High spatial resolution alkalinity and pH measurements by IIM-CSIC group along 24.5°N during the R/V Hespérides WOCE Section A05 cruise.

July 14 - August 15, 1992

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ABBREVIATIONS AND ACRONYMS

2ndQC	Secondary Quality Control
AAIW	Antartic Intermediate Water
AABW	Antartic Bottom Water
AMOC	Atlantic Meridional Overturning Circulation
A_T	Total Alkalinity
^{14}C	Radiocarbon
$CaCO_3$	Calcium carbonate
C_{ANT}	Anthropogenic CO_2
CFCs	Chlorofluorocarbons
CARINA	CARbon IN the Atlantic
CCHDO	Carbon Hydrographic Data Office
CDIAC	Carbon Dioxide Information Analysis Center
CLIVAR	The Climate Variability and Predictability
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
CRM	Certified Reference Material
CSIC	Consejo Superior de Investigaciones Científicas
C_T	Dissolved Inorganic Carbon
GLODAP	Global Ocean Data Analysis
IIM	Instituto de Investigaciones Marinas
LSW	Labrador Sea Water
NADW	North Atlantic Deep Water
NBS	National Bureau of Standards
pH_{NBS15}	pH on the NBS scale and referred to 15°C
pH_{SWS25}	pH on the SWS and referred to 25°C
QCed	Quality controlled
RSMAS	Rosenstiel School of Marine and Atmospheric Science
SWS	Sea Water Scale
U.S.A.	United States of America
WAVES	Web Accessible Visualization and Extraction System
WCRP	World Climate Research Programme
WOCE	World Ocean Circulation Experiment

ABSTRACT

This report presents the carbon dataset collected during the R/V BIO Hespérides oceanographic cruise along 24.5°N latitude (WOCE A05 section) in 1992, by the Instituto de Investigaciones Marinas (IIM) CO_2 group. The IIM CO2 dataset has never been reported in public databases though has already been used in three works on carbon transports and distributions across the 24.5°N section in the North Atlantic (Brown *et al.*, 2010; Macdonald *et al.*, 2003; Rosón *et al.*, 2003). It consists in dissolved inorganic carbon (C_T) calculated from total alkalinity (A_T) and pH direct potentiometric measurements performed in 107 stations of the section that include the sampling of the Florida Strait for CO_2 measurements. The current CO_2 dataset reported for the WOCE A05 in the CLIVAR & Carbon Hydrographic Data Office (CCHDO) and the Carbon Dioxide Information Analysis Center (CDIAC) was collected at 33 stations of the same cruise, by the Rosenstiel School of Marine and Atmospheric Science (RSMAS) and consists in C_T, A_T, and pH direct measurements from titrations of seawater. Due to the better spatial coverage achieved in the IIM dataset in relation to the available one on CDIAC and CCHDO sites, this work aims to provide these CO_2 data together with a quality control analysis. With this purpose, the IIM dataset was subjected to a secondary quality control (2ndQC) following the procedures used in CARINA (CARbon IN the Atlantic), which basically consisted in crossovers analysis to quantify possible systematic biases. After the crossover analysis the data were bias-adjusted by -4μmol kg^{-1} for A_T and -0.009 units for pH. The IIM quality controlled dataset measurements allows to obtain high spatial resolution C_T, A_T, and pH distributions along the WOCE A05 section.

Keywords: Carbon dioxide, pH, alkalinity, carbon cycle, World Ocean Circulation Experiment, hydrographic measurements, quality control, North Atlantic Ocean.

1. BACKGROUND INFORMATION

The ocean plays an important role as a sink for carbon dioxide (CO_2) released to the atmosphere. At least, oceans have absorbed about one third of all anthropogenic CO_2 emissions produced in the last three centuries (Sabine *et al.*, 2004) and, in this context, the North Atlantic Ocean plays an important part in absorbing, and especially accumulating, emitted CO_2 (Vázquez-Rodríguez *et al.*, 2009). This basin is considered to contain 23% of the global oceanic anthropogenic CO_2 (Sabine et al., 2004) so it is crucial in its penetration and balancing in the whole ocean. Once CO_2 is in solution, dissolved inorganic carbon (C_T) levels rise and chemical balances of the CO_2 system in seawater are affected leading to the formation of hydrogen ions that lower seawater pH while consuming carbonate (CO_3^{2-}) ions. These ions control the rate of calcium carbonate ($CaCO_3$) precipitation and dissolution in the ocean, which in turn constrain the amount of carbon that is buried in the sediments during extended periods of time. Overall, the atmospheric CO_2 removing capacity of the ocean will decrease in the future as a consequence of the continuous oceanic entrance of atmospheric CO_2 (Feely *et al.*, 2004). But, how marine carbon cycle will evolve in the future is still one of the main issues in Ocean Sciences (Sabine and Tanhua, 2009).

