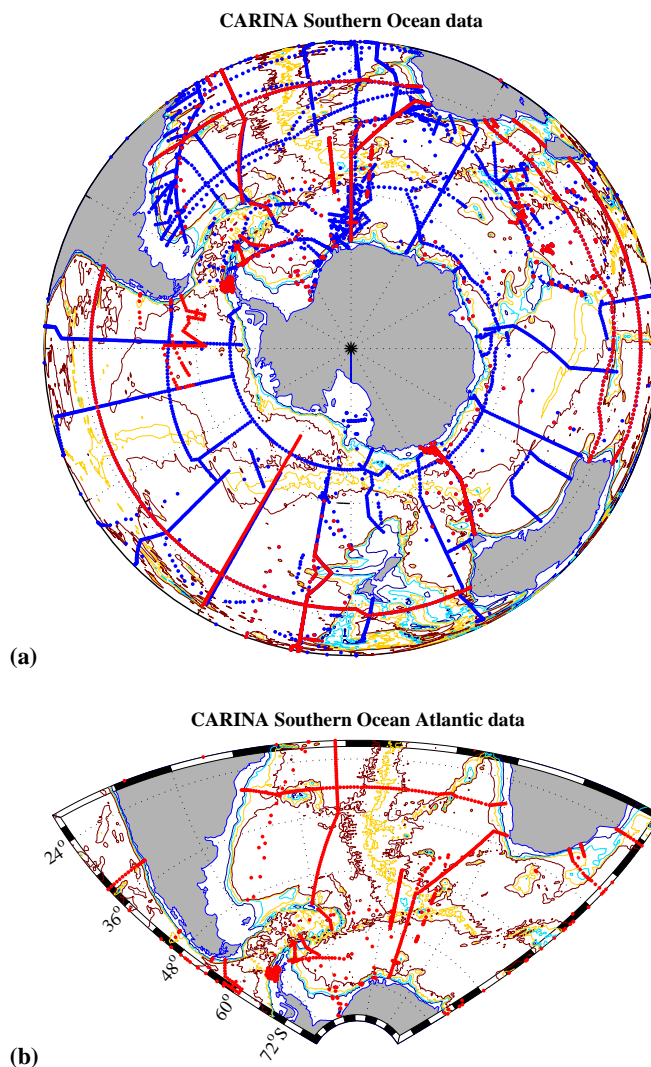


Figure 1. Map of the Southern Ocean with station positions, (a) of all CARINA cruises in red and GLODAP reference cruises in blue, and (b) of CARINA cruise in the Atlantic sector.

along WOCE section A16S which runs across the Antarctic Circumpolar Current is part of the data set.

Besides the 11 new CARINA cruises, 20 cruises from the GLODAP database were incorporated in the analysis as reference cruises (Table 1); these cruises have been evaluated before (Key et al., 2004). Note that the uncorrected, i.e. the GLODAP data as contributed by the data originators, were used in the present analysis. Below we focus on the new CARINA data. There are about twice as many nutrient and oxygen data points as TCO_2 and total alkalinity data (Fig. 2a), which is probably related to the long analysis times of the TCO_2 and alkalinity measurements. Chlorofluorocarbons (CFCs) are also included in Fig. 2a, as they are part of the CARINA database. However, the Southern Ocean CFCs have not been quality controlled. Not surprisingly, most of

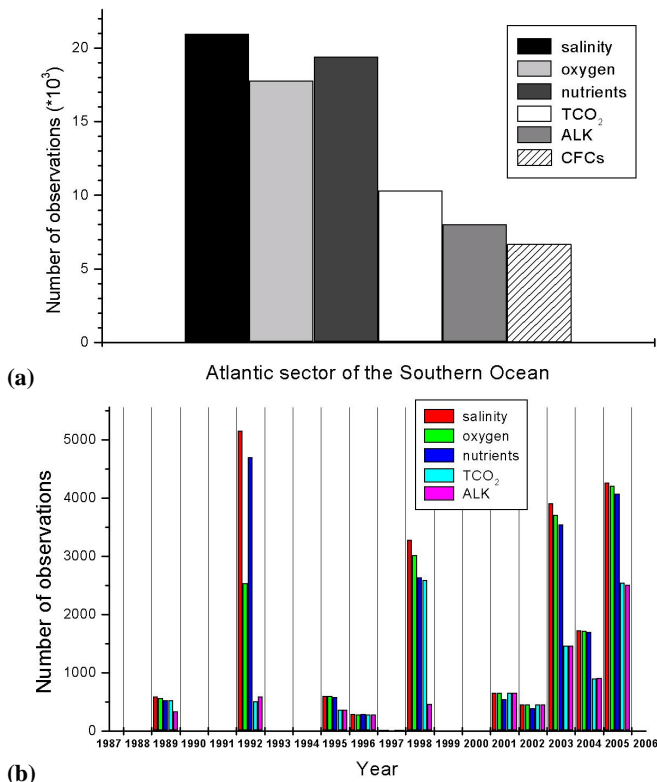


Figure 2. Data distribution in the Southern Ocean CARINA database (Atlantic part) (a) Total number of samples for different variables. The nutrient count represents any one measurement of the three variables nitrate, phosphate and silicate at a certain station and depth. CFCs are included in Southern Ocean CARINA, but have not been quality controlled. (b) Number of measurements performed in the respective years. Note that the distributions include some interpolated and calculated variables.

the CARINA Southern Ocean data originate from the post-GLODAP era, i.e., from 2000 or later (Fig. 2b). However, also older data not included in the GLODAP database were retrieved, dating back as early as 1989.

