

**Comparison of Inorganic Carbon System Parameters Measured in the Atlantic Ocean
from 1990 to 1998 and Recommended Adjustments**

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ABSTRACT

As part of the global synthesis effort sponsored by the Global Carbon Cycle project of the National Oceanic and Atmospheric Administration (NOAA) and U.S. Department of Energy, a comprehensive comparison was performed of inorganic carbon parameters measured on oceanographic surveys carried out under auspices of the Joint Global Ocean Flux Study and related programs. Many of the cruises were performed as part of the World Hydrographic Program of the World Ocean Circulation Experiment and the NOAA Ocean-Atmosphere Carbon Exchange Study. Total dissolved inorganic carbon (DIC), total alkalinity (TAlk), fugacity of CO₂, and pH data from twenty-three cruises were checked to determine whether there were systematic offsets of these parameters between cruises. The focus was on the DIC and TAlk state variables. Data quality and offsets of DIC and TAlk were determined by using several different techniques. One approach was based on crossover analyses, where the deep-water concentrations of DIC and TAlk were compared for stations on different cruises that were within 100 km of each other. Regional comparisons were also made by using a multiple-parameter linear regression technique in which DIC or TAlk was regressed against hydrographic and nutrient parameters. When offsets of greater than 4 $\mu\text{mol/kg}$ were observed for DIC and/or 6 $\mu\text{mol/kg}$ were observed for TAlk, the data taken on the cruise were closely scrutinized to determine whether the offsets were systematic. Based on these analyses, the DIC data and TAlk data of three cruises were deemed of insufficient quality to be included in the comprehensive basinwide data set. For several of the cruises, small adjustments in TAlk were recommended for consistency with other cruises in the region. After these adjustments were incorporated, the inorganic carbon data from all cruises along with hydrographic, chlorofluorocarbon, and nutrient data were combined as a research-quality product for the scientific community.

ABBREVIATED TERMS

AOML	Atlantic Oceanographic and Meteorological Laboratory
AOU	apparent oxygen utilization
AWI	Alfred-Wegener-Institut für Polar und Meeresforschung
BATS	Bermuda Atlantic Time-Series Station
BIO	Bedford Institute of Oceanography
BSH	Bundesamt für Seeschifffahrt und Hydrographie
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CRM	certified reference material
CSIC	Consejo Superior de Investigaciones Científicas
CTD	conductivity-temperature-depth sensor
DIC	total dissolved inorganic carbon
DOE	U.S. Department of Energy
$f\text{CO}_2$	fugacity of carbon dioxide
GCC	global carbon cycle
IEO	Instituto Español de Oceanografía
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
LDEO	Lamont-Doherty Earth Observatory
LODYC	Laboratoire d'Océanographie Dynamique et de Climatologie
LPO	Laboratoire de Physique des Océans
MLR	multiple-parameter linear regression
NBS	National Bureau of Standards
NOAA	National Oceanic and Atmospheric Administration
OACES	Ocean-Atmosphere Carbon Exchange Study
ODV	Ocean Data View
ORSTOM	Institut Français de la Recherche Scientifique pour le Développement en Coopération
PMEL	Pacific Marine Environmental Laboratory
RSMAS	Rosenstiel School of Marine and Atmospheric Science
SIO	Scripps Institute of Oceanography
SOC	Southampton Oceanography Centre
SOMMA	single-operator multiparameter metabolic analyzer
Talk	total alkalinity
UEA	University of East Anglia
US JGOFS	U.S. Joint Global Ocean Flux Study
WHOI	Woods Hole Oceanographic Institution
WHP	World Hydrographic Program
WOCE	World Ocean Circulation Experiment

1. INTRODUCTION

Various gases present in the Earth's atmosphere, such as water vapor (H_2O), carbon dioxide (CO_2), ozone (O_3), nitrous oxide (N_2O), methane (CH_4), and chlorofluorocarbons (CFCs), absorb thermal infrared (IR) radiation, creating the phenomenon commonly called the "greenhouse effect." Human industrial and agricultural activities have led to a rapid increase in concentrations of these "greenhouse gases," raising concerns over potential climate change. Of the greenhouse gases, CO_2 is the most important in terms of future global warming. Only about half of the anthropogenic CO_2 emitted remains in the atmosphere; the remainder is absorbed by the ocean and terrestrial biosphere. An excellent summary of the current state of knowledge on the greenhouse gases and projected increases can be found in the reports of the Intergovernmental Panel on Climate Change (IPCC) (Houghton et al. 1995, 2001). Predicting possible global climate change caused by CO_2 emissions requires forecasts of atmospheric CO_2 growth. This in turn necessitates obtaining temporal and spatial data from oceans and land that can be used to model the sequestration and storage of CO_2 in the oceans and terrestrial biosphere. Analysis of existing CO_2 measurements is fundamental to understanding the various uptake and storage processes (sinks) for CO_2 that have been observed to change on seasonal to decadal time scales. Future decisions on regulating emissions of greenhouse gases should be based on accurate models that have been adequately tested against accurate measurements.

During the 1990s, measurements of the oceanic inorganic carbon system, which are composed of total dissolved inorganic carbon (DIC), fugacity of CO_2 ($f\text{CO}_2$),¹ total alkalinity (TAlk), and pH, were taken on the World Hydrographic Program (WHP) cruises of the World Ocean Circulation Experiment (WOCE) and those of the Ocean-Atmosphere Carbon Exchange Study (OACES) of the National Oceanic and Atmospheric Administration (NOAA) (Fig. 1). These measurements have provided a benchmark of unsurpassed accuracy for the ocean inventory of CO_2 and other properties. The inorganic carbon measurements performed by U.S. investigators were cosponsored by NOAA and the U.S. Department of Energy (DOE) as part of the U.S. Joint Global Ocean Flux Study (US JGOFS) Program. In addition to the U.S. cruises, the Atlantic synthesis included a significant number of cruises sponsored by the science agencies of the foreign nations. This report addresses the consistency of oceanic inorganic carbon system parameter measurements taken from 1990 to 1998 in the northern and southern Atlantic Ocean and lists adjustments to some of the DIC and TAlk measurements based on careful analysis of the full data set.

The analysis of the large-scale data quality of inorganic carbon system parameters for the Atlantic syntheses data set followed the procedures outlined in Lamb et al. (2001) and Feely et al. (1999) with the objective of determining the consistency of inorganic carbon data among the different cruise data. The focus was on the DIC and TAlk state variables used in the calculation of the anthropogenic CO_2 inventory and for studies of biogeochemical carbon cycling. Four approaches were followed to determine whether there were systematic offsets in the cruise data sets.

- A. Inorganic carbon system values in deep water were compared where cruise tracks cross, hereafter referred to as "crossover analyses."
- B. Multiple-parameter linear regressions (MLRs) of DIC or TAlk with potential temperature, salinity, oxygen, silicate, and nitrate were created from data of cruises that followed a similar

¹The fugacity of CO_2 is the partial pressure of carbon dioxide ($p\text{CO}_2$) corrected for non-ideality of the gas (Weiss 1974). $f\text{CO}_2 \approx 0.996 p\text{CO}_2$; the terms are often used interchangeably.

cruise track. The calculated values were then compared with the measured parameters for each of the cruises.

- C. On cruises where more than two carbon system parameters were measured, the internal consistency between parameters was evaluated by using known thermodynamic relationships between the parameters.
- D. Finally, regional MLR regressions of DIC or TAlk with potential temperature, salinity, oxygen, silicate, and nitrate were created from all data in a particular region; data deemed good based on the previous checks were used. These fits were used together with hydrographic data from individual cruises to investigate differences between the calculated DIC or TAlk and the measured values.

The cruise lines used are shown in Fig. 1, and the distribution of data vs time and latitude are presented in Figs. 2 and 3, respectively. Observations decreased in 1995 and 1996 because the WOCE/WHP and OACES programs were focusing on the Indian Ocean during those years. The observations vs latitude show a reasonably uniform coverage for the carbon system parameters. Of note is the absence of alkalinity data in the Atlantic sector of the Southern Ocean.

In the crossover analyses, the four inorganic carbon system parameters (DIC, $f\text{CO}_2$, TAlk, and pH) were compared in density space referenced to 4000 dB (σ_4) at 53 locations where cruises overlapped throughout the Atlantic Ocean (Fig. 1, Table 1). Such comparisons have been made for oceanic carbon parameters in the Indian Ocean (Johnson et al. 1998, Millero et al. 1998, Sabine et al. 1999) and the Pacific Ocean (Lamb et al. 2001). Similar comparisons are under way for nutrient data (Gordon et al. 1998) and CFC data (Smethie, personal communication).

The analyses presented in this report are the basis for recommending adjustments to the data sets to form a consistent basin-wide unified data set. The corrected working data set, which includes the original carbon data as well, is provided as two large datafiles at the following web site: http://www.aoml.noaa.gov/ocd/oaces/atlantic_synthesis.html. The Atlantic data set in combination with those from the Indian and Pacific oceans will provide the first comprehensive global data set of DIC and TAlk to the research community. The Carbon Dioxide Information Analysis Center (CDIAC) web site (<http://cdiac.esd.ornl.gov/oceans/home.html>) will house all three corrected data sets. Data from the individual cruises can be found on the CDIAC site as well.

Crossover Locations in the North and South Atlantic

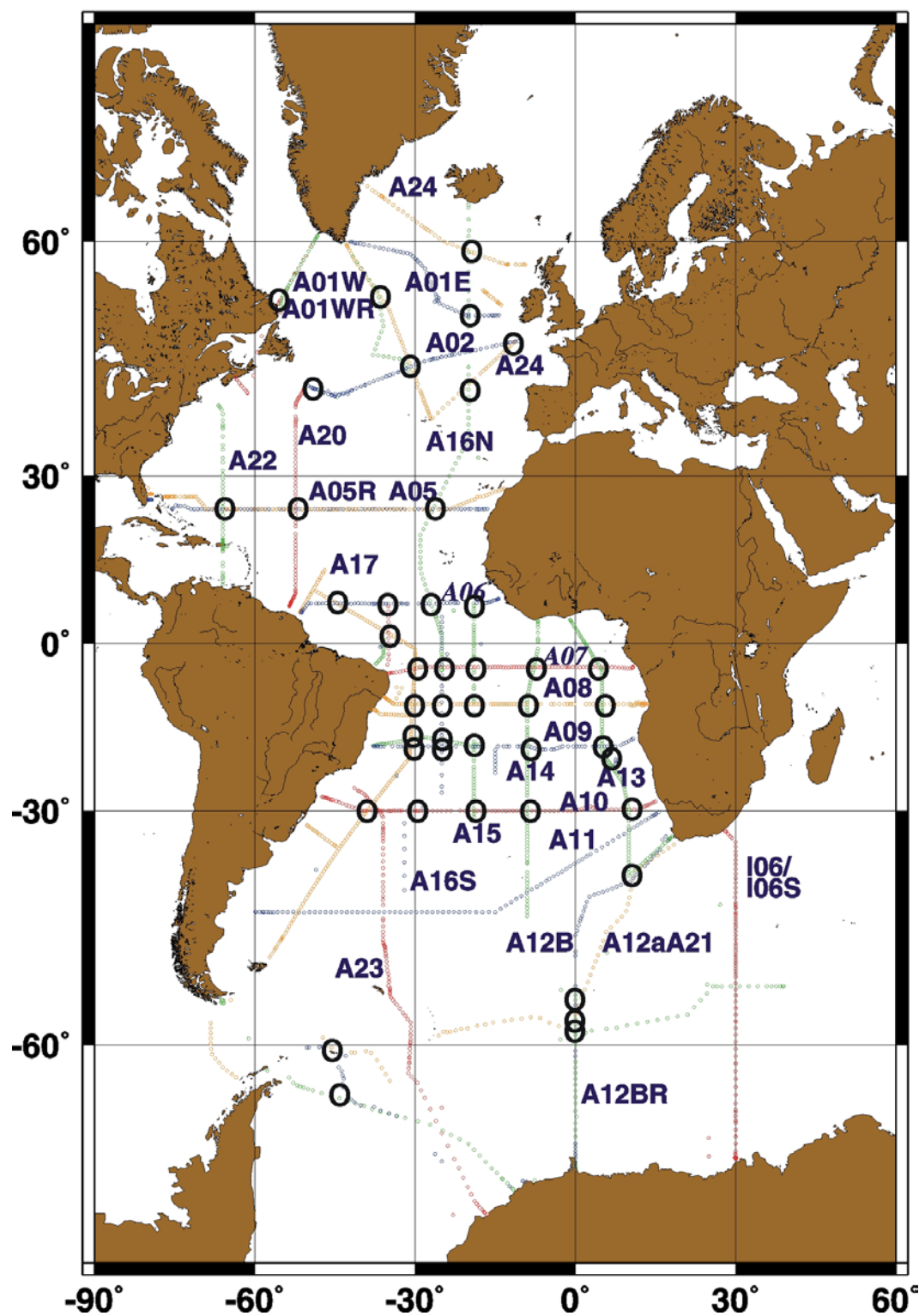


Fig. 1. Cruise tracks and crossover points (depicted as circles) for the Atlantic synthesis effort.

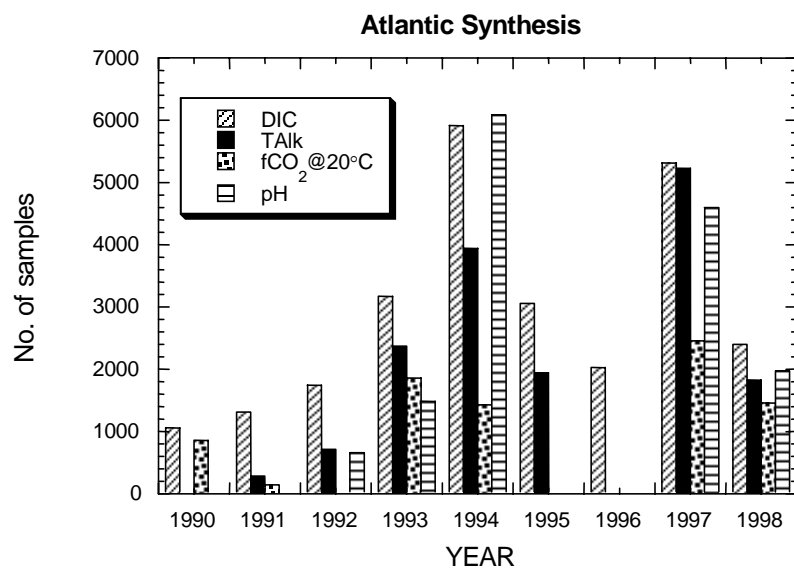


Fig. 2. Number of samples vs the year that the cruise was performed. (Note: the tally excludes A06 and A07.)