In the nineties, the World Ocean Circulation Experiment (WOCE), as a part of the World Climate Research Programme (WCRP), was the first attempt to study physical processes that affect oceanic circulation globally and, together with the inclusion of systematic chemical measurements and the repetition of some of these sections through time, allow describing trends of different seawater variables. Regarding CO_2 system dynamics in seawater, large amounts of direct C_T and total alkalinity (A_T) measurements have been collected since a few decades ago.

Included in the WOCE project, the WOCE A05 section, across 24.5°N in the North Atlantic subtropical gyre (Fig. 1), has been occupied several times since 1957, allowing multi-decadal-scale variability studies which were specially focused in the meridional transport of mass and heat. In 1992, the section was included in the net of selected hydrographic cruises to be studied within the frame of the WOCE Project and high spatial resolution in situ carbon system measurements were taken for the first time. Since then, five occupations have been conducted, in 1992, 1998, 2004, 2010 and 2011, providing a great opportunity to analyze and quantify changes in pH, carbon budget, and natural and anthropogenic carbon in the North Atlantic. In 1992, two different carbon system datasets were obtained: a shorter one, of C_T and A_T measurements, taken by the group of the Rosenstiel School of Marine and Atmospheric Science (RSMAS) University of Miami, Florida, which was reported in the CLIVAR & Carbon Hydrographic Data Office (CCHDO) and the Carbon Dioxide Information Analysis Center (CDIAC) databases after an accurate quality control (Millero *et al.*, 2000); and a larger dataset, consisting in pH and A_T measurements, obtained by the CO_2 group of the Instituto de Investigaciones Marinas (IIM-CSIC) of Vigo, Spain. This last dataset has never been reported in global hydrographic data centers despite having been quality controlled, also, in the first Atlantic synthesis on carbon measurements from 1990 to 1998 (Wanninkhof *et al.*, 2003) that supposed a big effort to assess the consistency of large-scale inorganic carbon data among the different cruises performed during this time period. In addition, the IIM dataset has been used in three studies (Brown *et al.*, 2010; Macdonald *et al.*, 2003; Rosón *et al.*, 2003) where C_T, A_T and anthropogenic CO_2 meridional fluxes in the North Atlantic were analyzed. Since this dataset includes four times more data than the available in CCHDO or CDIAC, it allows to reduce uncertainties in the estimations of C_T fluxes and inventories, and enables a better description of the carbon system variables over time along the A05 section.