If TCO₂ was measured (on 6 cruises in the Atlantic sector; Table 1), this was done with the precise coulometric method (Dickson et al., 2007). Some of the older TCO₂ data from the GLODAP database, which are used as a reference (see below), have been measured with the less accurate potentiometric acid titration. In most cases certified reference material (CRM) was used, which was introduced by A. G. Dickson (Scripps Institution of Oceanography) in 1991. Total alkalinity was measured by means of potentiometric titration, with an open or closed cell. On the Spanish cruises (expocode starting with 29HE) and the Good-Hope line (90AV20041104) the slightly modified method by Perez and Fraga (1987) and Mintrop et al. (2000) was applied. CRM values for total alkalinity were not available until 1996 (Dickson et al., 2007), so fewer data sets could be validated for alkalinity than for TCO₂. Dissolved oxygen

was generally measured using automated Winkler titration. Nutrients were measured using colorimetric techniques. Detailed information about methods, precision and accuracy of the individual cruises can be found in cruise reports or in the readme files which accompany the adjustment data of individual cruises in the online table (http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html), and it is also included in the header of the individual cruise files in exchange format.

3 Computational analysis approach

A common quality control procedure has been developed for all CARINA regions – see Tanhua et al. (2009) for a detailed description. It can be divided into three successive steps, i) a crossover analysis which compares deep measurements collected at nearby stations during two different cruises in order to detect any systematic offset, ii) the cruise-to-cruise differences (offsets) are evaluated together for the whole Southern Ocean data set, variable by variable, in order to identify the cruises that could require an adjustment, and iii) the suggested adjustments are applied and crossover analyses of deep measurements are performed again in order to check the internal consistency of the dataset after correction. The quality control of the CARINA Atlantic sector of the Southern Ocean dataset has been performed following these three steps, as was done for all other CARINA regions. A brief description, including specific features applied to the Southern Ocean, is presented below.

Crossover analysis consists of an objective comparison of data deeper than 1500 m depth with density anomaly (σ_4) rather than depth as the ordinate. Shallower data were excluded because of possible seasonal variability and long-term trends. Variability of biologically-mediated quantities in the abyssal ocean is assumed to be minor as compared to possible offsets between different data sets. Density was used instead of depth to exclude first order variability in the deep ocean hydrography. A crossover point is always between two different cruises; however, the number of stations per cruise is variable, depending on the occurrence of stations within a pre-determined distance from the crossover point. The default circle around a crossover point was taken to be the distance of two degrees of latitude (= 222 km). Crossover analysis was performed with an automatic routine for all possible combinations of cruises and their variables. The analysis used here is based on the running cluster routine; see Tanhua et al. (2009) for details. In some few cases (indicated in Sect. 4) results from the alternative cnaX routine was used for closer assessment. The cnaX routines in principle perform the same job as the running cluster routine, however, the details are different and control by the user is higher – details can be found in Tanhua et al. (2009). It should be appreciated that the results of both routines are generally very similar. Crossover results (both offset numbers and diagrams) of all individual pairs of cruises that

were used for computing and assessment of the final adjustment to the cruise data can be found in the online table (http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html).

In addition to the automated crossover work, manual crossover analysis was carried out. Here the data analyst treated each crossover position separately. The analyst had the possibility to vary the input conditions, such as the distance from the crossover position, the minimum depth of the deep data (but always >1500 m), the number of stations, or applying two or more clusters of stations when the cruises cover large distances in hydrographically different regions. Unfortunately, manual crossover data are not available for all crossover points due to the addition of cruise data after the initial manual checks. It should be appreciated, though, that the results of the manual and automatic routines are generally in good agreement (Tanhua et al., 2009). The results of the automatic crossover analysis were utilized for further data processing. Manual crossover results were used for qualitative validation, in case of doubt about the magnitude of the suggested offset. Similarly, comparisons with results from an automatic crossover analysis with a distance of 111 km in north-south direction but with 222 km in east-west were done, reflecting the zonal structure of the Southern Ocean hydrography (denoted by files with the ending “_short” in the online table with crossover and adjustment results).

Crossover analysis computes cruise-to-cruise offsets for certain variables. It also produces the mean offset of all variables of one particular cruise against all other cruises with which it has crossover points. The mean offset of a variable of a particular cruise gives a first indication of the accuracy and consistency of the variables. To achieve consistency within the entire database, an inversion analysis was performed based on the Johnson et al. (2001) algorithm. Inversions produce a correction (factor) that should be applied to the data for optimal consistency of the data set. Note that the correction goes in the opposite way compared to the offset determined by the crossovers. Details about the implementation to the CARINA data can be found in Tanhua et al. (2009). The inversion analysis was carried out with CARINA data from the entire Southern Ocean, i.e. including those from the Indian and Pacific sectors (Lo Monaco et al., 2009; Sabine et al., 2009). Two methods of inversions were available, Weighted Least Squares (WLSQ) and Weighted Dampened Least Squares (WDLSQ), of which we chose the latter. Weight in this case is equivalent to maximum allowable adjustment, which varied between different cruises as assessed from the data, metadata and crossover results. WLSQ was found to be less useful because it does not sufficiently employ the known high accuracy of particular cruises, and thus gives too much weight to less reliable cruises. The adjustments to be applied to the cruise data were determined using the corrections of the inversion analysis. Variables were evaluated cruise by cruise, and only adjustments above a defined threshold were applied (0.005 for salinity, $4 \mu\text{mol kg}^{-1}$ for TCO_2 , $6 \mu\text{mol kg}^{-1}$ for alkalinity,

2% for nutrients and 1% for oxygen). These envelopes have been fixed equally for all CARINA regions. The results of the inversion were painstakingly checked by manually verifying every single cruise and variable. In particular, the validation includes ensuring that the inversion results conformed to crossover offsets of core cruises or cruises that were deemed highly reliable based on other information (e.g. CRM evaluations). All available information on crossover results (different versions), metadata and the hydrographic region of the crossovers was utilized. In some cases this led to suggested adjustments that diverged from the inversion results. The suggested adjustments were evaluated at a meeting with the whole Southern Ocean synthesis group in Paris in June 2008. All considerations about the decision in favor of or against an adjustment are documented in the online table (http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html).