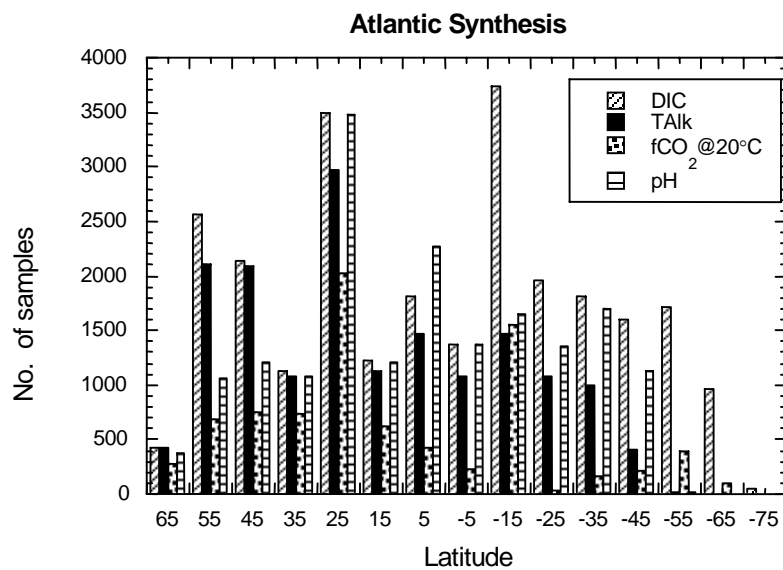


Fig. 3. Number of samples vs latitude. (Note: the tally excludes A06 and A07.)

Table 1. Cruises used in the Atlantic synthesis

No.	Cruise name EXPO code ^a	Research vessel	Period	Chief scientist ^b	Carbon-related data contributor ^b	Variables in data set ^b
1	A21/A12 06MT11_5	R/V <i>Meteor</i> 11/5	1/23/90–3/8/90	W. Roether/Univ. of Bremen	T. Takahashi/LDEO	Hydrogr., Nutr., DIC, $f\text{CO}_2$, CFC
2	A09 06MT15_3	R/V <i>Meteor</i> 15	2/10/91–3/23/91	G. Siedler/Univ. of Kiel	D. Wallace/Univ. of Kiel	Hydrogr., Nutr., DIC, TALK, $f\text{CO}_2$, CFC
3	A16S OACES91_1/2	R/V <i>Baldridge</i>	7/11/91–9/2/91	D. K. Atwood/AOML	R. Wanninkhof/AOML	Hydrogr., Nutr., DIC, $f\text{CO}_2$, TALK, underw. $f\text{CO}_2$
4	A01E 06MT18_1	R/V <i>Meteor</i> 18/1	9/2/91–9/26/91	D. Meincke/Univ. of Hamburg	D. Wallace/Univ. of Kiel	Hydrogr., Nutr., DIC, TALK, underw. $f\text{CO}_2$
5	A12B 06AQANTX_4	<i>Polarstern</i>	5/21/92–8/5/92	P. Lemke/Univ. of Kiel	M. Hoppema/Univ. of Bremen	Hydrogr., Nutr., DIC
6	A05 29HE06_1	R/V <i>Hesperides</i>	7/15/92–8/16/92	G. Parrilla/IEO, Spain	A. Rios/CSIC, Spain	Hydrogr, Nutr., DIC, TALK, pH
7	A10 06MT22_5	R/V <i>Meteor</i> 22	12/27/92–1/31/93	R. Onken/Univ. of Kiel	D. Wallace/Univ. of Kiel	Hydrogr., Nutr., DIC, TALK, CFC, underw. $f\text{CO}_2$
8	A11 74DI199_1	R/V <i>Discovery</i>	12/22/92–2/1/93	P. Saunders/SOC	N/A	Hydrogr., Nutr., CFC
9	A07 35A3CITHER1_2	R/V <i>L'Atalante</i>	1/2/93–2/10/93	A. Moliere/LODYC	C. Oudot/ORSTOM, Brest, France	Hydrogr., Nutr., DIC, TALK, $f\text{CO}_2$, pH, CFC
10	A06 35A3CITHER1_2	R/V <i>L'Atalante</i>	2/13/93–3/19/93	A. Moliere/C. Colin	C. Oudot/ORSTOM, Brest, France	Hydrogr., Nutr., DIC, TALK, $f\text{CO}_2$, pH, CFC
11	A16N OACES93	R/V <i>Baldrige</i>	7/4/93–8/30/93	R. Wanninkhof/AOML	R. Wanninkhof/AOML	Hydrogr., Nutr., DIC, TALK, $f\text{CO}_2$, pH, CFC, underw. $f\text{CO}_2$
12	A17 3230CITHER2_1/2	R/V <i>M Ewing</i>	1/4/94–3/22/94	L. Memery/LODYC	D. Wallace/A. Rios	Hydrogr., Nutr., DIC, TALK, pH, CFC, underw. $f\text{CO}_2$
13	A15 316N142_3	R/V <i>Knorr</i>	4/3/94–5/21/94	W Smethie/LDEO	C. Goyet/WHOI	Hydrogr., Nutr., DIC, TALK
14	A08 06MT28_1	R/V <i>Meteor</i>	3/29/94–5/11/94	T. Mueller/Univ. of Kiel	D. Wallace/Univ. of Kiel	Hydrogr., Nutr., DIC, $f\text{CO}_2$
15	A14 35A3CITHER3_1	R/V <i>L'Atalante</i>	1/17/95–2/11/95	M. Arhan/LPO	D. Wallace/A. Rios	Hydrogr., Nutr., DIC, TALK, pH, CFC, underw. $f\text{CO}_2$
16	A13 35A3CITHER3_2	R/V <i>L'Atalante</i>	2/22/95–3/28/95	M. Arhan/LPO	D. Wallace/Univ. of Kiel A. Rios/CSIC, Spain	Hydrogr., Nutr., DIC, TALK, CFC
17	A23 74JC10_1	RSS <i>JC Ross</i>	3/20/95–5/6/95	B. King/SOC K. Heywood/UEA	Robertson/SOC, England	Hydrogr., Nutr., DIC, $f\text{CO}_2$, CFC
18	A01W 18HU95011_1	R/V <i>Hudson</i>	6/7/95–7/5/95	J. Lazier/BIO, Canada	P. Jones/BIO, Canada	Hydrogr., Nutr., DIC, TALK, CFC
19	IO6 35MF103_1	R/V <i>M. Dufresne</i>	2/20/96–3/22/96	A. Poisson/Univ. of Paris	A. Poisson/Univ. of Paris	Hydrogr., Nutr., DIC, TALK, CFC

Table 1 (continued)

No.	Cruise name EXPO code ^a	Research vessel	Period	Chief scientist ^b	Carbon-related data contributor ^b	Variables in data set ^b
20	A12BR (SR04) 06AQANTXIII_4	<i>Polarstern</i>	3/17/96–5/20/96	E. Fahrbach/AWI	M. Hoppema/Univ. of Bremen	Hydrogr., Nutr., DIC, CFC
21	A02 06MT39_3	R/V <i>Meteor</i>	6/11/97–7/3/97	P. Koltermann/BSH	D. Wallace/Univ. of Kiel	Hydrogr., DIC, Talk
22	A20 316N151_3	R/V <i>Knorr</i>	7/17/97–8/10/97	R. Pickart/WHOI	F. Millero/RSMAS C. Sabine/PMEL; D. Wallace	Hydrogr., Nutr., DIC, Talk, <i>f</i> CO ₂ , pH, CFC
23	A22 316N151_4	R/V <i>Knorr</i>	8/15/97–9/3/97	T. Joyce/WHOI	F. Millero/RSMAS C. Sabine, D. Wallace	Hydrogr., Nutr., DIC, Talk, <i>f</i> CO ₂ , pH, CFC
24	A24 316N151_2	R/V <i>Knorr</i>	8/15/97–9/3/97	L. Talley/SIO	F. Millero/RSMAS D. Wallace/Univ. of Kiel	Hydrogr., Nutr., DIC, Talk, <i>f</i> CO ₂ , pH
25	A05R OACES98	R/V <i>Brown</i>	1/24/98–2/23/98	K. Lee/AOML	R. Wanninkhof/AOML	Hydrogr., Nutr., DIC, Talk, pH, <i>f</i> CO ₂ , CFC
26	A01WR (AR07W) 18HU98023_1	CCGS <i>Hudson</i>	6/22/98–7/8/98	P. Jones/BIO, Canada	P. Jones/BIO, Canada	Hydrogr., Nutr., DIC, Talk, CFC

^aThe official EXPO code for the OACES cruises were unavailable, the ones reported here were created for this report.

^bAbbreviations:

AOML	Atlantic Oceanographic and Meteorological Laboratory
AWI	Alfred-Wegener-Institut für Polar und Meeresforschung
BIO	Bedford Institute of Oceanography
BSH	Bundesamt für Seeschifffahrt und Hydrographie
CFC	chlorofluorocarbon
CSIC	Consejo Superior de Investigaciones Científicas
DIC	total dissolved inorganic carbon
<i>f</i> CO ₂	fugacity of carbon dioxide
hydrogr.	hydrography
IEO	Instituto Español de Oceanografía
LDEO	Lamont-Doherty Earth Observatory
LODYC	Laboratoire d'Océanographie Dynamique et de Climatologie
LPO	Laboratoire de Physique des Océans
nutr.	nutrients
ORSTOM	Institut Français de la Recherche Scientifique pour le Développement en Coopération
PMEL	Pacific Marine Environmental Laboratory
RSMAS	Rosenstiel School of Marine and Atmospheric Science
SIO	Scripps Institute of Oceanography
SOC	Southampton Oceanography Centre
Talk	total alkalinity
UEA	University of East Anglia
underw.	underway
WHOI	Woods Hole Oceanographic Institution

2. ANALYTICAL METHODS

Several significant advances in the chemical analysis of inorganic carbon system parameters occurred immediately prior to and during the inorganic carbon survey on the WOCE/WHP and OACES cruises. Many of the DIC measurements were performed by using a coulometer, often connected to a single-operator multiparameter metabolic analyzer (SOMMA), which has greater precision than previous techniques. For the U.S. cruises and many of the (later) foreign cruises, standard operating protocols were applied following the techniques outlined in the *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water* (DOE 1994). Certified reference materials (CRMs) were used on all U.S. cruises and on many non-U.S. cruises as secondary standards for DIC analyses. Discussion of the preparation and use of CRMs for DIC and TAlk is presented in detail in Dickson, Afgan, and Anderson (accepted) and Dickson, Anderson, and Afgan (submitted) (see also http://www-mpl.ucsd.edu/people/adickson/CO2_QC/). The CRMs consisted of natural seawater that was filtered, sterilized, and poisoned. Certification of the CRMs for DIC is based on manometric analyses in the shore-based laboratory of C. D. Keeling of Scripps Institution of Oceanography (SIO) over a period of several years. The CRMs were bottled in large batches into 500-mL borosilicate glass containers, sealed to prevent contamination, and shipped to the users. They were then analyzed at sea interspersed with samples over the course of each of the cruises as a way of verifying accuracy. Because CRMs were routinely analyzed for DIC during most cruises, groups analyzing TAlk on those cruises often measured CRMs for their alkalinity content. This enabled post-cruise corrections to be made to TAlk data based on archived CRMs that were analyzed at C. D. Keeling's laboratory and at the laboratory of F. Millero in Miami.

Insufficient metadata precluded a determination of which cruises had adjustments applied for TAlk based on CRM analyses. CRMs were not available for the other two carbon parameters discussed in this report ($f\text{CO}_2$ and pH). However, for some of the cruises the CRMs were used to normalize the pH values by calculating the pH of the CRMs from the certified TAlk and DIC values. Analyses of salinity, nutrients, and O_2 followed WOCE WHP protocol (WOCE 1994).

Analytical procedures differed between cruises. SOMMAs were used for all of the cruises that had U.S. investigators performing the DIC measurements (Johnson et al. 1993). For non-U.S. investigators, other procedures were used, ranging from use of coulometers with manual or automated pipettes to analysis by gas chromatography (Table 2). For some cruises, DIC was determined from TAlk and pH. The TAlk was measured by potentiometric titration logging of either a full titration curve (referred to as "Full" in Table 2) (Millero et al. 1993) or single-point titrations ("1-point") (Perez and Fraga 1987). For cruises A6 and A7, we were unable to find the appropriate metadata describing how the alkalinities were measured. The pH measurements were done by electrode, spectrophotometric, or potentiometric determination (Byrne and Breland 1989). Discrete $f\text{CO}_2$ was measured by equilibration of a discrete sample with a headspace with known initial concentration and by subsequent IR analysis (Wanninkhof and Thoning 1993) or gas chromatography (Chipman, Marra, and Takahashi 1993, Neil et al. 1997).