Due to the better spatial coverage of the section achieved in the IIM CO_2 dataset, our main goal with this report is to review and refine these CO_2 system measurements to enlarge the available North Atlantic CO_2 information for future carbon studies.
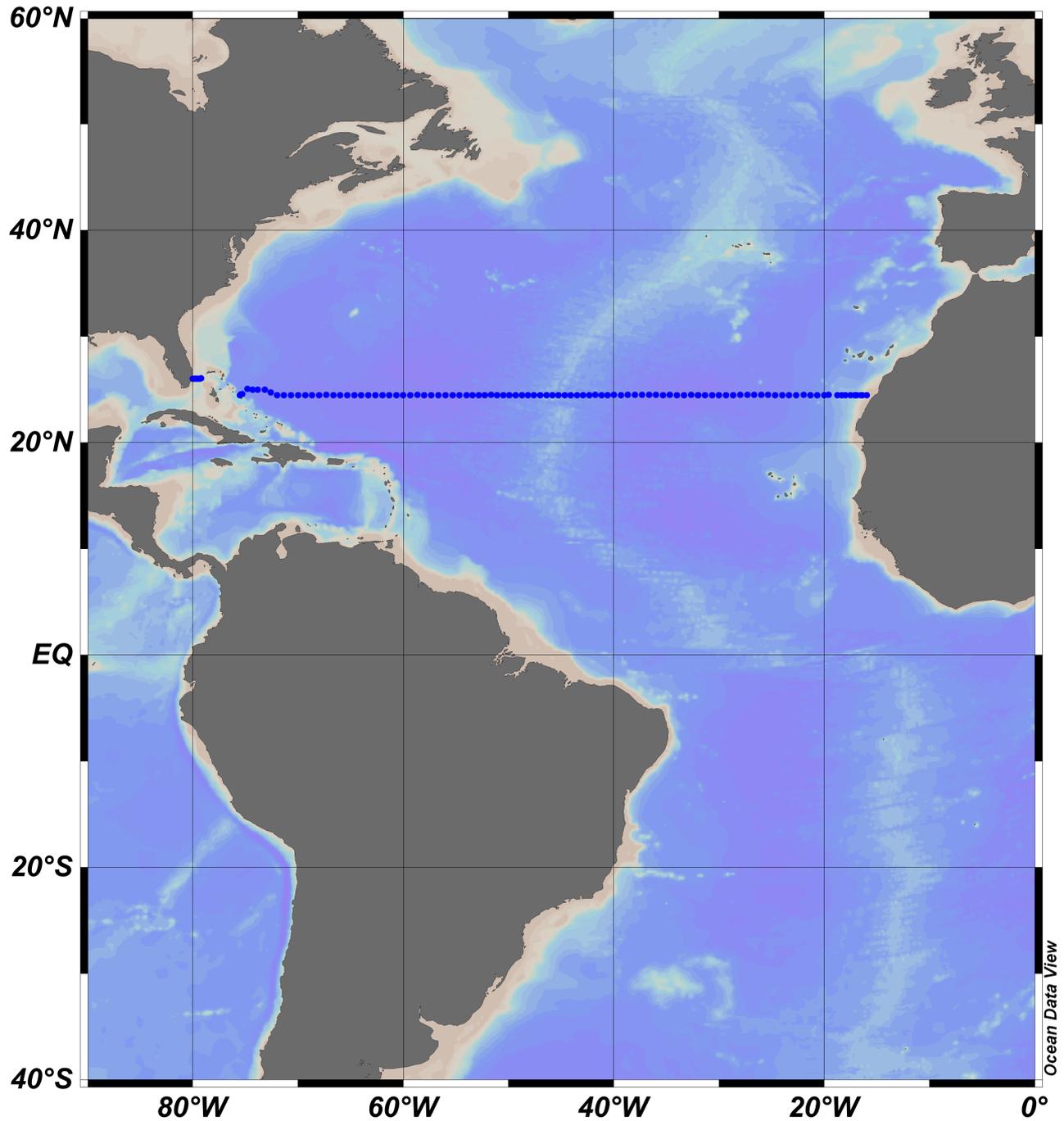
Fig 1. Cruise track of the WOCE A05 section on board the R/V BIO Hespérides.

2. DESCRIPTION OF THE EXPEDITION

The cruise HE06 (WOCE A05 section) was carried out between 14 July and 15 August 1992 along 24°N on board the R/V Hespérides from Cadiz (Spain) to Miami (Florida, U.S.A.). Full-depth CTD profiles were performed at 112 hydrographic stations. At each station, water samples were taken at different depths for different chemical analyses including salinity, oxygen, nutrients, chlorofluorocarbons (CFCs), pH, A_T, C_T, primary production, aluminium and radiocarbon (^{14}C). The cruise track and station locations are shown in Fig. 1. A detailed description of the cruise can be found in Millero *et al.*, (2000): http://cdiac.ornl.gov/oceans/ndp_074/.