The final check for consistency was conducted by running the crossover and inversion analyses on the cruise data after the adjustments had been applied. Again the results were evaluated for all cruises and their variables. In some few cases there was a need for modifying the previous results. The suggested adjustments to the cruise data were only considered final after this last check and these are shown in Table 1.

4 Results and recommendations

A composite of the corrections suggested by the final inversion analysis for CARINA cruises in the Atlantic sector of the Southern Ocean and a suite of reference cruises from the GLODAP database (without the GLODAP corrections applied) are presented after applying the corrections suggested by the initial inversion analysis (Figs. 3–9). The final adjustments applied to all cruise data are summarized in Table 1. These differ in some very few cases with the corrections suggested by the inversion analysis because the adjustment needed to be modified after analyzing the causes. Numbers in the figures denote the corrections, computed by the final inversion, which must be applied to obtain the optimally consistent data set either in an additive or in a multiplicative way. In all diagrams the envelope of accepted variations of that particular variable has been drawn. Note that in a few cases no statistically meaningful crossover analysis could be performed due to a lack of other cruises or stations in the vicinity of a particular cruise; for such cruises the inversion analysis does not yield a correction. Adjustments in such cases were estimated using any information available. In some cases not even the latter has been possible. Such cruises are marked NC (not considered) in Table 1. In the following sections the results are described by variable. We focus on the CARINA data, while the GLODAP data are treated in less detail. This bears on the fact that the GLODAP data were primarily included as reference to enhance the performance of the quality control procedures.

Table 1. Cruises included in the CARINA Southern Ocean database in the Atlantic sector (upper part) provided together with cruises from the GLODAP synthesis (lower part) of the same region, identified with their expocodes and numbered according to the cruise summary table in Key et al. (2009). Of the CARINA cruises three were chosen as core cruises because of their high quality. Of the GLODAP cruises, all but one are reference cruises (column core/ref). Cruise information includes the data originators and the suggested adjustments for different properties investigated. Adjustments for salinity, TCO₂ and alkalinity are additive, i.e. no adjustment at value 0, while adjustments for the remaining variables are multiplicative, i.e. no adjustment at value 1. NA denotes not available; this may be because the property was not measured, or data could not be retrieved. NC denotes not considered; data of such a cruise could not be used for crossover analysis because of lack of stations from other cruises for comparison. Such data are still contained in the database.

CARINA # or common name	Expocode	core/ref (1 true, 0 not true)	Sal (/10 ³) (+)	NO ₃ (x)	PO ₄ (x)	SiO ₃ (x)	Oxy (x)	TCO ₂ (μmol kg ⁻¹) (+)	TA (μmol kg ⁻¹) (+)	Nutrient analyst	Oxygen analyst	CO ₂ PI	Chief scientist
CARINA cruises													
1	06AQ19920929	0	0	1	1	0.93	0.99	0	-8	K. Bakker	R. Manuels	M. Stoll, J. Rommets	V. Smetacek
4	06AQ19980328	0	0	1	1	NC	NC	0	NA	K. Bakker	A. Wisotzki	M. Hoppema, R. Bellerby	E. Fahrbach
58	29HE19951203	0	NC	NC	0.98	NC	0.99	NA	0	C. Castro	C. Castro	A. Ríos	R. Anadón, M. Estrada
59	29HE19960117	0	NC	NC	1	0.93	1	NA	-6	C. Castro	C. Castro	A. Ríos	R. Anadón, M. Estrada
61	29HE20010305 ^a	0	0	1	1	1	0.99	-6 ^b	-6	C. Castro	M. Álvarez	A. Ríos	A. Ríos
62	29HE20020304 ^a	1	0	1	1	1	1	0 ^b	0	C. Castro	C. Castro	A. Ríos	F. Perez
87	33RO20050111 ^a	1	0	1	1.03	1	1	0	0	R. Wanninkhof, F. Millero	R. Wanninkhof, F. Millero	R. Wanninkhof, F. Millero	R. Wanninkhof, S. Doney
113	49NZ20031106 ^a	1	0	1	1	1	1	0	0	M. Aoyama, S. Watanabe	Y. Kumamoto, S. Watanabe	A. Murata	Y. Yoshikawa
127	58A119890214	0	-0.005	1	0.90	1	0.99	6	-15	L. Anderson	L. Anderson	L. Anderson	L. Anderson
182	90AV20041104	0	0	1.02	1	1	1	0 ^b	0	V. Zubarevich	P. Branellec	M. Álvarez	S. Gladyshev, S. Speich
183	91AA19971204	0	0	NA	NA	NA	1	-4	0	NA	A. Fransson	M. Chierici, A. Fransson	D. Turner
Reference cruises													
ANTV/1,2	06AQ19860627	1	0	1.03	1	1	1	12	0	J. C. Jennings, L. I. Gordon	J. C. Jennings, L. I. Gordon	D. Chipman	E. Augstein, G. Hempel
ANTVIII/2	06AQ19890906	1	0	1	0.95	1.02	1	NA	NA	J. C. Jennings	J. C. Jennings	NA	E. Augstein
ANTX/4	06AQ19920521	1	0	0.98	0.98	0.98	1	0	NA	K. U. Richter	A. Wisotzki	M. Hoppema	P. Lemke
ANTX/7	06AQ19921203	0	NC	NC	NC	NC	NC	NC	NA	K. U. Richter	E. Fahrbach	M. Hoppema	E. Fahrbach
ANTXIII/4	06AQ19960317	1	0	1.02	1	1.05	1.01	-4	NA	K. Bakker	E. Fahrbach	M. Hoppema	E. Fahrbach
AJAX	316N19831007	1	0	1	1	0.98	0.99	8	0	PACODF ^c	PACODF ^c	T. Takahashi	J. Reid, W. Nowlin
ARC	316N19831113	1	0	poor	0.88	poor	1	NA	NA	N.N.	N.N.	NA	A. Gordon
Marathon7	31WT19841001	1	0	1	0.98	1	0.99	NA	NA	L. Gordon	L. Gordon	NA	A. Gordon
S04I	320619960503 ^c	1	0	1	1	1	1	0	0	PACODF ^c	PACODF ^c	F. Millero, T. Takahashi	J. Swift, T. Whitworth
Cither2	323019940104 ^a	1	0	1	1	0.98	1	0	-8	X. Álvarez-Salgado, C. G. Castro	H. Mércier	L. Bingler/ L. Arlen, A. Ríos/G. Rosón	L. Mémerly
Cither3-1	35A319950111	1	0	1	1.02	1	1	4	-8	X. Álvarez-Salgado	H. Mércier	L. Bingler, A. Ríos	H. Mércier
Cither3-2	35A319950222	1	0	1.025	1.055	1	1	4	0	P. Morin	M. Arhan	L. Bingler, A. Gonzales	M. Arhan
CIVA1	35MF19930123 ^c	1	0	0.98	0.98	0.98	1	0	0	J. F. Minster, J. Escalier	A. Poisson, B. Schauer	A. Poisson, C. Brunet	A. Poisson
CIVA2, I06S	35MF19960220 ^c	1	0	0.96	0.97	0.90	1	0	0	J. F. Minster	A. Poisson	A. Poisson, N. Metz	A. Poisson
A11, D199	74DI19921222	1	0	0.98	1.04	1	1.015	NA	NA	D. Hydes	P. Chapman	NA	P. M. Saunders
S04, D200	74DI19930206	1	0	1	1	1	0.96	NA	NA	D. Kirkwood	D. Kirkwood	J. Robertson ^d	R. Dickson
A23	74JC19950320	1	0	1	1.02	1	1.025	poor	NA	R. Sanders	R. Sanders	J. Robertson	K. Heywood, B. King
Wepolex	90MS19811009	1	-0.006	NA	NA	NA	NA	-4 ^b	-15	NA	NA	C. Chen	A. Gordon, E. Sarukhanyan
Geosecs	Geosecs Atlantic	1	0	1	1.02	1	0.99	0	-10	PACODF ^c	PACODF ^c	NA	NA
SAVE	SAVE	1	0	1	1	1	1	4	0	PACODF ^c	PACODF ^c	T. Takahashi	T. Takahashi