Table 2. Analytical methods used to measure the carbon system parameters

No.	Cruise name	Period	Dissolved inorganic carbon	Total alkalinity ^a	CO ₂ fugacity	pH
1	A21/A12	1/23/90–3/8/90	Coulometer	—	Gas chromatography ^b	—
2	A09	2/10/91–3/23/91	SOMMA ^c	Full ^d	—	—
3	A16S	7/11/91–9/2/91	SOMMA	Full	Infrared analysis ^e	—
4	A01E	9/2/91–9/26/91	SOMMA	Full	—	—
5	A12B	5/21/92–8/5/92	Coulometer	—	—	—
6	A05	7/15/92–7/23/92	Calculated	1-point	—	Electrode
7	A10	12/27/92–1/31/93	SOMMA	Full	—	—
8	A11	12/22/92–2/1/93	—	—	—	—
9	A07	1/2/93–1/10/93	Gas chromatography	—	Gas chromatography	Electrode
10	A06	1/2/93–3/19/93	Gas chromatography	—	Gas chromatography	Electrode
11	A16N	7/4/93–8/30/93	SOMMA	Full	Infrared analysis ^e	Spectrophotometric
12	A17	1/4/94–3/22/94	SOMMA	1-point	—	Potentiometric ^f
13	A15	4/3/94–5/21/94	SOMMA	Full	—	—
14	A08	3/29/94–5/11/94	SOMMA	—	Gas chromatography ^g	—
15	A13	2/20/95–3/2/95	SOMMA	1-point	—	—
16	A14	1/12/95–2/16/95	SOMMA	1-point	—	Potentiometric
17	A23	3/20/95–5/6/95	Coulometer	—	Gas chromatography ^h	—
18	A01W	6/95–7/95	Coulometer	Full	—	—
19	A12BR	3/17/96–5/20/96	Coulometer	—	—	—
20	A02	6/11/97–7/3/97	SOMMA	Full	—	—
21	A20	7/17/97–8/10/97	SOMMA	Full	—	Electrode
22	A22	8/15/97–9/3/97	SOMMA	Full	—	Electrode
23	A24	8/15/97–9/3/97	SOMMA	Full	—	Electrode
24	A05R	1/24/98–2/23/98	SOMMA	Full	Gas chromatography ^g	Spectrophotometric
25	A01WR	6/22/98–7/8/98	Coulometer	Full	—	Electrode

^aDetermined by potentiometric titration, either a full curve (“Full”) or a single-point (“1-point”) titration.

^b500-mL samples, analysis by gas chromatography. (Chipman, D. W., J. Marra, and T. Takahashi. Primary production at 47° N and 20° W in the North Atlantic Ocean: A comparison between the ¹⁴C incubation method and mixed layer carbon budget observations. *Deep-Sea Research II* 40, 151–69, 1993.)

^cSingle-operator multiparameter metabolic analyzer.

^dAnalyzed shoreside.

^e500-mL samples, infrared analysis. [Wanninkhof, R., and K. Thoning. Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods. *Mar. Chem.* 44 (2–4), 189–205, 1993.]

^fA17C only.

^g60- or 120-mL samples, analysis by gas chromatography. (Neill, C., K. M. Johnson, E. Lewis, and D. W. R. Wallace. Small volume, batch equilibration measurement of *f*CO₂ in discrete water samples. *Limnol. Oceanogr.* 42, 1774–83, 1997.)

^hMeasured at 4°C.

3. PROCEDURES TO DETERMINE OFFSETS

The quality of all data used in the analyses was extensively controlled by the investigators responsible for the measurements. Therefore, significant care was taken to avoid suggesting erroneous corrections. This is why different and largely independent approaches were used to look for biases. Adjustments were recommended only if there were clear-cut and consistent differences of greater than 4 $\mu\text{mol/kg}$ for DIC and 6 $\mu\text{mol/kg}$ for TAlk. The cutoffs correspond to about twice the precision of the measurements performed on the cruises based on replicate and deep-water comparisons. Issues of data variability with depth and/or station-to-station variability were more frequent than clear-cut offsets. Sometimes the variability was large enough to question the integrity and utility of the cruise for the purposes of large-scale integration.

Several methods were used to assess the consistency among DIC and TAlk data from the cruises. For the first method, cruise-to-cruise comparisons of measurements were performed at crossover points for deep water (>1500 m). The assumption was that variability in deep water would be very small and that the anthropogenic signal, which would complicate the comparison of cruise data spanning eight years, would be negligible. The analysis was performed in density space to avoid biases due to movement of water masses. The method incorporated the implicit assumption that there were no systematic biases with density over the time period. Several recent investigations have shown changes in properties throughout the water column, but limited time-series work suggests that the changes are smaller than the level of agreement we are striving for (4 $\mu\text{mol/kg}$ for DIC and 6 $\mu\text{mol/kg}$ for TAlk). For instance, the time series station data at Bermuda show constancy in deep-water DIC values to within 3 $\mu\text{mol/kg}$ (Fig. 4) (Nick Bates, personal communication).

In total, 53 crossovers were investigated. The breakdown of carbon parameters compared at the crossovers is shown in Table 3. As the table indicates, 20 of the 53 total crossovers had DIC as a common parameter for the junction of cruises; 16 had comparable TAlk and DIC data on both cruises. For 17 of the crossovers, three or four carbon system parameters were measured on both cruises.

Table 3. Parameters compared at the crossovers

Parameter	No. of crossovers
DIC only	19
DIC and TAlk only	17
DIC and $f\text{CO}_2$ only	0
DIC and pH only	0
Three or four parameters	17
Total	53

The second method was used for cruises that covered a similar cruise track. It involved an MLR of DIC or TAlk with parameters known to influence DIC or TAlk levels and/or those that are known to regress with DIC or TAlk. The measurements for the overlapping cruises were combined for depths generally greater than 1500 m, and the regression coefficients were determined for DIC or TAlk with T, S, SiO_2 , apparent oxygen utilization (AOU), and NO_3 . The calculated DIC or TAlk values from this MLR were then compared with the measured values to determine systematic differences among cruises. This method of comparison was applied to ten cruises that overlapped in space.

The third method involved assessment of internal consistency for cruises in which three or more inorganic carbon system parameters were measured. In this approach, the thermodynamic relationships of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) were used to calculate DIC from TAlk and $f\text{CO}_2$ or pH (or to calculate TAlk from DIC and $f\text{CO}_2$ or pH). The calculated values were then compared with the measured values. When significant differences are found between calculated and measured values, this approach does not a priori establish which of

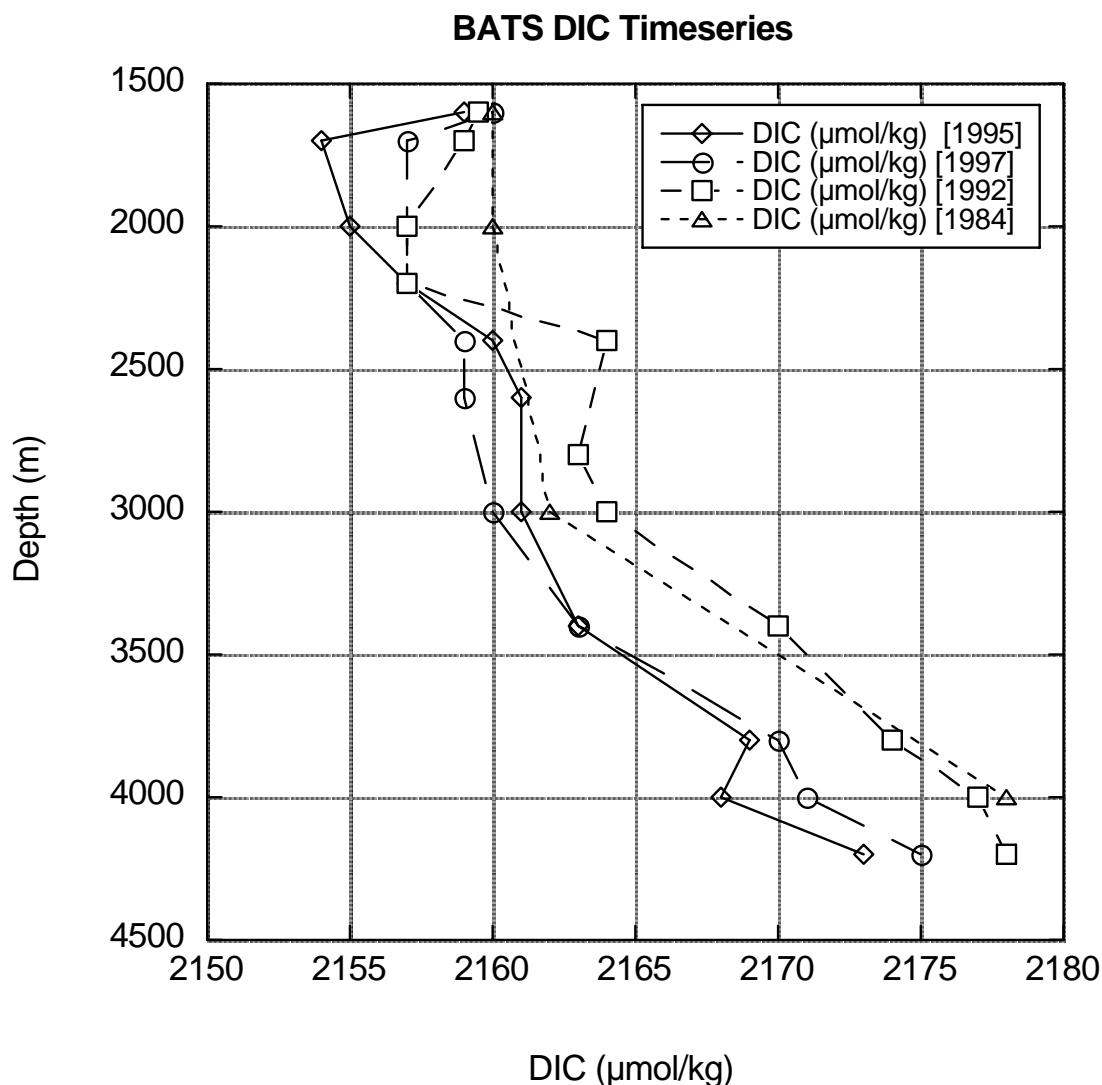


Fig. 4. Plot of deep DIC at the Bermuda time series station (BATS). The circles are data for 1997, the diamonds for 1995, and the open squares for 1992. The open triangles are samples from nearby Hydrostation S for 1984, analyzed by manometry by C. D. Keeling of the Scripps Institute of Oceanography. The small changes are a combination of inaccuracy in measurements and water-mass movement (data courtesy of Nick Bates, Bermuda Biological Station for Research).

the three parameters is in error, but the results can be used with the other methods to identify the culprit. Ten cruises had three or four inorganic carbon system parameters for which this approach could be applied.

The fourth method used the same MLR technique as was used in the overlapping cruise comparisons, but it was applied to cruises in a particular region. The regression fit was determined by using the cruises that had met the crossover criteria in a particular region for depths greater than 1500 m. The relevant data from all cruises were separated into three regions with distinctly different fits for the regressions: (1) The subtropical and polar regions north of 15° N, (2) the equatorial region between 15° N and 15° S, and (3) the subtropical and polar region

south of 15° S. The DIC and TAlk data for the individual cruises within each region were then compared with the calculated values from the corresponding regressions.

3.1 Crossover Analyses

Before the detailed crossover analyses were performed, all relevant parameters at crossover locations were inspected for overall data integrity. Data were imported into Ocean Data View (ODV), a data-visualization program available as freeware at <http://www.awi-bremerhaven.de/GEO/ODV/>. For each crossover, all stations within a 1° (≈100 km) radius of each other were included for analysis. Individual ODV profiles were created of the carbon parameters, temperature, salinity, oxygen, nitrate, phosphate, and silicate vs full water depth. Each crossover plot was visually inspected for offsets among the cruises that might be consistent across the hydrographic, nutrient, and carbon parameters. Such consistent offsets might indicate that different water masses were sampled on the two cruises. This first look also allowed us to detect errors such as improper recording of the measurement temperature for $f\text{CO}_2$ or an incorrectly labeled reference scale or measurement temperature for pH. After this visual inspection was completed, more rigorous approaches were performed to quantify offsets in carbon system parameters.

The crossover analyses involved the comparison of one to four inorganic carbon-system parameters (DIC, $f\text{CO}_2$, TAlk, and pH) at each crossover against the density referenced to 4000 dB, σ_4 . σ_4 was calculated from conductivity-temperature-depth sensor (CTD) salinity, CTD temperature, and pressure with the algorithms of Millero and Poisson (1981). When pressure was not included in the provided data set, the algorithms of Saunders and Fofonoff (1976) were used to calculate it from depth. A commercial plotting program, KaleidaGraph, was then used to create plots. Within each plot, an expanded area representing deep-water values was then selected (typically $\sigma_4 \approx 45.5\text{--}45.9$) and was plotted separately (Fig. 5). A second-order polynomial fit of the relevant carbon system parameter vs σ_4 was determined for this limited σ_4 range for each of the stations included in the crossover. For many of the crossovers, a strong curvature of DIC or TAlk vs density in the bottom waters complicated the curve-fitting analysis. Thus, the deepest water (Antarctic bottom water) often was not included in the regression. For high southern latitude crossovers, the inorganic carbon parameters were plotted against depth because the water masses south of 40° S have a very narrow density range.