3. DESCRIPTION OF METHODS FOR CARBON PARAMETERS

3.1. CO_2 parameters measurements

The IIM group took inorganic CO_2 measurements of seawater in almost each station of the section (Fig. 2a), by sampling 107 full depth profiles for A_T and pH analysis. All the sampled stations are summarized in Table 1 and procedures for chemical analysis are described in Rosón *et al.*, (2003). The pH was measured potentiometrically in the NBS scale with a combined glass electrode associated to a thermocompensator and referred to 15°C (Pérez and Fraga, 1987a). The method had a shipboard precision of 0.005 units, based on 184 replicate analysis corresponding to two different oceanographic bottles fired at the same depth at each station (Ríos and Rosón, 1996). A_T measurements were made by titration of seawater with potentiometric endpoint detection (Pérez and Fraga, 1987b), reaching a precision of ±1 µmol kg^{-1}. Total dissolved inorganic carbon was calculated from measured pH_{NBS15} and A_T using equilibrium constants of Mehrbach *et al.*, (1973) and the boric acid constants reported by Lyman (1956). The calculations were checked for accuracy three times during the cruise against Dickson standards of seawater, comparing estimated C_T from pH and A_T measurements done in a number of samples of the Certified Reference Materials (CRMs, Batch#12) with the certified C_T concentration given for that batch (1984 µmol kg^{-1}). Following this methodology, both analytical errors of pH (±0.005) (Pérez and Fraga, 1987a) and A_T (±2 µmol kg^{-1}) (Pérez and Fraga, 1987b) produce together an error of ±4 µmol kg^{-1} in C_T calculations (Zirino, 1985).

In the RSMAS dataset, C_T, A_T, and pH were determined from titrations of seawater samples collected at 33 stations of the whole section (Fig. 2b). The titration systems were calibrated with CRMs. Procedures followed for sample analysis are described in Millero *et al.*, (2000). They basically consisted in the use of three titration systems to determine A_T and C_T. The pH values were determined in the seawater scale, from the initial titrations voltage reading relative to TRIS buffers. The accuracy/precision of the measured parameters was estimated to be ±7 µmol kg^{-1}/±2 µmol kg^{-1} for A_T, ±7 µmol kg^{-1}/±5 µmol kg^{-1} for C_T, and ±0.02/±0.005 for pH. This carbon dataset followed the corresponding quality review at the Carbon Dioxide Information Analysis Center (CDIAC) ensuring proper data examination to supply accurate carbon information for researchers. The full dataset is available at the CDIAC website (http://cdiac.ornl.gov/oceans/ndp_074/) or at the CCHDO website (http://cchdo.ucsd.edu/cruise/29HE06_1). The quality controlled version of the dataset, without questionable or bad measurements, is available on the Global Ocean Data Analysis (GLODAP) bottle database search tool: Web Accessible Visualization and Extraction System (WAVES, http://cdiac3.ornl.gov/waves/discrete/) through the OUTPUT option.