^a Also in North Atlantic data base.

^b TCO₂ calculated from alkalinity and pH.

^c Also in Indian Ocean sector (Lo Monaco et al., 2009).

^d CO₂ measured but data not available due to unreliable CRMs.

^e PACODF is Physical and Chemical Ocean Data Facility; this is the former name of the analytical group at Scripps now known as CCHDO.

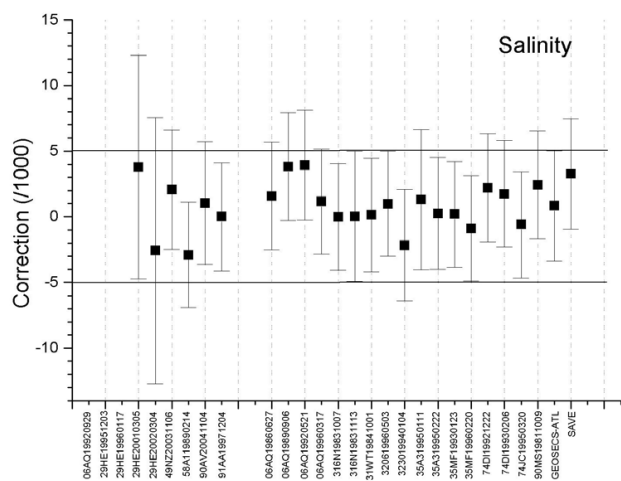


Figure 3. Results (with standard deviation) of the final inversion analysis for salinity of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are additive. A positive correction means the original salinity data must be increased by that amount. Shown are the envelopes of ± 5 within which variation is accepted.

4.1 Salinity

Salinity is a traditional hydrographic variable that is measured by the precise salinometer (most of the CARINA cruises) or Conductivity Temperature Depth (CTD) devices with a high accuracy due to widely accepted use of IAPSO standard seawater. In line with this, only two cruises, 58A119890214 (#127) and 90MS19811009 (GLODAP), were slightly adjusted, while the remaining cruises exhibit variations within the accepted envelope of ± 0.005 (Fig. 3). Although the inversion analysis suggested no significant correction, cruise 58A119890214 was adjusted because of the significant offsets with a few reliable Polarstern cruises. Decadal variability of salinity in the deep Southern Ocean is well-known (Robertson et al., 2002), but the magnitude is generally less than 0.01 (Fahrbach et al., 2004). As almost all cruises show only variations within the ± 0.005 range, water mass variability does not seem to have been very large.

4.2 TCO₂

Three CARINA cruises were subject to a TCO₂ adjustment.

29HE20010305 (cruise #61) has most crossover points in the Atlantic region north of 30° S; the adjustment is based on those (see also Pierrot et al., 2009). In addition, note that TCO₂ in the original data set of 29HE20010305 had been calculated from pH and alkalinity. We thus used these TCO₂ values only for enhancing the number of crossover points. TCO₂ values in the final CARINA database have been cal-

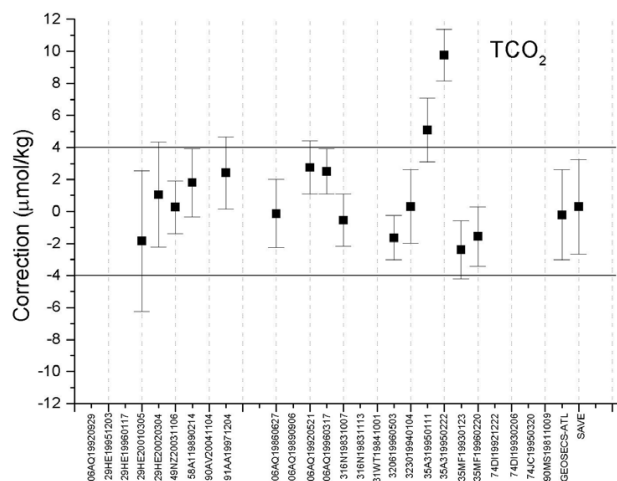


Figure 4. Results (with standard deviation) of the final inversion analysis for TCO₂ of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are additive. A positive correction means the original TCO₂ data must be increased by that amount. Shown are the envelopes of ± 4 within which variation is accepted.

culated from pH and alkalinity, which were subject to the regular analyses for adjustment.