Table 4 provides a summary of the derived constants M_0 , M_1 , M_2 , and r^2 from the polynomial $X = M_0 + M_1(\sigma_4) + M_2(\sigma_4)^2$ curve-fitting routine for each station profile, where X is a value for DIC, TAlk, $f\text{CO}_2$, or pH. The correlation coefficient r^2 indicates the goodness of fit and often is a good indicator of precision of the data for a particular station. The calculated curve for each station in each crossover analysis was divided into ten evenly spaced σ_4 intervals, on average, 0.04 units apart, over the data range ($\sigma_4 \approx 45.5\text{--}45.9$). The value of X was calculated for each point in the interval from the derived M_0 , M_1 , and M_2 for each of the stations. In all cases, the data bracketed the σ_4 interval. The average difference between station profiles was then determined and was used as the calculated offset in Table 4. The standard deviation of the difference of the ten points indicated whether the offset values were systematic or scattered around the mean. As a convention, the calculated difference is always the value for a crossover station being subtracted from the first cruise/station of that crossover listed in Table 4. A search radius of 1° (≈100 km) sometimes included more than one station from a given cruise. This situation offered the opportunity to assess offsets of data for adjacent stations for a particular cruise as well as

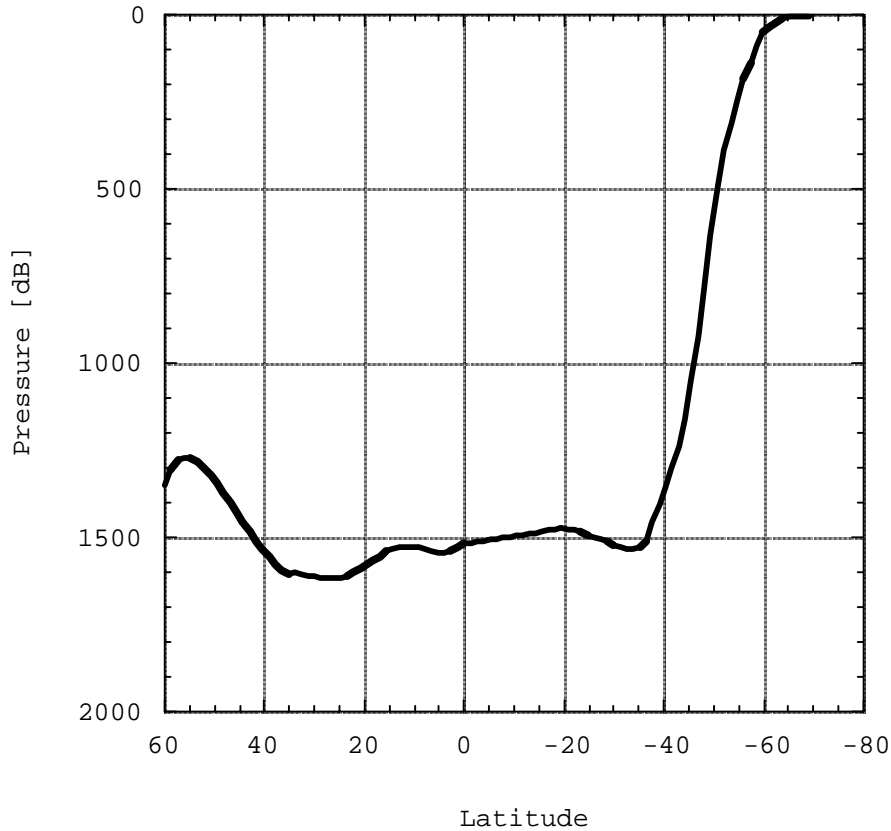


Fig. 5. Depth of isopycnal 45.5 (σ_4) in the Atlantic Ocean based on cruises A16N, A16S, and A23.

differences between cruises. Table 5 contains information similar to Table 4, but it is ordered according to the cruise. This table contains an average of the means of the crossovers listed for each cruise and is useful for determining whether parameters on a particular cruise show consistent offsets. Plots of the crossovers can be found on the following website:
http://www.aoml.noaa.gov/ocd/oaces/atlantic_synthesis.html.

3.2 The Regional Multiple-Parameter Linear Regression Method for Checking for Offsets in DIC and TALK

A regional MLR was applied to corroborate any offsets in the crossover comparisons of DIC and TALK data. The regional MLR was performed to determine whether DIC and TALK data for particular cruises were consistent in a regional context. For this check, a somewhat subjective assessment was made to determine which cruises to use as controls to create the MLR and which to use as unknowns. In general, the unknowns had larger offsets in the crossover analyses and/or had more scatter in the data. Several iterations were performed with different subsets of cruises used as controls to determine the coefficients. This was done to ensure consistency in cruise data

Table 4. Summary of crossover analysis results by location^a

Location	Cruise	Station	Dissolved inorganic carbon			Total alkalinity			pH		CO ₂ fugacity			
			Ave ^b	StDev ^c	R ^{2d}	Ave	StDev	R ²	Ave	StDev	R ²	Ave	StDev	R ²
66° W, 24.2° N	A22	42			0.753			0.767			0.611			
	A22	44	-1.9	1.1	0.804	-1.4	2.4	0.892	-0.0015	0.0031	0.730			
	A05	84	-3.4	3.1	1.000	-2.1	4.7	0.892	0.0383	0.0113	0.364			
66° W, 24.2° N	A22	42			0.753			0.767			0.611			
	A22	44	-0.9	2.0	0.804	-1.4	2.4	0.892	-0.0016	0.0031	0.730			0.729
	A05R	85	-3.4	4.6	0.714	-0.3	3.0	0.870	0.0119	0.0012	0.625	6.8	3.6	0.280
55° W, 53.4° N	A05R	86	-1.5	0.4	0.909	9.0	10.4	1.000	0.0148	0.0022	0.708	7.0	4.0	0.952
	A01W	3			0.916			0.922						
	A01W	4	-0.7	0.3	1.000	-1.5	7.9	1.000						
52.3° W, 24.2° N	A01W	5	-1.0	4.1	0.428	-3.3	3.9	0.990						
	A01WR	26	-7.93	2.95	0.961	-29.9	9.9	0.736						
	A01WR	28	-3.15	3.5	0.864	-27.5	7.1	0.770						
	A01WR	30	1.15	2.02	1.000	-19.9	5.2	1.000						
	A01WR	32	1.78	0.34	0.880	-26.3	13.3	0.753						
	A20	47			0.984			0.955			0.915			
	A20	48	-0.7	0.1	0.979	0.5	0.8	0.965	-0.0008	0.0020	0.852			
	A05	62	-0.7	2.3	0.999	-3.5	7.0	1.000	-0.0016	0.0059	0.999			
52.3° W, 24.2° N	A05	64	-4.5	5.9	1.000	-4.4	7.7	1.000	0.0051	0.0371	0.200			
	A20	47			0.971			0.976			0.908			
	A20	48	-0.7	1.4	0.979	0.6	0.7	0.969	-0.0004	0.0020	0.869			
50° W, 43.5° N	A05R	66	-2.5	2.8	0.886	-4.5	1.4	0.975	0.0130	0.0003	0.789			
	A05R	67	-5.7	1.0	0.975	-6.9	3.9	0.992	0.0123	0.0009	0.880			
	A20	8			0.903			0.751						
47.2° W, 60.2° S	A20	10	-3.9	5.0	0.287	-10.9	11.2	0.176						
	A02	334	2.7	0.9	0.948	-11.4	13.9	0.827						
	A02	336	-6.9	9.8	0.936									
	A12	122			0.963									
44.5° W, 7.4° N	A12B	640	1.3	0.5	0.524									
	A06	140			0.786			0.502			0.970			
	A17	200							-0.0509	0.0487	0.821			
44° W, 64° S	A17	201	5.4	14.9	0.832	2.2	11.8	0.933	-0.0477	0.0497	0.615			
	A17	202							-0.0512	0.0456	0.848			
	A12BR	94			0.933									
	A12B	630	0.9	0.4	0.960									
	A12B	631	3.6	2.9	0.977									

Table 4 (continued)

Location	Cruise	Station	Dissolved inorganic carbon			Total alkalinity			pH		CO ₂ fugacity			
			Ave ^b	StDev ^c	R ^{2d}	Ave	StDev	R ²	Ave	StDev	R ²	Ave	StDev	R ²
39° W, 30° S	A17	72			0.715			0.951						
	A17	75	-6.0	4.4	0.769	0.0	2.2	0.784						
	A10	11	2.0	3.5	0.872	25.1	2.5	0.847						
	A10	13	0.5	3.9	0.726									
38° W, 29° S	A23	115			1.000									
	A17	75	-2.6	4.0	0.963									
	A17	78	-6.5	2.8	0.984									
37° W, 30° S	A23	115			0.985									
	A10	15	-4.5	4.5	0.918									
36.6° W, 54° N	A24	115			0.710			0.492						
	A01W	55	0.5	0.7	0.616	15.3	4.9	0.296						
	A01W	57	-1.3	2.3	0.913	-8.6	17.6	0.277						
	A01W	58	-1.0	2.2	0.725	4.0	9.8	0.563						
35° W, 7.5° N	A06	154			0.603			0.519			0.995			
	A06	156	-15.5	8.3	0.894	-15.4	5.2	0.894	0.0042	0.0057	0.989			
	A07	158	-11.7	12.1	0.818	-9.5	10.6	0.882	0.0096	0.0055	0.988			
	A07	119	-13.0	2.5	0.581	-8.7	5.4	0.151	0.0102	0.0063	0.989			
35° W, 2° N	A17	180									0.873			
	A17	181							-0.0001	0.0008	0.903			
	A17	182			0.935			0.939	-0.0106	0.0009	0.895			
	A17	183							-0.0208	0.0030	0.962			
	A07	110	-26.1	2.6	0.271	-15.5	6.9	0.021	0.0351	0.0384	0.980			
	A07	112	-15.5	10.9	0.835	-8.5	2.0	0.093	0.0380	0.0343	0.889			
31.6° W, 45.8° N	A01W	77			0.755			0.201						
	A01W	78	0.6	1.5	0.757	1.2	14.4	0.924						
	A02	307	-0.8	1.4	0.888	-16.0	8.4	0.622						
31° W, 46.2° N	A24	131			0.868			0.898						
	A24	132				5.5	7.9	1.000						
	A24	133	-1.6	1.3	0.857	-1.2	1.4	0.776						
	A24	135	-1.3	1.8	0.927	-1.2	1.4	0.823						
	A01W	76	2.8	0.3	0.878	18.2	16.4	0.539						
	A01W	77	2.9	1.0	0.755	12.9	8.7	0.201						
30.4° W, 11.4° S	A01W	78	3.5	1.7	0.757	11.8	10.6	0.924						
	A17	145			0.833									
	A17	148	6.4	5.0	0.996									
	A08	186	6.4	5.4	0.655									
	A08	188	8.7	7.0	0.859									

Table 4 (continued)

Location	Cruise	Station	Dissolved inorganic carbon			Total alkalinity			pH		CO ₂ fugacity				
			Ave ^b	StDev ^c	R ^{2d}	Ave	StDev	R ²	Ave	StDev	R ²	Ave	StDev	R ²	
30.8° W, 46.1° N	A24	131			0.868			0.898							
	A24	132				0.3	0.8	0.879							
	A24	133	−1.3	1.7	0.906	−1.1	1.1	0.776							
	A24	135	−1.4	1.4	0.927	−1.4	1.4	0.823							
	A02	305	0.4	2.1	0.815	−4.5	2.2	0.444							
	A02	307	2.3	0.2	0.888	−1.9	2.3	0.056							
30.8° W, 18.8° S	A17	102			0.939			0.986							
	A17	105	−3.3	1.0	0.931	3.3	1.4	0.989							
	A09	143	0.2	4.5	0.802	−6.9	3.0	0.945							
30.8° W, 17.8° S	A17	105			0.945			0.816							
	A17	108	−1.5	1.8	0.921	−1.5	1.3	0.929							
	A15	134	2.1	1.6	0.936	14.4	0.7	0.938							
	A15	136	0.0	2.8	0.962	15.1	0.9	0.994							
30° W, 5° S	A17	157			0.543			0.970			0.959				
	A17	158							−0.0043	0.0025	0.904				
	A17	159							−0.0030	0.0019	0.899				
	A17	160	6.0	2.2	0.790	0.9	1.1	0.962	−0.0068	0.0048	0.858				
28.5° W, 29.5° S	A07	78	−5.0	3.4	0.353	−5.8	2.8	0.251	0.0253	0.0270	0.995				
	A07	80	−1.5	8.6	0.516	5.2	1.4	0.367	0.0281	0.0292	0.962				
	A16S	31			0.752			0.456							
	A10	36	1.0	1.0	0.605	2.3	4.6	0.781							
	27° W, 24° N	A16N	38			0.963			0.965			0.914			
		A16N	48	−0.4	0.7	0.990	1.3	1.2	0.866	0.0008	0.0010	0.948			
26.8° W, 24° N	A05	21	−5.5	7.9	0.926	−5.5	6.9	0.888	0.0148	0.0212	0.409				
	A16N	38			0.905			0.977			0.569			0.963	
	A16N	48	−0.6	3.1	0.869	0.8	0.5	0.777	−0.0003	0.0005	0.631	−2.7	5.3	0.662	
	A05R	26	−0.4	1.3	0.847	−2.3	1.3	0.757	−0.0001	0.0034	0.936	7.5	5.2	0.996	
26.8° W, 7° N	A05R	27	0.3	1.3	1.000				−0.0033	0.0024	0.981	10.6	4.8	0.900	
	A16N	24			0.984			0.937			0.997				
	A16N	25	4.2	1.8	0.994	6.0	1.9	0.989							
	A06	172	0.5	1.6	0.782	−9.3	−9.3	0.465	−0.2750	0.0270	0.941				
	25° W, 67.2° S	A23	19			0.903									
		A12BR	83	−29.8	0.3	0.903									
25° W, 19° S	A16S	23			0.789										
	A09	151	5.1	1.1	0.921										
25° W, 17° S	A16S	22			0.519			0.115							
	A15	122	1.7	3.0	0.738	−7.6	5.3	0.989							

Table 4 (continued)

Location	Cruise	Station	Dissolved inorganic carbon			Total alkalinity			pH		R ²	CO ₂ fugacity		
			Ave ^b	StDev ^c	R ^{2d}	Ave	StDev	R ²	Ave	StDev		Ave	StDev	R ²
25° W, 11° S	A16S	18			0.815			0.731						0.927
	A08	194	0.1	1.8	0.882	3.8	2.0	0.898				−19.1	13.3	0.426
	A08	196	−0.9	4.1	0.515	3.7	4.7	0.387				−31.5	14.9	0.302
25° W, 4.5° S	A16N	2			0.866			1.000						
	A16N	3	0.3	0.5	0.930	−15.3	20.0	0.988			0.961			
	A16N	4	3.7	4.6	0.671	−7.2	19.1	0.992	0.0047	0.0119	0.857			
	A16N	5	3.8	4.0	0.775	−9.4	20.4	0.880						
	A07	70	−1.3	13.9	0.171	−23.2	14.7	0.271	−0.2472	0.0261	0.962			
25° W, 4° S	A16S	12			0.905			0.860						0.712
	A07	70	−4.1	7.3	0.559	−50.5	9.6	0.244	−0.3048	0.0630	0.985			
20° W, 52° N	A16N	69			0.958			0.997						
	A16N	70	0.8	1.2	0.972	4.7	2.7	0.979						
	A16N	71	0.2	1.7	0.988	0.2	5.5	0.999						
	A01E	607	1.5	2.8	0.998	−58.7	17.1	0.985						
	A01E	610	2.3	2.6	0.999									
19.9° W, 43.8° N	A24	14			0.990			0.974			0.881			0.606
	A24	16	−2.6	0.9	0.941	0.7	1.1	0.969	0.0115	0.0106	0.833			
	A16N	61	−1.3	1.6	0.987	−5.2	3.1	1.000	−0.0050	0.0111	0.668	0.9	9.8	0.932
	A16N	63	−3.2	0.6	0.966	−4.4	3.3	0.863	−0.0084	0.0129	0.903	7.5	10.7	0.970
19.8° W, 59.1° N	A24	67			1.000			0.890						0.994
	A24	69				3.1	1.9	0.748			0.877			
	A16N	76	−1.4	7.1	0.963	0.1	2.8	0.985				13.3	3.5	0.998
	A16N	77	−4.6	9.8	0.874	3.3	3.1	0.758	−0.0168	0.0044	0.968	−7.0	22.6	0.746
	A16N	78	−1.7	8.7	0.763	3.3	2.0	0.828	−0.0175	0.0032	0.913	3.7	18.0	0.718
19° W, 7.5° N	A15	28			0.956			0.983						
	A06	184	−24.2	2.2	0.601	−33.8	5.2	0.437						
	A06	186	−11.2	6.5	0.718	−18.2	4.8	0.838						
	A06	188	−22.5	1.2	0.672	−30.8	5.2	0.716						
19° W, 30° S	A15	106			0.846			0.613						
	A10	46	−4.8	6.3	0.914									
	A10	48	−2.8	1.5	0.871	−0.6	1.3	0.806						
19° W, 19° S	A15	82			0.976									
	A09	161	−7.7	1.6	0.785									
19° W, 11° S	A15	66			0.976									
	A15	68	−2.6	7.1	0.994									
	A08	204	6.4	2.9	0.982									
	A08	206	−0.3	3.7	0.984									