2a

2b
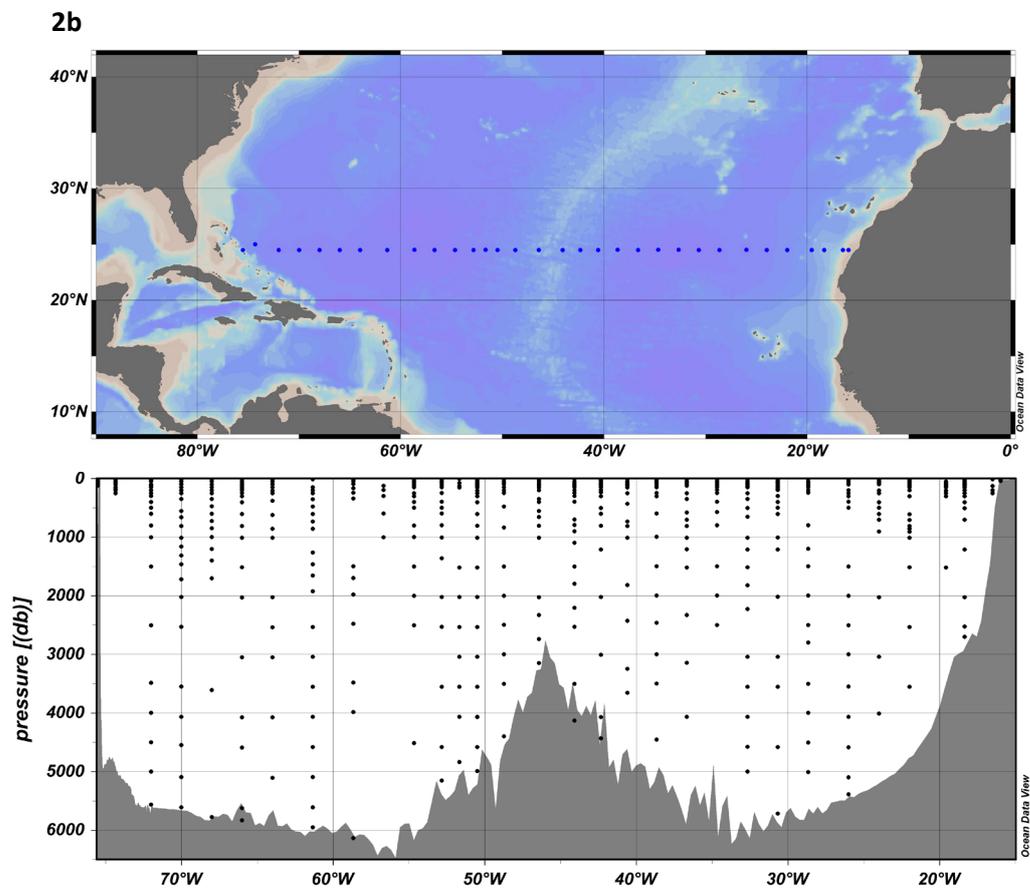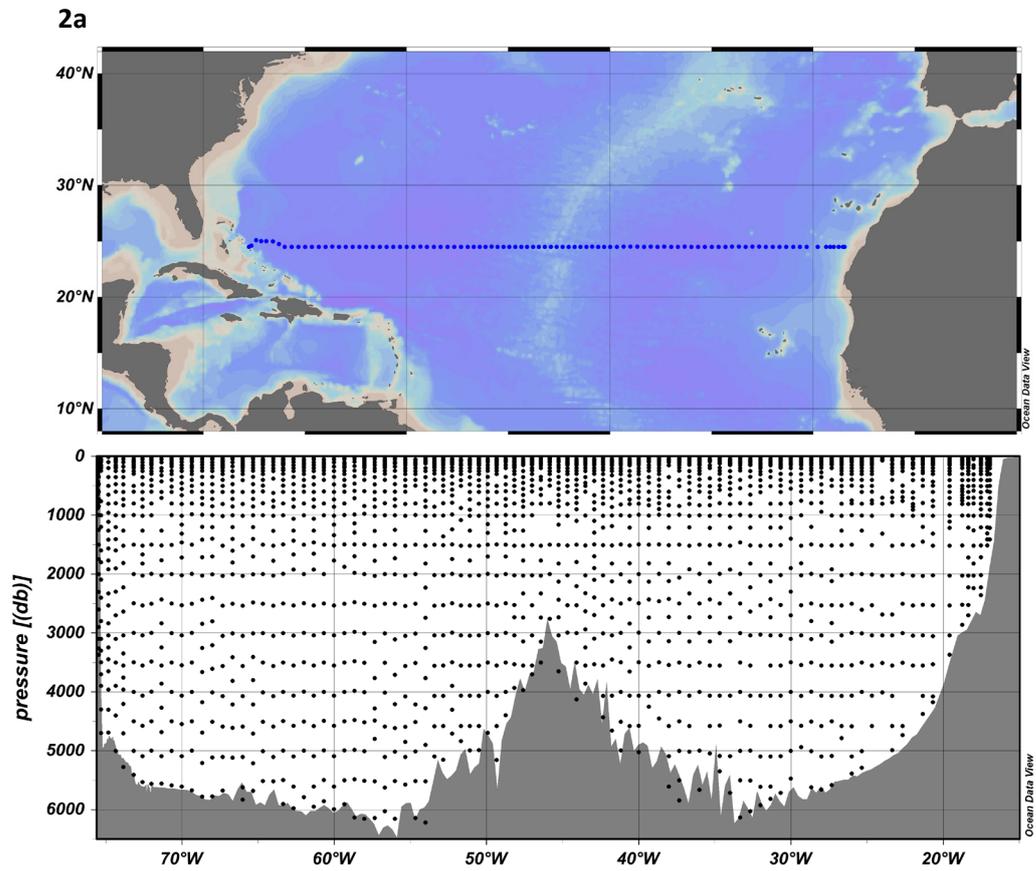
Fig 2. Sampling stations and depths for CO$_2$ measurements along WOCE section A05. 2a) Sampling stations performed by IIM CO$_2$ group for pH$_{NBS15}$ and total alkalinity (A$_T$) concentration determinations. 2b) Sampling stations performed by RSMAS CO$_2$ group for alkalinity (A$_T$) and dissolved inorganic carbon (C$_T$) determinations.