Since **58A119890214** (cruise #127) is an older cruise from 1989 and the TCO₂ adjustment is positive ($+6 \mu\text{mol kg}^{-1}$), the validity of the adjustment needs to be verified in the context of recent uptake of anthropogenic CO₂. TCO₂ data from 58A119890214 were measured before the era with common CRMs and thus an accuracy problem is not unlikely. The adjustment appears justified because the offset of 58A119890214 with cruise 06AQ19960317 (7 years difference) in the deep Weddell Sea is 9–13 $\mu\text{mol kg}^{-1}$. This is definitely too much in these waters, the annual increase of anthropogenic CO₂ being significantly less than 1 $\mu\text{mol kg}^{-1}$ (Hoppema et al., 2001; Hauck, 2008).

91AA19971204 (cruise #183) was biased by a crossover with 06AQ19860627, which is clearly too low (Table 1). In view of crossovers with 06AQ19920521, the adjustment was set to $-4 \mu\text{mol kg}^{-1}$, as confirmed by the final inversion analysis (Fig. 4).

Additionally, we recommend adjustments to six GLODAP cruises (Table 1), of which three did not receive an adjustment in the earlier GLODAP analyses (Key et al., 2004) – the other three were not in the main GLODAP database (being older historical data) and thus did not receive an adjustment either:

Cruise **06AQ19960317** has an offset of $+9 \mu\text{mol kg}^{-1}$, and an adjustment of $-4 \mu\text{mol kg}^{-1}$ is suggested by the regional analysis. Also in the Indian sector this cruise appears to be high (Lo Monaco et al., 2009).

Cruise **35A319950111** has only few crossover points, but the offset with our core cruise 49NZ20031106 appears to

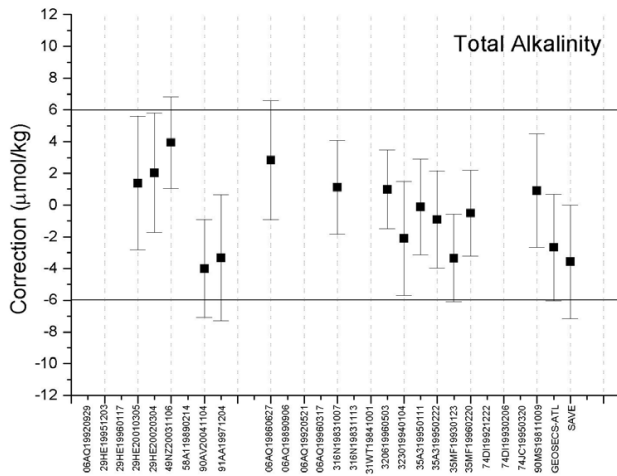


Figure 5. Results (with standard deviation) of the final inversion analysis for total alkalinity of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are additive. A positive correction means the original total alkalinity data must be increased by that amount. Shown are the envelopes of ± 6 within which variation is accepted.

justify the adjustment of $+4 \mu\text{mol kg}^{-1}$, which was suggested by the final inversion analysis.

Cruise **35A319950222** has a negative offset, which is confirmed by the regional and final check analyses. An adjustment of $+4 \mu\text{mol kg}^{-1}$ is therefore suggested which also complies with the crossover with core cruise 49NZ20031106.

From the other cruises, we recommend **06AQ19860627** to be adjusted up by $12 \mu\text{mol kg}^{-1}$. Although being an older cruise, we think this is justified because the offsets with similarly old cruises like 90MS19811009 and 06AQ19920521 are high. Cruise **316N19831007** is recommended to be adjusted up by $8 \mu\text{mol kg}^{-1}$ while similar arguments hold here.

4.3 Total alkalinity

After the final inversion analysis, all alkalinity data lie within the envelope of accepted variation of $\pm 6 \mu\text{mol kg}^{-1}$ (Fig. 5). For accomplishing this, four CARINA and four GLODAP cruises had been adjusted. No decadal trend of alkalinity in the deep Southern Ocean is known and therefore the adjustments are all thought to be robust. Because most of the TA data have been produced in a time that CRMs for alkalinity were not available, offsets between cruises are not unexpected.

06AQ19920929 (cruise #1) has only one or two crossover points (depending on the distance between stations). Inversion analysis could not contribute any suggestion. The adjustment of $-8 \mu\text{mol kg}^{-1}$ is based on a comparison with Geosecs-Atlantic.

29HE19960117 (cruise #59) is adjusted down by $6 \mu\text{mol kg}^{-1}$. This cruise covers a small region west

of the Antarctic Peninsula (Fig. 1), where only cruise 29HE19951203 and GLODAP cruise Geosecs-Atlantic have some stations nearby. The latter cruise received an adjustment based on the inversion analysis, and this has been the basis for applying a small adjustment to 29HE19960117.

29HE20010305 (cruise #61) has most crossover points in the Atlantic north of 30°S (Velo et al., 2009). The adjustment of $-6 \mu\text{mol kg}^{-1}$ is fully consistent for the Atlantic and Southern Ocean crossover data.