Table 4 (continued)

[illegible]

Table 4 (continued)

Location	Cruise	Station	Dissolved inorganic carbon			Total alkalinity			pH			CO ₂ fugacity		
			Ave ^b	StDev ^c	R ^{2d}	Ave	StDev	R ²	Ave	StDev	R ²	Ave	StDev	R ²
5° E, 11.5° S	A13	195			0.909									
	A13	198	3.9	2.9	0.927									
	A08	254	2.6	0.9	0.894									
	A08	256	1.8	0.3	0.932									
5° E, 19° S	A13	179			0.981									
	A13	182	-3.0	2.1	0.995									
	A09	212	-2.6	1.8	0.995									
	A09	214	-5.8	0.8	0.991									
7° E, 22.6° S	A13	170			1.000									
	A13	173	5.2	1.8	0.955									
	A09	217	-1.3	2.8	0.978									
10° E, 29.8° S	A13	148			0.961									
	A13	151	0.6	1.2	0.962									
	A10	87	5.8	4.0	0.981									
	A10	89	1.4	1.7	0.914									
10° E, 40° S	A13	130			0.848									
	A12B	551	-7.8	3.5	0.816									
	A12B	552	-5.6	8.0	0.841									

^aAll values are the difference between the first station and the second (or subsequent one). Italicized values are from cruises that were not retained in the synthesis.

^bAve = Average difference of 10 equally spaced points on the two least squares second-order polynomial lines of property versus σ_4 between nominally $\sigma_4 = 45.5$ and 45.9 . The average difference between stations, "Ave," for the same cruise is an indication of the station to station variability in data.

^cStDev = Standard deviation of the average difference of ten equally spaced points on the two lines.

^dR² = Goodness of fit for the line. An R² of one indicates that only three points were in the selected range, which yields a perfect fit for the second order polynomial.

Table 5. Summary of crossover analysis results by cruise^{a,b}

Cruise	Crossover	Location	Dissolved inorganic carbon		Total alkalinity		pH		CO ₂ fugacity	
			Ave	StDev	Ave	StDev	Ave	St Dev	Ave	St Dev
A01E	A16N	20° W, 52° N	-1.89	0.53	58.69	17.14				
A01W	A24	36.6° W, 54° N	0.62	0.95	-3.58	11.96				
	A24	31° W, 46.2° N	-3.07	0.36	-14.31	3.45				
	A01WR	55° W, 53.4° N	-2.04	4.50	-25.90	4.26				
	A02	31.6° W, 45.8° N	-0.81	1.43	-16.02	8.44				
A01WR	A01W	55° W, 53.4° N	2.04	4.5	25.90	4.26				
A02	A20	50° W, 43.5° N	2.08	6.77	11.39	13.87				
	A01W	31.6° W, 45.8° N	0.81	1.43	16.02	8.44				
	A24	30.8° W, 46.1° N	-1.33	1.34	3.18	1.84				
	A24	11.2° W, 49.2° N	-0.06	7.6	4.28	2.39				
A05	A22	66° W, 24.2° N	3.42	3.1	2.13	4.69	-0.04	0.01		
	A20	52.3° W, 24.2° N	2.6	2.63	3.95	0.64	-0.002	0.01		
	A16N	27° W, 24° N	5.52	7.92	5.55	6.91	-0.01	0.02		
A05R	A22	66° W, 24.2° N	2.46	1.34	-4.33	6.57	-0.01	0	-6.92	0.11
	A20	52.3° W, 24.2° N	4.1	2.26	5.71	1.66	-0.01	0		
	A16N	26.8° W, 24° N	0.05	0.55	2.3	1.28	0.002	0	-9.05	2.16
A06	A17	44.5° W, 7.4° N	5.38	15	2.21	11.81	-0.05	0.002		
	A07	35° W, 7.5° N	-12.32	0.9	-8.67	5.43	0.01	0.006		
	A16N	26.8° W, 7° N	-0.54	1.6	9.30	1.29	0.28	0.030		
A07	A15	19° W, 7.5° N	19.27	7.07	27.60	8.28				
	A06	35° W, 7.5° S	12.32	0.9	8.67	5.43	0.01	0.0006		
	A13	4.8° E 4.7° S	-3.27	8.9						
	A14	8° W, 4.5° S	24.68	2.4	24.93	2.25	-0.06	0.005		
	A17	35° W, 2° N	20.77	7.5	12.02	4.92	-0.04	0.002		
	A17	30° W, 5° S	3.25	2.5	0.34	7.78	-0.03	0.002		
	A16S	25° W, 4° S	4.15	7.3						
A08	A16N	25° W, 4.5° S	1.28	14	23.22	14.73	0.25	0.03		
	A17	30.4° W, 11.4° S	-7.50	1.63						
	A16S	25° W, 11° S	0.37	0.69	-3.75	0.07			25.33	8.80
	A13	5° E 11.5° S	-2.21	0.57						
	A14	9° W, 11.5° S	-0.34	0.13	-11.53	0.82				
	A15	19° W, 11° S	-3.05	4.69						

Table 5 (continued)

Cruise	Crossover	Location	Dissolved inorganic carbon		Total alkalinity		pH		CO ₂ fugacity	
			Ave	StDev	Ave	StDev	Ave	St Dev	Ave	St Dev
A09	A17	30.8° W, 18.8° S	-0.18	4.53	6.95	3.01				
	A13	5° E 19° S	4.18	2.26						
	A13	7° E 22.6° S	1.26	2.82						
	A14	9° W, 19° S	1.34	2.21						
	A16S	25° W, 19° S	-5.11	1.13						
A10	A15	19° W, 19° S	7.69	1.64						
	A17	39° W, 30° S	-1.23	1.04	-25.1	2.47				
	A13	10° E 29.8° S	-3.64	3.13						
	A14	9° W, 30° S	-4.90	2.43						
	A16S	28.5° W, 29.5° S	-1.04	1.03	-2.27	4.58				
A12	A23	37° W, 30° S	4.51	4.53						
	A15	19° W, 30° S	3.84	1.42	0.56	1.29				
	A12B	0° 57° S	-0.46	1.70						
	A12B	47.2° W, 60.2° S	1.34	0.5						
	A12BR	0° 58.5° S	-1.70	0.81						
A12B	A12BR	0° 55.5° S	-2.31	0.65						
	A12BR	44° W, 64° S	-2.25	1.86						
	A12	0° 57° S	0.46	1.70						
	A12	47.2° W, 60.2° S	-1.34	0.50						
	A13	10° E 40° S	6.71	1.56						
A12BR	A12B	44° W, 64° S	2.25	1.86						
	A23	25° W, 67.2° S	29.78	0.30						
	A12	0° 58.5° S	1.70	0.81						
	A12	0° 55.5° S	2.31	0.65						
	A07	4.8° E 4.7° S	3.27	8.9						
A13	A08	5° E 11.5° S	2.21	0.57						
	A09	5° E 19° S	-4.18	2.26						
	A09	7° E 22.6° S	-1.26	2.82						
	A10	10° E 29.8° S	3.64	3.13						
	A12B	10° E 40° S	-6.71	1.56						
A14	A07	8° W, 4.5° S	-24.68	2.4	-24.93	2.25	0.03	0.005		
	A08	9° W, 11.5° S	0.34	0.13	11.53	0.82				
	A09	9° W, 19° S	-1.34	2.21	2.72	1.74				
	A10	9° W, 30° S	4.9	2.43						

Table 5 (continued)

Cruise	Crossover	Location	Dissolved inorganic carbon		Total alkalinity		pH		CO ₂ fugacity	
			Ave	StDev	Ave	StDev	Ave	St Dev	Ave	St Dev
A15	A17	30.8° W, 17.8° S	-1.05	1.47	-14.74	0.49				
	A16S	25° W, 17° S	-1.68	2.97	7.56	5.31				
	A10	19° W, 30° S	-3.84	1.42	-0.56	1.29				
	A06	19° W, 7.5° N	-19.27	7.07	-27.60	8.28				
	A09	19° W, 19° S	-7.69	1.64						
	A08	19° W, 11° S	3.05	4.69						
A16S	A10	28.5° W, 29.5° S	1.04	1.03	2.27	4.58				
	A09	25° W, 19° S	5.11	1.13						
	A15	25° W, 17° S	1.68	2.97	-7.56	5.31				
	A08	25° W, 11° S	-0.37	0.69	3.75	0.07			-25.33	8.80
	A07	25° W, 4° S	-4.15	7.3						
A16N	A05	27° W, 24° N	-5.52	7.92	-5.55	6.91	0.01	0.02		
	A05R	26.8° W, 24° N	-0.05	0.55	-2.3	1.28	-0.002	0	9.05	2.16
	A06	26.8° W, 7° N	0.54	1.6	-9.30	1.29	-0.28	0		
	A07	25° W, 4.5° S	-1.28	14	-23.22	14.73	-0.25	0		
	A01E	20° W, 52° N	1.89	0.53	-58.69	17.14				
	A24	19.9° W, 43.8° N	2.21	1.34	4.78	0.57	0.007	0	-4.2	4.72
A17	A24	19.8° W, 59.1° N	1.54	0.25	-2.23	1.85	0.02	0.0005	-3.34	10.17
	A06	44.5° W, 7.4° N	-5.38	15	-2.21	11.81	0.05	0		
	A10	39° W, 30° S	1.23	1.04	25.1	2.47				
	A07	35° W, 2° N	-20.77	7.5	-12.02	4.92	0.04	0		
	A07	30° W, 5° S	-3.25	2.5	-0.34	7.78	0.03	0		
	A08	30.4° W, 11.4° S	7.5	1.63						
	A09	30.8° W, 18.8° S	0.18	4.53	-6.95	3.01				
	A23	38° W, 29° S	4.56	2.8						
	A15	30.8° W, 17.8° S	1.05	1.47	14.74	0.49				
	A20	52.3° W, 24.2° N	-2.6	2.63	-3.95	0.64	0.002	0.01		
A20	A05R	52.3° W, 24.2° N	-4.1	2.26	-5.71	1.66	0.01	0		
	A02	50° W, 43.5° N	-2.08	6.77	-11.39	13.87				
	A05	66° W, 24.2° N	-3.42	3.1	-2.13	4.69	0.04	0.01		
A22	A05R	66° W, 24.2° N	-2.46	1.34	4.33	6.57	0.01	0	6.92	0.11
	A17	38° W, 29° S	-4.56	2.8						
A23	A10	37° W, 30° S	-4.51	4.54						
	A12BR	25° W, 67.2° S	-29.78	0.3						

Table 5 (continued)

Cruise	Crossover	Location	Dissolved inorganic carbon		Total alkalinity		pH		CO ₂ fugacity	
			Ave	StDev	Ave	StDev	Ave	St Dev	Ave	St Dev
A24	A01W	36.6° W, 54° N	-0.62	0.95	3.58	11.96				
	A01W	31° W, 46.2° N	3.07	0.36	14.31	3.45				
	A02	30.8° W, 46.1° N	1.33	1.34	-3.18	1.84				
	A02	11.2° W, 49.2° N	0.06	7.6	-4.28	2.39				
	A16N	19.9° W, 43.8° N	-2.21	1.34	-4.78	0.57	-0.007	0	4.2	4.72
	A16N	19.8° W, 59.1° N	-1.54	0.25	2.23	1.85	-0.02	0.0005	3.34	10.17

^aCrossover values are the differences between values for each cruise and the value for the crossover cruise (column 1). Italicized values are from cruises that were not retained in the synthesis.

^bIf more than one station of a cruise was used in a crossover, the mean values are given for the averages and standard deviations.

used to create the regressions. DIC and TALK data from greater than 1500 m were fit with an MLR as a function of common hydrographic parameters. After calculation of the linear regression, it was possible to investigate the residuals for evidence of systematic differences between the various cruises. Details of the procedure can be found in Key (1999, 2000). The data quality of the independent variables was checked in the regional MLR technique to minimize potential biases resulting from an artificial offset in one of the independent variables.

The following regressions were solved for the coefficients α_x and β_x :

$$DIC = \alpha_1 + \alpha_2 S + \alpha_3 \theta + \alpha_4 AOU + \alpha_5 NO_3 + \alpha_6 SiO_2 \quad (1)$$

$$TALK = \beta_1 + \beta_2 S + \beta_3 \theta + \beta_4 NO_3 + \beta_5 SiO_2 \quad (2)$$

where

α and β = constants,
 S = salinity,
 θ = potential temperature, °C,
 AOU = apparent oxygen utilization, $\mu\text{mol/kg}$,
 NO_3 = nitrate, $\mu\text{mol/kg}$,
 SiO_2 = silicate, $\mu\text{mol/kg}$.

The coefficients were determined from regressions of the data from the cruises listed as “control” in Tables 6 and 7. The independent variables used for the fits (θ , S , AOU , SiO_2 for TALK; and θ , S , AOU , SiO_2 , NO_3 for DIC) are closely related to response variables (DIC and TALK). Potential temperature, θ , and salinity, S , for example, represent physical factors that influence DIC and TALK, while AOU accounts for the biological effects. However, several different parameters can represent the same process. The choice of parameters used to represent the processes that affect DIC and TALK were based on previous work in the Pacific (Lamb et al. 2001).

The Atlantic Ocean is divided into three regions: (1) north of 15° N, (2) between 15° N and 15° S, and (3) south of 15° S. Water mass characteristics for each of these regions are different, and thus the coefficients of the MLR are different.

For DIC, the cruises used as controls in region 1 (north of 15° N) included A01E, A01W, A02, A05R, A16N, A20, A22, and A24 (see Table 6 for details). The cruises used as “unknown” were A05 and A01WR. In region 2 (between 15° N and 15° S), the cruises used as controls included A08, A13, A14, A15, A16N, and A20. Those used as unknowns were A06, A07, A16S, A22, and A17. In region 3 (south of 15° S) the controls were A10, A13, A14, A15, and A16S. The unknowns were A09, A12, A12B, A12BR, A17, A21, and IO6. The Indian Ocean cruise IO6 along 30° E was included in the Atlantic synthesis as a boundary cruise between the Indian and Atlantic oceans. Data from IO6 were consistent with other Indian Ocean data based on similar quality checks (Millero et al. 1998, Sabine et al. 1999). The correlation coefficient, standard error, and coefficients for the best-fit equations obtained from the controls for each region for depths greater than 1500 m are as follows.

- Region 1—north of 15° N, $N = 3130$, $R^2 = 0.95$, residual standard error = 3.44 $\mu\text{mol/kg}$

$$DIC = 2519.890 - 11.741 S + 1.418 T + 0.369 AOU + 0.896 NO_3 + 0.693 SiO_2 \quad (3)$$

- Region 2—between 15° N and 15° S, $N = 1751$, $R^2 = 0.93$, residual standard error = 5.72 $\mu\text{mol/kg}$

$$DIC = 783.944 + 38.214 S + 0.369 T + 0.033 AOU + 1.375 NO_3 + 0.974 SiO_2 \quad (4)$$

- Region 3—south of 15° S, $N = 1388$, $R^2 = 0.95$, residual standard error = 4.68 $\mu\text{mol/kg}$

$$DIC = 4546.784 - 69.213 S + 5.210 T + 0.009 AOU + 0.385 NO_3 + 0.887 SiO_2 \quad (5)$$

Predicted DIC values were computed with these equations and were compared with observed values. The mean difference between observed DIC and the predicted DIC (i.e., observed minus predicted) for each of the cruises is given in Table 6.

For TALK, the cruises used as controls in region 1 included A05, A05R, A16N, A22, and A24. The unknown cruises were A01E, A01W, A02, and A20. In region 2, the controls were A14, A15, A16N, A16S, and A22. The unknowns were A06, A07, A08, A17, and A20. In region 3, the

Table 6. Results of the multiple-parameter linear regression checks of dissolved inorganic carbon (observed – predicted)

Location	Cruise	Mean	StDev	n	Type
North of 15° N	A05	–0.40	8.39	175	Unknown (calc) ^a
	A01WR	–0.83	3.01	145	Unknown
	A01E	–0.78	2.98	227	Control
	A01W	0.86	3.77	355	Control
	A02	0.98	2.12	223	Control
	A05R	1.73	3.55	642	Control
	A16N	1.38	3.22	307	Control
	A20	–3.49	1.94	451	Control
	A22	–2.24	2.92	410	Control
15° N to 15° S	A24	1.66	2.54	515	Control
	A06	14.95	12.39	550	Unknown
	A07	10.60	12.09	640	Unknown
	A17	–3.39	3.02	662	Unknown
	A16S	–47.91	12.94	33	Unknown
	A22	9.00	2.21	42	Unknown
	A08	0.54	5.87	652	Control
	A13	–2.82	4.80	283	Control
	A14	0.31	2.40	182	Control
	A15	–2.01	3.05	229	Control
	A16N	–1.74	3.51	255	Control
	A20	–1.00	1.74	150	Control
	A09	4.81	7.76	309	Unknown
	A12	–7.66	6.26	164	Unknown
	A12B	–2.75	6.82	74	Unknown
South of 15° S	A12BR	–4.70	6.86	40	Unknown
	A17	–0.63	4.30	456	Unknown
	A21	–7.37	11.45	72	Unknown
	A23	–21.11	14.46	18	Unknown
	I06	–16.47	11.51	418	Unknown
	A10	–0.24	4.56	468	Control
	A13	2.58	4.56	437	Control
	A14	0.14	3.58	212	Control
	A15	–4.09	2.28	233	Control
	A16S	–2.62	3.59	38	Control

^aCalculated from pH and total alkalinity.

controls were A10, A14, A15, and A16S. The unknowns were A09, A12, A21, A23 and A17. The best-fit MLR equations obtained from the control cruises for TAlk are as follows.

- Region 1—north of 15° N, $N = 1759$, $R^2 = 0.93$, residual standard error = 4.2 $\mu\text{mol/kg}$

$$TAlk = -450.510 + 77.811 S - 3.706 T + 2.570 NO_3 + 0.808 SiO_2 \quad (6)$$

- Region 2—between 15° N and 15° S, $N = 737$, $R^2 = 0.78$, residual standard error = 6.9 $\mu\text{mol/kg}$

$$TAlk = 808.654 + 43.164 S - 18.971 T + 3.765 NO_3 + 0.408 SiO_2 \quad (7)$$

- Region 3—south of 15° S, $N = 754$, $R^2 = 0.67$, residual standard error = 8.4 $\mu\text{mol/kg}$

$$TAlk = -634.340 + 84.305 S - 3.401 T + 0.588 NO_3 + 0.560 SiO_2 \quad (8)$$

TAlk values were computed with these equations and were compared with observed values. The mean difference between observed TAlk and the predicted TAlk (i.e., observed minus predicted) for each of the cruises are given in Table 7.

Table 7. Results of the multiple-parameter linear regression checks of total alkalinity (observed – predicted)

Location	Cruise	Mean	StDev	n	Type
North of 15° N	A01E	69.61	20.23	39	Unknown
	A01W	-13.94	20.18	337	Unknown
	A01WR	-5.66	10.95	128	Unknown
	A02	3.50	5.71	225	Unknown
	A20	-5.86	3.76	411	Unknown
	A05	0.44	7.92	193	Control
	A05R	-0.82	4.48	366	Control
	A16N	0.48	4.00	312	Control
	A22	-0.85	2.89	371	Control
15° N to 15° S	A24	0.73	2.38	517	Control
	A06	28.85	14.58	544	Unknown
	A07	21.17	13.49	629	Unknown
	A08	-2.97	7.43	639	Unknown-calc ^a
	A17	4.87	4.80	727	Unknown
	A20	-2.46	5.03	147	Unknown
	A14	4.97	3.63	234	Control
	A15	-3.22	4.02	223	Control
	A16N	-0.90	6.41	208	Control
South of 15° S	A16S	-7.41	15.48	35	Control ^b
	A22	26.54	2.61	37	Control ^b
	A09	9.85	8.95	60	Unknown
	A17	6.24	4.53	477	Unknown
	A12	-13.05	7.67	164	Unknown-calc ^a
	A21	-12.86	7.76	4	Unknown-calc ^a
	A23	-8.16	21.81	36	Unknown-calc ^a
	IO6	-11.39	10.22	398	Unknown
	A10	-0.99	9.80	228	Control
	A14	6.16	5.33	255	Control
	A15	-4.48	3.99	229	Control
	A16S	-7.57	8.24	42	Control

^aCalculated from pH and total alkalinity.

^bThese cruises should have been treated as an unknown. However, because of the small number of samples, it does not affect the coefficients determined in the multiple-parameter linear regression.

3.3 The Multiple-Parameter Linear Regression Method for Checking Overlapping Cruises

Several of the cruise lines were completely or partially reoccupied during the 1990s, and the MLR technique was used to compare the overlapping cruise data as well. This method is preferable to direct comparison because biogeochemical variables often co-vary in a systematic fashion in water masses. Water mass movement between the times of investigation is thus (partially) accounted for in the MLR technique. The following cruises were compared: A05 with A05R, A16N with A16S, A01W with A24, A01W with A01WR, and A12B with A12BR. The suffix “R” stands for repeat occupation.² The coefficients for the MLR were determined by combining data from both cruises in question. Multiple-parameter linear fits of the form

$$DIC = \alpha_1 + \alpha_2 S + \alpha_3 \theta + \alpha_4 AOU + \alpha_5 NO_3 + \alpha_6 SiO_2,$$

and

$$Talk = \beta_1 + \beta_2 S + \beta_3 \theta + \beta_4 NO_3 + \beta_5 SiO_2$$

were created for the combined data set, and the average differences between the observed points and calculated values (observed minus predicted from the fit) were determined (Table 8).

The MLR was applied over different depth ranges, depending on number of samples and the density structure. In general, samples at depths greater than 1500 m were used to avoid biases from variations in the upper water column. For the A16N/A16S comparison between 4° N and 4° S along 25° W, the criteria were relaxed to include depths up to 200 m to get a sufficient number of samples. Because both cruises were run in the summer, seasonal variability should not have unduly affected the values. For the high-northern-latitude A24 and A01W cruises, only samples deeper than 3000 m were analyzed because the high-latitude regions experience deep ventilation and the two cruises did not overlap exactly in space. No significant differences were observed for DIC between overlapping cruises. Significant differences were observed for TALK for A24, A01W, and A01WR, but these differences were generally within one standard deviation. As described below, these results were used as corroborative evidence of systematic offsets between cruises.

3.4 Other Inorganic Carbon System Parameters

The primary uses for pH and fCO_2 measurements in this work are to determine the internal consistency of the inorganic carbon measurements when three or four carbon parameters were measured and to calculate TALK or DIC on the cruises when these state variables were not measured. In these cases, DIC and pH (or fCO_2) are used to determine TALK, and TALK and pH (or fCO_2) are used to calculate DIC. The fCO_2 and pH data on cruises were compared by using the same crossover analyses as DIC and TALK, but no recommendations are made regarding adjustments because the paucity of fCO_2 and pH data makes it difficult to sufficiently evaluate these parameters.

3.4.1 pH

Electrodes or spectrophotometry were used to measure pH. The spectrophotometric pH measurements have excellent precision, of 0.001 or better (McElligott et al. 1998). Because pH is

²Throughout this report the standard WOCE/WHP cruise identifiers were used except for the repeat occupations, which are listed by the WOCE/WHP primary cruise identifier with an “R” attached rather than the official WOCE/WHP repeat cruise designation, “ARXX.”

Table 8. Summary of comparisons of overlapping cruises

Overlap	Nominal position		Cruise name/ WOCE line	Dates of occupation	Station range	Depth range	Dissolved inorganic carbon			Total alkalinity		
	Longitude range	Latitude range					Ave	StDev	Number of samples	Ave	StDev	Number of samples
A05/A05R	23.85° W	24.5° N	A5R	28 Jan to 16 Feb 1998	22	>1500	0.4	3.0	534	0.0	4.4	313
	69.13° W	24.5° N	A5R		89							
	23.34° W	24.5° N	A5	24 July to 11 Aug 1992	17	>1500	-1.6	8.1	144	0.0	7.7	159
	69.33° W	24.5° N	A5		89							
A16S/A16N	25° W	4° N	A16S	16 July to 20 July 1991	7	>200	-1.0	6.1	99	-1.0	8.9	71
	25° W	4° S	A16S		12							
	25° W	4° S	A16N	8 July to 10 July 1993	4	>200	0.2	4.1	281	0.4	5.7	261
	25° W	4° N	A16N		14							
A01W/A24	41.96° W	58.84° N	A24	19 June to 21 June 1997	103	>3000	0.5	1.7	167	3.6	1.9	151
	37.07° W	54.84° N	A24		114							
	41.73° W	58.59° N	A01W	17 June to 19 June 1995	44	>3000	-0.5	1.5	111	-2.8	16.0	200
	37.07° W	55.03° N	A01W		55							
A01W/A01WR	53.98°	55.26° N	A01W	13 June to 26 June 1995	11	>1500	1.6	2.1	406	-7.1	13.7	247
	48.28° W	58.59° N	A01W		43							
	53.82° W	55.41° S	A01WR	28 June to 3 July 1998	48	>1500	-1.7	2.8	151	5.2	13.1	271
	49.16° W	59.74° S	A01WR		97							
A12B/A12BR	0° W	55° S	A12B	8 June to 27 July 1992	576	>1500	0.0	2.5	195			
	48.65° W	60.17° S	A12B		641							
	3.06° E	58.60° S	A12BR	3 April to 7 May 1996	29	>1500	0.0	2.5	452			
	50.84° W	63.73° S	A12BR		99							

very sensitive to changes in TAlk and DIC, it can be used to discern minute changes in them. For example, for North Atlantic deep water with DIC = 2192 $\mu\text{mol/kg}$, TAlk = 2349 $\mu\text{mol/kg}$, and pH_{sw} (25°C) = 7.7417, a 1- $\mu\text{mol/kg}$ change in DIC will result in a 0.0023 change in pH. However, the accuracy of the measurements is not well quantified and is currently under debate (DelValls and Dickson 1998, Millero et al. submitted). CRMs were used to normalize pH values on cruises A13, A14, and A17 by calculating pH from the certified DIC and TAlk values and from the dissociation constants recommended by Mehrbach et al. (1973). The measured pH values were then normalized to the mean calculated CRM value for each cruise (Ríos and Perez 1999)

Eleven of the 24 cruises had pH measurements. Different analysis techniques were used, and the pH values were recorded on different reference scales. Metadata provided with the pH measurements often were not sufficient to fully comprehend methods and corrections. A summary of the metadata is provided in Table 9. Much of the pH data were reported at 25°C on the seawater scale [pH_{sw} (25°C)]. The data from A16N, A17C, and A14 that were not reported at 25°C and on the SW scale were corrected to pH_{sw} (25°C) in order to perform the crossover analyses. The conversion was done by using the program of Lewis, Wallace, and Allison (1998) and by applying the carbonate dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). Because the temperature dependence of pH is not well known, these adjustments (and therefore the crossover comparison) should be viewed with caution.