58A119890214 (cruise #127) was adjusted down by as much as $15 \mu\text{mol kg}^{-1}$. Crossover points with 316N19831007 and 06AQ19860627 rendered qualitative information that alkalinity of 58A119890214 is much too high. Anderson et al. (1991), who presented the alkalinity data of this cruise, compared their data basin-wide with those of Poisson and Chen (1987), here represented by expocode 90MS19811009, and found no significant difference. Using this information and the fact that 90MS19811009 is adjusted down by $15 \mu\text{mol kg}^{-1}$ as based on the inversion analysis, we adjusted 58A119890214 by the same amount.

Two GLODAP cruises are recommended to get an adjustment here, and these had not been corrected in the GLODAP analysis:

323019940104 was adjusted down by $8 \mu\text{mol kg}^{-1}$. This is based consistently on crossovers both in the Atlantic Ocean and the Southern Ocean, and is in perfect agreement with an assessment of the quality of the alkalinity data in the cruise report (Rfos et al., 2005).

For cruise **35A319950111** also an adjustment of $-8 \mu\text{mol kg}^{-1}$ was applied. This is based on offsets with the Geosecs-Atlantic and SAVE cruises, but above all with core cruise 49NZ20031106; all of these offsets point to the same correction.

4.4 Nitrate

The results of the final inversion analysis (Fig. 6) and the adjustments (Table 1) show that the variation of the nitrate data was relatively large. It was not possible to get all the data within the envelope of accepted variation of 2% for nutrients, not even after applying the suggested adjustments. One should realize that the inversion analysis optimizes the offsets between many different cruises and the fact that after applying corrections there is still variation beyond 2% indicates the overall accuracy is less than 2%. This is not surprising because nutrient measurements lack common CRMs, and inter-comparison exercises reveal major offsets between laboratories (e.g., Aoyama et al., 2007).

Only one of the CARINA cruises was given an adjustment for nitrate (Table 1). After the initial inversion **90AV20041104** (cruise #182) did not need a correction. After the final inversion, however, an adjustment seemed necessary (Fig. 6). The offsets with reliable cruises (06AQ19920521, 06AQ19960317 and 316N19831007) give further evidence that an adjustment of 1.02 is justified.

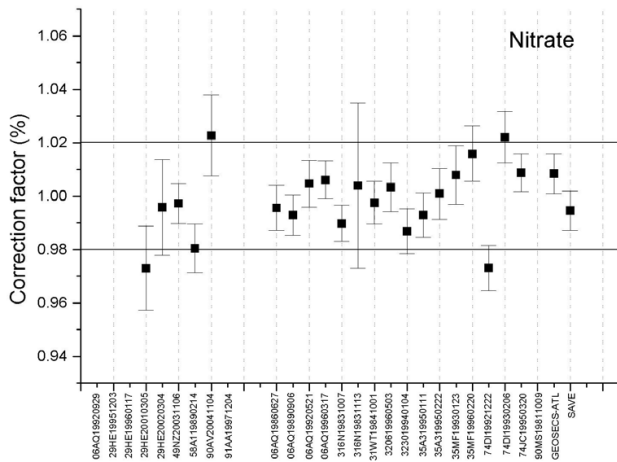


Figure 6. Results (with standard deviation) of the final inversion analysis for nitrate of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are multiplicative. A correction means the original nitrate data must be multiplied by that amount. Shown are the envelopes of $\pm 2\%$ within which variation is accepted. Note that strictly the unit of the correction factor is % deviation from 1.

29HE20010305 (cruise #61) is slightly outside the 2% envelope in the final inversion analysis, but we refrained from adjusting the data. Most of the crossover points of this cruise occur in the Atlantic north of 30° S and these do not warrant an adjustment.

Seven GLODAP cruises are recommended to be adjusted with factors between 0.96 and 1.03 (Table 1), while nitrate data of one cruise (316N19831113) were discarded because of large scatter:

Cruise **74DI19921222** appeared to be outside the 2% envelope after the final inversion. Its offset with several cruises (Geosecs-Atlantic, SAVE, 49NZ20031106) showed the nitrate values to be relatively high, and thus an adjustment of 0.98 was given.

For cruise **74DI19930206** the final inversion computes a correction slightly above the accepted boundary of 1.02. The crossovers with seven cruises, however, show a very consistent picture with no significant offset. We therefore decided for no adjustment.

4.5 Phosphate

Similar to nitrate, the cruise-to-cruise variation of the phosphate data is very large, even so large that of all variables the largest number of adjustments had to be applied to the phosphate data. The quality control has achieved a good result as evidenced by Fig. 7, where most phosphate data are now within the accepted envelope of $\pm 2\%$. Three CARINA cruises were adjusted.

29HE19951203 (cruise #58) is a problematic case, because it has only two cross-over points. It is, however,

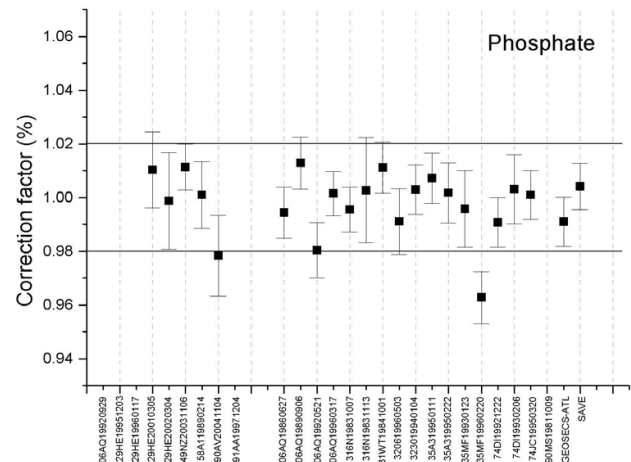


Figure 7. Results (with standard deviation) of the final inversion analysis for phosphate of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are multiplicative. A correction means the original phosphate data must be multiplied by that amount. Shown are the envelopes of $\pm 2\%$ within which variation is accepted. Note that strictly the unit of the correction factor is % deviation from 1.

clearly high compared to nearby cruise 29HE19960117 and Geosecs-Atlantic seems to confirm this. The inversion analysis suggests a correction as well.

33RO20050111 (cruise #87) received an adjustment of 1.03 as based on the inversion results for the Atlantic Ocean (not the Southern Ocean). This adjustment is fully consistent with the crossover offset with Southern Ocean core cruise 49NZ20031106.

As to **58A119890214** (cruise #127) the adjustment is quite large with 0.90. This is suggested both by the inversion analysis and by the mean offset against five cruises in the interior Weddell Sea. If the offset is that large the question as to the quality is justified; however, the standard deviations of the crossovers are in the usual range, so the large adjustment appears justified and still the data quality is sufficient.

Adjustments are recommended for 11 GLODAP cruises (Table 1). After the final inversion analysis all but one cruise were within the range of acceptable deviations (Fig. 7). Cruise **35MF19960220** was given an initial correction of 0.98 largely following the inversion result. However, after the final inversion analysis (where adjacent data had been corrected) the data were still found to be too high. A larger adjustment of 0.97 was therefore decided to bring the data closer to the accepted range without making them inconsistent with respect to neighboring cruises.

4.6 Silicate

Two CARINA cruises were adjusted by 0.93 each (Table 1). **06AQ19920929** (cruise #1) has only few crossover points in the common running cluster crossover analysis, but in the

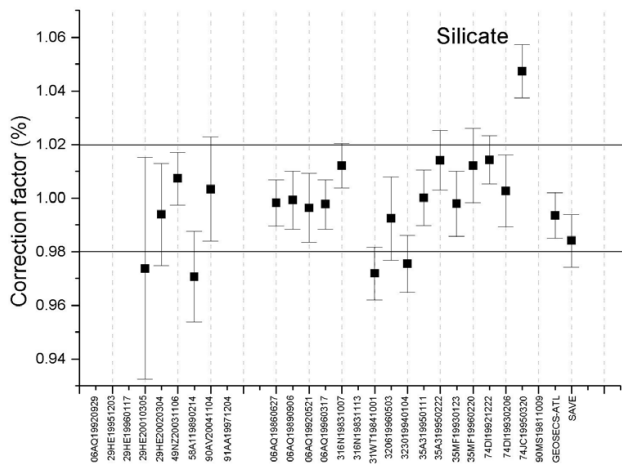


Figure 8. Results (with standard deviation) of the final inversion analysis for silicate of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are multiplicative. A correction means the original silicate data must be multiplied by that amount. Shown are the envelopes of $\pm 2\%$ within which variation is accepted. Note that strictly the unit of the correction factor is % deviation from 1.

cnaX crossover and inversion analysis (see Tanhua et al., 2009) an offset of 7% is computed. Based on this an adjustment of 0.93 is suggested.

29HE19960117 (cruise #59) has only two crossovers but they show that the silicate data are much too high. This is confirmed in a composite of all silicate data of the Weddell region as plotted versus potential temperature. Since no inversion results are available due to lack of data, the adjustment factor of 0.93 is based on the offsets.

No adjustment was given to **29HE20010305** (cruise #61) although the final inversion suggests a correction factor (Fig. 8). However, both in the Atlantic Ocean and in the Southern Ocean the mean offsets are within the 2% interval. Moreover, the spread in the crossover results is relatively large.

Nor did **58A119890214** (cruise #127) receive an adjustment, although the final inversion would suggest one. However, the mean offset against five Weddell cruises is insignificant which warrants no adjustment.

Seven GLODAP cruises are recommended to be adjusted with values between 0.90 and 1.05, while the silicate data of one cruise (316N19831113) were discarded because of poor quality and extremely large offsets ($>20\%$) to other cruises. Of these, three were still outside the 2% range after the final inversion (Fig. 8). Cruise **323019940104** was initially not given an adjustment although the inversion analysis suggested one. This was based on the insignificant offsets both in the Atlantic Ocean and in the Southern Ocean. However, after the final inversion the same correction factor was still suggested. An adjustment of 0.98 was therefore applied.

As to cruise **74JC19950320**, originally it had a relatively large adjustment of 0.96 based on the inversion results. However, after the final inversion (Fig. 8) the data appeared to be too low by about the same amount. Therefore, finally no adjustment was given.

After the final inversion, cruise **31WT19841001** is outside the 2% interval. No adjustment was suggested because of the favorable offsets with several reliable cruises such as Geosecs-Atlantic, SAVE and 323019940104.

4.7 Oxygen

Although data of four CARINA cruises were adjusted, the adjustment was small with 0.99 each. For **06AQ19920929** (cruise #1) the cnaX crossover and inversion analysis is the only information available and it suggests an adjustment amounting to 0.99.

29HE19951203 (cruise #58) has only two crossovers. Both suggest this cruise is too high, which is in line with the inversion which supports an adjustment of 0.99.

29HE20010305 (cruise #61) has small offsets both in the Atlantic Ocean and in the Southern Ocean, somewhat higher in the former region than in the latter. The inversions suggest a correction factor of 0.98 for the Atlantic and 0.99 for the Southern Ocean. The cnaX crossover and inversion analysis (Tanhua et al., 2009), which combines both regions, suggests a correction factor of 0.99, which was decided to be the adjustment.

58A119890214 (cruise #127) has a mean offset against six Weddell cruises of 1.017 indicating it is too high. The inversion analysis initially suggested no significant correction; however, the final inversion (Fig. 9) revealed that these oxygen data are likely too high indeed. We therefore suggest an adjustment of 0.99 for this cruise.