Table 9. Summary of metadata for cruises with pH measurements

Cruise	Method	Temp. (°C)	Calibration ^a	Principal investigator	Remarks ^b
A05 ^c	Potentiometric	25	Yes	Ríos	OK
A5R	Spectroscopic	25	Yes	Millero	OK
A06	Potentiometric	<i>d</i>	<i>d</i>	<i>d</i>	No
A07	Potentiometric	<i>d</i>	<i>d</i>	<i>d</i>	No
A14	Potentiometric	15 ^e	Yes	Ríos	No ^e
A16N	Spectroscopic	20	Yes	Millero	OK
A16S	Potentiometric	25	No	Millero	No
A17C ^e	Potentiometric	15 ^e	No ^e	Ríos	No ^e
A20 ^f	Potentiometric	25	Yes	Millero/Sabine	No
A22 ^f	Potentiometric	25	Yes	Millero Sabine	No
A24 ^f	Potentiometric	25	Yes	Millero/Sabine	No

^aYes = pH values are normalized by using certified reference materials (CRMs) calibrated on shore. No = pH values were not referenced to CRMs.

^bRecommendation of Kitack Lee and Frank Millero whether pH is reliable for crossover analysis and internal consistency. OK = recommended, No = not recommended.

^cMeasured on the National Bureau of Standards (NBS) scale at 15°C but reported at 25°C seawater scale by principal investigator (A. Ríos).

^dUnknown.

^eReported on the NBS scale.

^fNot deemed reliable (Millero, personal communication).

A16N data were provided on the seawater scale at 20°C. The correction to 25°C was performed by using the measured DIC and pH_{sw} (20°C) and the Lewis, Wallace, and Allison (1998) program. The A14 and A17 data were provided on the National Bureau of Standards (NBS) scale at 15°C. Correction to 25°C on the seawater scale was done by first calculating $f\text{CO}_2$ from DIC and pH_{nbs} (15°C), and then by using the DIC and calculated $f\text{CO}_2$ to determine pH_{sw} (25°C). Both the original reported pH data and the converted data are presented in the working synthesis data files.

3.4.2 Fugacity of CO₂

The fugacity of CO₂ was measured throughout the water column on seven cruises. Like pH, the measurements were performed at a fixed temperature. Agreement between cruises was good (see Table 4), considering that there were no liquid reference materials and that gas standards used by different groups were not intercalibrated. The precision of the measurements depends on the methodology, but in general it was better than 2 μatm for surface waters (<500 μatm) and within 1% of the measured value for deep water. The $f\text{CO}_2$ (20°C) is very sensitive to changes in TAlk and DIC, particularly in deep water. For example, for North Atlantic deep water with DIC = 2192 $\mu\text{mol/kg}$, TAlk = 2349 $\mu\text{mol/kg}$, and $f\text{CO}_2$ (20°C) = 757 μatm , a 1 $\mu\text{mol/kg}$ change in DIC will result in a 5- μatm change in $f\text{CO}_2$ (20°C). Thus a commonly quoted DIC precision of 2 $\mu\text{mol/kg}$ corresponds to a 10 μatm uncertainty in $f\text{CO}_2$ (20°C) for deep water. The only crossover that exhibited significant differences was that of A16S and A8 (see Table 5). Based on the internal consistency analyses (see Sect. 3.5), the difference in measured TAlk and calculated TAlk [from DIC and $f\text{CO}_2$ (20°C)] for A16S of -3.6 $\mu\text{mol/kg}$ suggests that the A16S deep-water $f\text{CO}_2$ (20°C) measurements are low by 10 to 15 μatm .

3.5 Internal Consistency Checks

For cruises in which more than two inorganic carbon system parameters were measured, it is possible to assess the agreement of the inorganic carbon data by an internal consistency check. With knowledge of the apparent carbonate dissociation constants and two carbon system parameters, the other two can be calculated. Although there remains controversy about the accuracy of the carbonate-dissociation constants, there is increasing evidence that those of Merzbach et al. (1973) as refit by Dickson and Millero (1987) yield consistent results (Lee et al. 2000, Millero et al. submitted). Internal consistency checks were performed for cruises where three or four parameters were measured. The results are presented in Table 10.

Table 10. Summary of internal consistency on Atlantic CO₂ data sets

Cruise	pH + TAlk $\Delta\text{DIC}^{a,b}$		pH + DIC $\Delta\text{TAlk}^{a,b}$		$f\text{CO}_2$ + TAlk $\Delta\text{DIC}^{a,b}$		$f\text{CO}_2$ + DIC $\Delta\text{TAlk}^{a,b}$	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
A06 ^c	87.5	37.1	-87.5	40.4	-92.9	7.9	92.9	9.5
A07 ^c	89.4	34.5	-89.4	37.5	-83.4	10.5	83.4	12.6
A14	-4.6	3.8	4.8	4.0				
A17	-7.2	4.3	7.5	4.5				
A20	3.3	2.9	-3.6	3.1	0.3	3.0	-0.4	3.4
A22	0.7	2.9	-0.9	3.1	-2.3	2.4	2.5	2.8
A24	-8.6	3.8	8.9	4.0	-2.9	3.9	3.2	4.5
A16N	-3.7	3.6	3.8	4.2	-0.9	4.5	1.0	5.1
A16S					3.3	11.6	-3.7	13.5
A05R	-1.6	4.2	1.6	4.4	0.4	6.4	-0.5	7.4

^aThe Δ is measured minus calculated quantity. The parameters preceding the deltas are the input parameters used for the calculations.

^bAbbreviations: TAlk: total alkalinity, DIC: total dissolved inorganic carbon, $f\text{CO}_2$: carbon dioxide fugacity.

^cNot recommended for use in this synthesis.

Of the cruises listed in Table 10, A06 and A07 are not recommended for use in the synthesis because of inconsistent data and because of the absence of appropriate metadata. A17 and A24 show significant differences in measured and calculated TAlk and DIC. For A24 this appears to be an issue with the pH measurements because the calculation with $f\text{CO}_2$ shows reasonable agreement. For A17, Ríos and Perez (1999) show better agreement, having used the original Mehrbach (1973) constants. Because the crossover differences in DIC and TAlk for A17 with

other cruises are smaller than the internal consistency offset, we attribute this to issues with the applied internal consistency method. When the constants used in our analysis are applied, the difference is consistent over the entire DIC range (Fig. 6) but with a trend with latitude. The pH data for A20, A22, and A24 were measured by potentiometry and, according the responsible investigator (Millero), do not have the accuracy for a robust crossover analysis.

4. RECOMMENDATIONS

The data included in the Atlantic synthesis data set come from diverse sources, and the intercomparisons are complicated by the dynamic nature of the Atlantic Ocean; shifts in bottom-water characteristics have been documented. Therefore, we are being conservative and only recommend adjustments in the synthesis data set when there are clear biases of greater than 4 $\mu\text{mol/kg}$ for DIC and 6 $\mu\text{mol/kg}$ for TAlk. The recommendations are solely for the purpose of this analysis, to produce an internally consistent basin-wide data set of DIC and TAlk that can be used to quantify large-scale characteristics. Data sets that were deemed of insufficient quality for this analysis can have significant intrinsic merits for other applications.

Overall, the data appear to be of high quality, and only a few cruises showed consistent biases for each method. Variability within profiles and between stations often was of the same magnitude as the cruise-to-cruise differences (see Table 4). If adjustments had to be applied, the assessments were somewhat subjective because the statistical evidence of the different methods of comparison had to be weighed in an arbitrary manner. Our approach, as outlined in Sects. 4.1 and 4.2, consisted of first looking at the crossover results (see Tables 4 and 5) for offsets between cruises. From this comparison it was determined whether an offset appeared consistent for a particular cruise at all crossovers with other cruises. Table 5, which has the crossovers ordered per cruise, is particularly useful for this check. DIC anomalies of greater than 4 $\mu\text{mol/kg}$ and TAlk anomalies greater than 6 $\mu\text{mol/kg}$ prompted closer scrutiny. If cruises showed a consistent bias, it was determined whether a similar bias was apparent in the regional MLR, internal consistency, and overlapping cruise regressions. Cruise-by-cruise narratives for crossovers with offsets of DIC greater than 4 $\mu\text{mol/kg}$ (Sect. 4.1) and TAlk greater than 6 $\mu\text{mol/kg}$ (Sect. 4.2) provide a rationale for the proposed adjustments.

In cases of overlapping cruises when only one of the cruises is used, the repeat cruise is recommended. Thus A05R, A01WR, A12BR, and A16N in the equatorial overlap section with A16S are suggested. The repeat cruises are also often closer in time to the other cruises in the synthesis, thereby decreasing the possibility of a temporal bias. However, these overlapping cruises are invaluable for many applications, and all of the individual cruises are retained in the data holdings. Also, the cruise tracks of overlapping cruises sometimes diverge for part of the tracks, and these segments should be included in basinwide analyses.

4.1 Narrative of DIC Adjustments

In consideration of all the analyses described in this report, we believe that cruises with consistent offsets in DIC of greater than 4 $\mu\text{mol/kg}$ should be considered for adjustments. The cruises with offsets of this magnitude are discussed in the following subsections.

A06 and A07. The 11 crossovers showed high variability and often large differences along with large standard deviations, suggesting significant variability over the density range investigated. The MLR indicated that these cruises had biases of 11 to 15 $\mu\text{mol/kg}$ with large standard deviations compared with other cruises in this region. These results suggest significant station-to-station differences and possible variability with depth. Therefore, these cruises are not recommended for use.

A08. A08 had crossovers with five other cruises. It was 8 $\mu\text{mol/kg}$ low compared with A17, but the other crossings were not more than 3 $\mu\text{mol/kg}$ lower than other cruises. The MLR showed the cruise to be in line with other cruises in the tropical region. No adjustment is recommended.

A09. A09 had crossovers with five other cruises. These crossovers showed that A09 had lower values than A16S ($-5 \mu\text{mol/kg}$) but higher values than A15 ($+8 \mu\text{mol/kg}$). It was almost $5 \mu\text{mol/kg}$ high with respect to the regional MLR but had a standard deviation of $8 \mu\text{mol/kg}$. An adjustment of $-4 \mu\text{mol/kg}$ would bring the values in line with most of the other transects, but this is at the borderline of suggested adjustments. Given the variability and inconsistency of the different comparisons, no adjustments are recommended.

A10. A10 had crossovers with six other cruises. A10 was $4 \mu\text{mol/kg}$ higher than A15 but was slightly low relative to the other cruises. It did not appear anomalous in the MLR; therefore, no adjustment is recommended.

A12B. A12B had crossovers with three other cruises. It was $7 \mu\text{mol/kg}$ high relative to A13 but showed no offset in multiple crossovers with A12 and A12BR. A12B also compared favorably with the MLR. Therefore, no adjustment is recommended.

A13. A13 had four crossovers with other cruises. It was low by $7 \mu\text{mol/kg}$ relative to A12B but compared favorably in crossovers with three other cruises and in the MLR. It is our assessment that the stations associated with the A13-A12B crossover must be slightly anomalous relative to the rest of the data from these cruises. No adjustment is recommended for A13.

A14. A14 had four crossovers with other cruises. It was $5 \mu\text{mol/kg}$ high with respect to A10 but compares favorably with A08 and A09 as well as in the MLR. Therefore, no adjustment is recommended.

A15. A15 had six crossovers with other cruises. It was $8 \mu\text{mol/kg}$ low compared with A09 and was consistently low compared with other cruises except crossover A08, which showed a large standard deviation. The regional MLR suggested that adding $4 \mu\text{mol/kg}$ would put the values in line with other cruises. This is a borderline case, but no adjustment is recommended.

A16S. A16S had five crossovers with other cruises. A16S was $5 \mu\text{mol/kg}$ higher than A09 but was consistent with crossovers from four other cruises. A16S was $48 \mu\text{mol/kg}$ low in the tropical Atlantic MLR, but only 33 samples were included in this analysis. The A16S MLR analysis for the South Atlantic was within $3 \mu\text{mol/kg}$. The internal consistency and overlap with A16N showed good agreement; thus no adjustment is recommended.

A16N. A16N had seven crossovers with other cruises. It was $6 \mu\text{mol/kg}$ lower than A05 but with a large standard deviation. The six other crossovers looked very good, as did the overlap MLR and regional MLR. No adjustments are recommended.

A17. A17 had seven crossovers with other cruises. A17 was $9 \mu\text{mol/kg}$ higher than A08 but was in good agreement with three other crossovers. The MLR showed good agreement in the southern region and a -3 offset in the tropical region. Visual inspection of the crossover plots did not show systematic trends. The internal consistency comparison suggested that either pH, DIC, or TAlk had a bias (Fig. 6). We suspect that the calculation involving pH is the culprit. The cruise covered a large region and traversed a series of boundary currents that could contribute to the differences. No adjustments are proposed.