Seven GLODAP cruises are recommended to be adjusted but also here the adjustments are mostly small. This fact and the small CARINA adjustments is evidence for the relatively good quality of the oxygen data. Cruise **06AQ19920521** has a positive offset with respect to five Weddell cruises, but the initial inversion did not suggest a significant correction factor. In the final inversion (Fig. 9) a small correction may be suggested but we refrained from it due to the spread of the crossover data.

No adjustment was given to cruise **35MF19960220** although the final inversion could be interpreted that it could require one. However, the crossovers are from a region with variability, while crossovers with some reliable cruises do not warrant an adjustment.

Cruise **35MF19930123** has no significant mean offset against three cruises. Based on the final inversion a small correction factor of 1.01 was considered. However, we did not apply any adjustment because of a small Indian sector bias due to larger variability in the region (Lo Monaco et al., 2009).

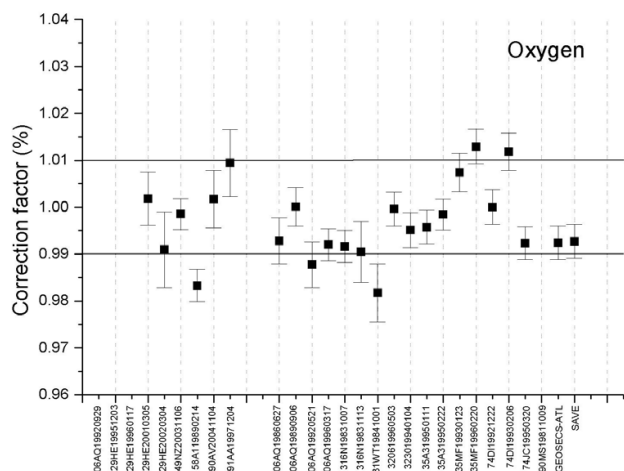


Figure 9. Results (with standard deviation) of the final inversion analysis for dissolved oxygen of CARINA and GLODAP reference cruises in the Atlantic sector of the Southern Ocean. The corrections are multiplicative. A correction means the original oxygen data must be multiplied by that amount. Shown are the envelopes of $\pm 1\%$ within which variation is accepted. Note that strictly the unit of the correction factor is % deviation from 1.

Finally, the final inversion suggests a correction for cruise **31WT19841001** (which it did not get after the initial inversion). A small offset to a few cruises corroborates the requirement of an adjustment. We decided to follow the suggestion by the final inversion and adjusted the data with a factor 0.99.

4.8 Overall accuracy

The overall accuracy of the merged CARINA-GLODAP Southern Ocean dataset was evaluated after the final adjustments had been applied (Table 1). We calculated the weighted mean (*WM*) for each parameter using the absolute value of the offset (*D*) of *L* crossovers with the uncertainty (σ), as follows:

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

Based on this analysis, the accuracy of the merged Southern Ocean dataset is 0.002 for salinity, $2.3 \mu\text{mol/kg}$ for TCO_2 , $5.1 \mu\text{mol/kg}$ for alkalinity, 0.8% for oxygen, 1.1% for nitrate, 1.3 % for phosphate and 1.2% for silicate.

5 Data access

The CARINA database is available at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html. It consists essentially of two parts. The first part is the 188 individual cruise files with

all the measured data and their flags all through the water column. These files are in WHP (WOCE Hydrographic Program) exchange format where the first lines consist of the condensed metadata. There are neither calculated nor interpolated values in the individual cruise files, and no adjustments have been applied to the values. In many cases there are additional variables in the individual cruise files that were not included in the secondary QC procedures of CARINA and in some cases they were excluded from the final data products. The second part of CARINA consists of three merged data files, divided into the three geographical regions of CARINA and thus one for the Southern Ocean. The following common variables are included in this file: salinity, CTD salinity, temperature, dissolved oxygen, nutrients (nitrate, phosphate, silicate), total CO_2 , total alkalinity, pH (at seawater scale at 25°C), CFC-11, CFC-12, CFC-113 and CCl_4 , SF_6 , ^{14}C , ^{13}C , ^3H , ^3He , and He. The data have been modified or complemented with, i) interpolated values for nutrients, oxygen and salinity, if those data are missing and if interpolation can be performed according to certain criteria as described in Key et al. (2009); and ii) calculated carbon variables (i.e., if TCO_2 and total alkalinity were measured, pH was calculated; see Key et al., 2009). Calculated and interpolated values have the quality flag “0”. Values in the merged data file have been adjusted according to Table 1. No specific software is needed to access the data; however, MATLAB software is offered to facilitate data usage.

6 Concluding remarks

A consistent data product has been produced largely within the confidence intervals ($4 \mu\text{mol kg}^{-1}$ for TCO_2 , $6 \mu\text{mol kg}^{-1}$ for total alkalinity, 2% for nutrients, 1% for oxygen) that were set before commencing the quality control work. This could only have been done by implementing rigorous quality control measures. Note that these intervals exist because of natural variability, but also due to measurement uncertainty. We consider systematic differences between cruises to be largely corrected by applying adjustments. Most adjustments were necessary for the nutrient data (in particular silicate) which again proves the need for reference material. The distribution and wide-spread use of these is likely to become a reality (Aoyama et al., 2007). For TCO_2 and total alkalinity such CRM has been there for almost two decades now. Despite of this, some recent cruises did need adjustments. This urges us to further enhance standardization, e.g. by more strictly using standard protocols for CRM measurements and data processing (Dickson et al., 2007).

This work in the Atlantic sector of the Southern Ocean constitutes a part of the larger CARINA Southern Ocean effort, which in turn is a combined effort with those in the Atlantic Ocean and Arctic Mediterranean Seas. Additionally, a similar synthesis effort is also underway for the Pacific Ocean, which thus almost closes the world-wide database.

All of these new efforts are superimposed on the previous world-wide GLODAP database. We think that the new data product will be very useful for much future work, both by observationalists and modelers.

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