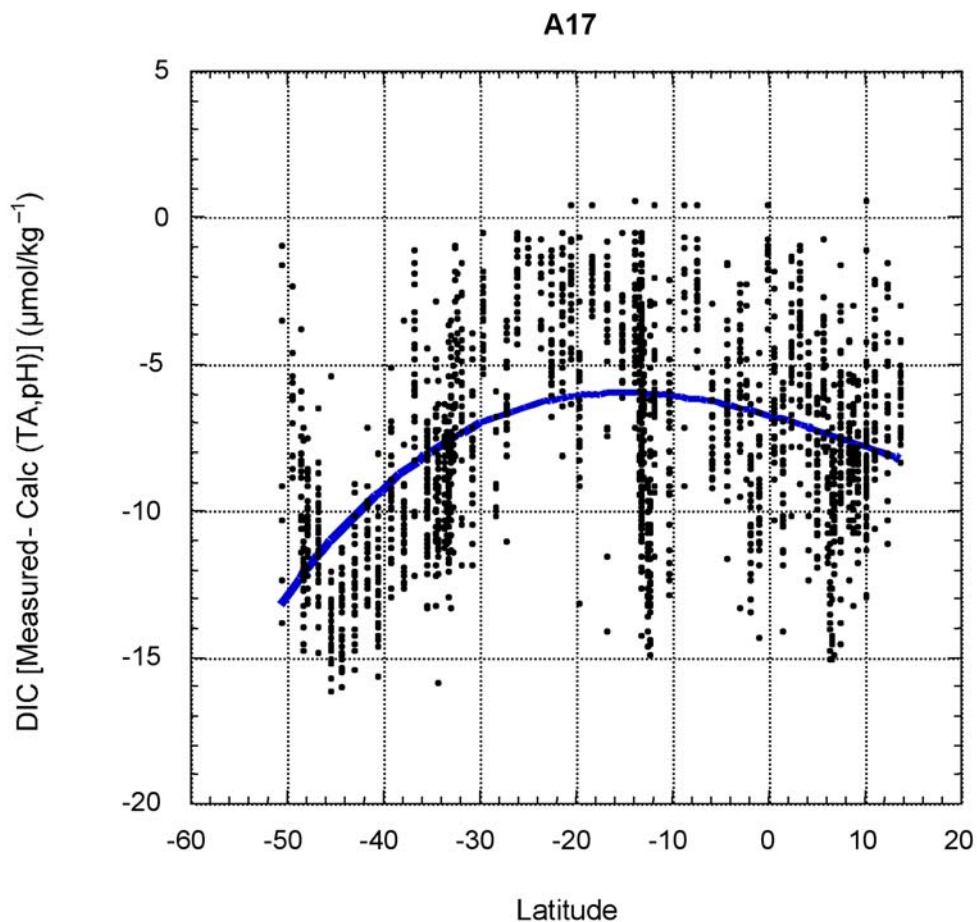


Fig. 6. Measured – calculated (from total alkalinity and pH) dissolved inorganic carbon vs latitude for A17. This trend and offset appears to be an artifact of the dissociation constants used in the calculations. This trend was not observed by Ríos and Perez, who used slightly different dissociation constants. (Ríos, A. F., and F. F. Perez. 1999. Improvements in potentiometric determinations of the CO₂ oceanic system using substandards and CO₂ reference materials. *Ciencias Marinas* 25: 31–49.)

A20. A20 had three crossovers. It was 4 μmol/kg lower than A05R and 2 to 3 μmol/kg lower than the other overlaps. In the regional MLR it was 3 μmol/kg lower, but the internal consistency with *f*CO₂ was excellent. Applying an adjustment of 2 to 3 μmol/kg would improve the consistency among cruises, but this adjustment is smaller than the overall consistency criteria. No adjustment is recommended.

A22. This cruise was 2 to 3 μmol/kg low based on two crossovers and the internal consistency check with *f*CO₂. The northern MLR also suggested that the A22 DIC values were low by 2 μmol/kg, but the tropical MLR suggests that the values are high. Applying an adjustment of 2 to 3 μmol/kg would generally improve the consistency among cruises but this is beyond the overall consistency criteria. No adjustment is recommended.

A23. A23 had three crossovers. There were significant problems with the coulometer (Robertson and Watson, personal communication), and the offsets were not consistent for this cruise. The high-latitude crossover with A12BR at 67° S showed a very consistent offset of –30 μmol/kg

throughout the water column. However, the crossover with A17 at 29° S showed that an offset increased with density, ranging from 0 to –10 $\mu\text{mol/kg}$. The DIC data for A23 is not recommended for use in the synthesis product.

4.2 Narrative of TAlk Adjustments

Alkalinity data showed greater differences than DIC data showed between cruises. Crossovers where deviations were greater than 6 $\mu\text{mol/kg}$ were checked in greater detail. Although adjustments of less than 6 $\mu\text{mol/kg}$ are discussed in the following narrative, we chose not to apply these adjustments, given the uncertainty of the overall data set and the reliability of the assessments at that level of accuracy. That is, for highly precise data sets it is possible to recommend adjustments of less than 6 $\mu\text{mol/kg}$, but the uncertainty for imprecise data is such that adjustment cannot be recommended with confidence.

A01E. There was only one crossover available for evaluation of the A01E alkalinity data. The crossover showed values that were 59 $\mu\text{mol/kg}$ greater than A16N with a standard deviation of 17. Such a large offset along with large deviation make the data highly questionable for our purposes. Therefore, it is recommended that the TAlk for cruise A01E not be used.

A01W. For A01W, there were three crossovers for TAlk. Cruise A01W showed values that were systematically low by 4 to 16 $\mu\text{mol/kg}$. The regional analysis showed an offset of 14 $\mu\text{mol/kg}$ in the same direction, albeit with a large standard deviation. Therefore, we recommend an upward correction of 14 $\mu\text{mol/kg}$ for the A01W TAlk values. The TAlk data for this cruise are very noisy, with apparent random scatter of ± 20 $\mu\text{mol/kg}$.

A01WR. A01WR had one crossover for TAlk and a significant section of overlap with A01W. The crossover showed a difference of 26 ± 4 $\mu\text{mol/kg}$ with A01W. The crossover occurs in a water depth of 300 m, however. The comparison of overlapping cruise tracks between A01W and A01WR using the MLR technique shows a difference of 12 $\mu\text{mol/kg}$. This difference is in accord with the proposed adjustment of A01W of 14 $\mu\text{mol/kg}$ and suggests that A01WR TAlk data do not need to be adjusted. The regional MLR showed an offset of –5.6 $\mu\text{mol/kg}$. Inspection of the data showed significant scatter with depth and changes from station to station of 10–20 $\mu\text{mol/kg}$. No adjustment is recommended for A01WR, but it must be recognized that the TAlk data for both A01W and A01WR are of dubious quality.

A02. A02 had four crossovers for TAlk. A02 showed a positive anomaly of 16 $\mu\text{mol/kg}$ with A01W, which was reduced to 2 $\mu\text{mol/kg}$ after the proposed adjustment to A01W. A positive anomaly of 11 $\mu\text{mol/kg}$ was also observed with the A20 crossover. However, two A24 crossovers showed an offset of 3 to 4 $\mu\text{mol/kg}$, and the MLR indicated good agreement. Given the inconsistent results, no adjustment is recommended.

A06 and A07. Based on nine crossovers, the offsets and scatter are such that we do not recommend including the data from A06 or A07 in the synthesis product.

A08. The two crossovers suggested that the values for A08 were 4 to 12 $\mu\text{mol/kg}$ low. The regional MLR was 3 $\mu\text{mol/kg}$ low, but we do not feel that there was sufficient evidence to suggest an adjustment.

A09. A single crossover with A17 suggested that the values are 7 $\mu\text{mol/kg}$ high. The regional regression implied a 10- $\mu\text{mol/kg}$ bias in the same direction. A downward correction of 7 $\mu\text{mol/kg}$ is proposed for A09 TAlk.

A10. There were three crossovers with TAlk for A10. A10 showed a large negative bias with respect to A17, but crossovers with A16S and A15 did not indicate a significant offset. The MLR did not suggest an offset either, so no adjustment is recommended.

A14. There were three crossovers of A14 with other cruises where TAlk was measured. It showed a 12- $\mu\text{mol/kg}$ high offset with A08 but was only 3 $\mu\text{mol/kg}$ high relative to A09. Both the tropical and southern MLR analyses suggested that values were high by about 5 to 6 $\mu\text{mol/kg}$. The internal consistency also suggested that the TAlk could be high by 5 $\mu\text{mol/kg}$. An adjustment of 5 $\mu\text{mol/kg}$ would bring values in better agreement with all analyses, but because this adjustment was less than the 6- $\mu\text{mol/kg}$ criterion, no adjustment was proposed for this synthesis.

A15. There were four crossovers for A15. A15 showed both 8- $\mu\text{mol/kg}$ high values (with respect to A16S) and 15- $\mu\text{mol/kg}$ low crossover values (with respect to A17), but both had large standard deviations. The regional MLR showed that the TAlk on the cruises was low by about 3 to 4 $\mu\text{mol/kg}$. Given the inconsistency of the results, no adjustment is recommended.

A16S. A16S had three crossovers. It showed an 8- $\mu\text{mol/kg}$ low bias with A15 and a low bias of similar magnitude with the regional MLR in both the tropical and southern regions (albeit with only 35 data points). The internal consistency showed a low bias in TAlk as well, assuming that DIC and $f\text{CO}_2$ are accurate. A 4- $\mu\text{mol/kg}$ increase would put the values in better agreement with the other cruises, but because this is less than the minimum adjustment criteria, no adjustment is recommended.

A17. There were six crossovers for A17. A17 showed both significantly high deviations (25 $\mu\text{mol/kg}$ with respect to A10 and 15 $\mu\text{mol/kg}$ compared to A15) and low deviations (-7 $\mu\text{mol/kg}$ with respect to A09) in the crossover analyses. The regional MLR suggested that the TAlk data are 5 to 6 $\mu\text{mol/kg}$ high compared with data from other cruises in the tropical and southern regions. The internal consistency suggested that the TAlk was high by 8 $\mu\text{mol/kg}$. A decrease in TAlk of 6 $\mu\text{mol/kg}$ for A17 TAlk would bring the values in better agreement. Because a decrease was suggested for A09 as well, the bias between these cruises remains of the same magnitude. However, this offset of 6 $\mu\text{mol/kg}$ is right at the recommended cutoff, and no adjustment is recommended.

A20. There were three crossovers of A20 with other cruises. The alkalinities for this cruise were measured with very high precision but showed systematic offsets in every procedure, except for the assessment of internal consistency conducted by $f\text{CO}_2$ and DIC. The TAlk values were low by 3 to 11 $\mu\text{mol/kg}$. The 11- $\mu\text{mol/kg}$ offset was observed with A02, whose TAlk was consistently higher than those of other cruises. A correction of 4 $\mu\text{mol/kg}$ would bring values in line, but no adjustments are proposed.

A24. A24 had six crossovers. A24 showed an offset with A01W but showed good agreement in the MLR analysis. If the suggested correction were applied to A01W, the crossover analysis would fall in line with A24. The assessment of internal consistency conducted by using TAlk, DIC, and pH showed an offset with pH; however, the pH data on this cruise were not of highest quality because they were measured by electrode. No adjustment to A24 TAlk data is proposed.

4.3 Omitted Cruises

Based on comprehensive comparisons, the DIC data for cruises A06, A07, and A23 are not included in the combined DIC data set. The following cruises are not included for TAlk: A06, A07, and A01E. The data from these cruises showed large offsets, large differences for different crossovers (see Table 4), and large scatter, limiting their use in this analysis. Omitting these data significantly decreases data coverage in the equatorial Atlantic.

There were several reoccupations of cruise lines during the decade. For interpretations where only a single cruise along the transect is needed, the repeat occupations later in time are recommended for use. These later cruises are believed to be of higher quality and may contain more parameters. They are also often closer in time to the other cruises. The recommended cruises are A05R (instead of A05), A01WR (instead of A01W), and A12BR (instead of A12B). In the case of A12B and A12BR, different cruise tracks were occupied, and there may be merit in retaining both, particularly because the data coverage is so sparse at high southern latitude.

4.4 Adjustments for the Repeat Lines

The following adjustments are proposed for parameters measured on the repeat lines.

4.4.1 Dissolved Inorganic Carbon

No adjustments are proposed for DIC. Although differences between crossovers were often greater than the stated precision of the measurements ($\approx 2 \mu\text{mol/kg}$), the differences were not consistent at the $4\text{-}\mu\text{mol/kg}$ level between different crossovers along a line, and/or the standard deviation of the differences were sufficiently large that the differences did not have a strong statistical significance.

4.4.2 Total Alkalinity

Crossover analyses and MLR analyses showed consistent offsets for two cruises (A01W and A09). We recommend adding $14 \mu\text{mol/kg}$ to all TAlk values in A01W and subtracting $7 \mu\text{mol/kg}$ for all TAlk data on A09. In the combined data set, A01WR was used instead of A01W because the cruise data are compatible with other data in the region and do not require any adjustments.

5. SUMMARY

The comprehensive analysis of the quality of the carbon data of the twenty-three cruises shows general good agreement and high quality. This is testament to the care that was taken in gathering and reducing the data. Extensive use of CRMs facilitated consistency of the DIC and TAlk data sets. Internal consistency calculations for cruises on which three or more carbon system parameters were measured suggest that the pH and, in particular, $f\text{CO}_2$ measurements on the cruises were consistent and of high quality as well. Based on the extensive analyses, we suggest that the DIC and TAlk of two cruises (A06 and A07) not be considered as appropriate for this synthesis. In addition, the TAlk values of A1E are significantly different from neighboring cruises and are not recommended for use, either. A23 has inconsistent DIC data, so these data are also not included in this synthesis. Of the lines that have repeat occupations, we recommend that the later (repeat) cruises be used as the primary data set. This is because the data are more consistent with the other data, in part, because of improved analysis techniques and because they often are closer in time to the other cruises, thus minimizing the effects of anthropogenic and natural variability. No specific adjustments in DIC are recommended. Although crossover analyses often show systematic differences in DIC greater than the assumed precision of $2 \mu\text{mol/kg}$, the differences either are not systematic for each crossover or do not show up in the regional multilinear analysis. TAlk values show greater inconsistency for some cruises, and adjustments of $+14 \mu\text{mol/kg}$ and $-7 \mu\text{mol/kg}$ are suggested for TAlk values on A01W and A09, respectively.

The caveats in the analysis and recommendations should be borne in mind. The purpose of the exercise was to create a mutually consistent data set of TAlk and DIC for the Atlantic Ocean based on data obtained on different cruises in the 1990s. This data set will be used to create gridded fields of DIC and TAlk for model validation and to determine basin-scale quantities such as anthropogenic CO_2 inventories, carbonate saturation levels, and other relevant large-scale phenomena. The analysis of consistency is primarily focused on deep-water quantities with the assumption that these values are invariant on the decadal timescale. In the well-ventilated Atlantic Ocean, where large-scale natural changes manifest themselves through much of the water column, this is not always the best assumption. Moreover, in this analysis we assume that there are no systematic differences with depth. No comparisons in the upper water column were made, both because of seasonal variability in the upper ocean and because the anthropogenic perturbations are most noticeable there.

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