Table 1. Summary of CO₂ system stations sampled by IIM group during the cruise. (*) Sampled parameter, (-) No sampled parameter.

Station	Longitude (°W)	Latitude (°N)	Bottom Depth (m)	Alkalinity	pHSWS25	Date
1	-15.97	24.50	53	-	-	20/7/2012
2	-16.41	24.50	117	-	-	20/7/2012
3	-16.50	24.50	575	-	-	20/7/2012
4	-16.93	24.50	1545	*	*	21/7/2012
5	-17.09	24.50	1936	*	*	21/7/2012
6	-17.51	24.49	2407	*	*	21/7/2012
7	-18.00	24.50	2224	*	*	21/7/2012
8	-18.34	24.49	2736	*	*	21/7/2012
9	-18.75	24.50	2948	*	*	22/7/2012
10	-	-	-	-	-	22/7/2012
11	-19.58	24.51	3393	*	*	22/7/2012
12	-20.00	24.50	3755	-	-	23/7/2012
13	-20.67	24.50	4186	*	*	23/7/2012
14	-21.33	24.50	4379	*	*	23/7/2012
15	-21.98	24.51	4705	-	-	24/7/2012
16	-22.67	24.50	4663	*	*	24/7/2012
17	-23.34	24.50	4914	*	*	24/7/2012
18	-24.00	24.50	5149	*	*	24/7/2012
19	-24.67	24.50	5120	*	*	25/7/2012
20	-25.34	24.51	5339	*	*	25/7/2012
21	-26.00	24.51	5297	*	*	25/7/2012
22	-26.67	24.51	4715	*	*	26/7/2012
23	-27.32	24.51	5595	*	*	26/7/2012
24	-28.00	24.52	5669	*	*	26/7/2012
25	-28.65	24.50	5723	*	*	26/7/2012
26	-29.33	24.50	4862	*	*	27/7/2012
27	-30.01	24.50	5479	*	*	27/7/2012
28	-30.67	24.50	5617	*	*	27/7/2012
29	-31.34	24.50	5717	*	*	28/7/2012
30	-32.00	24.50	5817	*	*	28/7/2012
31	-32.67	24.51	6426	*	*	28/7/2012
32	-33.34	24.50	6191	*	*	28/7/2012
33	-34.00	24.50	5737	*	*	29/7/2012
34	-34.68	24.51	5354	*	*	29/7/2012
35	-35.33	24.50	4966	*	*	29/7/2012
36	-36.01	24.51	5747	*	*	29/7/2012
37	-36.66	24.51	5008	*	*	30/7/2012
38	-37.33	24.51	5872	*	*	30/7/2012
39	-38.01	24.51	5606	*	*	30/7/2012
40	-38.66	24.51	4580	*	*	30/7/2012
41	-39.33	24.49	4194	*	*	31/7/2012
42	-40.00	24.51	5139	*	*	31/7/2012
43	-40.58	24.50	4551	*	*	31/7/2012
44	-41.16	24.50	5195	*	*	31/7/2012
45	-41.75	24.51	4640	*	*	1/8/2012
46	-42.33	24.50	4430	*	*	1/8/2012
47	-42.91	24.50	3605	*	*	1/8/2012
48	-43.50	24.50	3867	*	*	1/8/2012
49	-44.08	24.50	4182	*	*	1/8/2012
50	-44.67	24.50	2999	*	*	2/8/2012
51	-45.25	24.51	3658	*	*	2/8/2012
52	-45.83	24.50	2777	*	*	2/8/2012
53	-46.41	24.49	3518	*	*	2/8/2012
54	-47.00	24.50	3727	*	*	2/8/2012
55	-47.58	24.50	4021	*	*	3/8/2012
56	-48.16	24.49	3930	*	*	3/8/2012
57	-48.73	24.50	4541	*	*	3/8/2012
58	-49.33	24.50	5159	*	*	3/8/2012
59	-49.91	24.50	4758	*	*	3/8/2012
60	-50.49	24.50	4975	*	*	4/8/2012
61	-51.08	24.50	5040	*	*	4/8/2012
62	-51.66	24.51	4888	*	*	4/8/2012
63	-52.25	24.50	4789	*	*	4/8/2012
64	-52.83	24.50	5231	*	*	5/8/2012
65	-53.41	24.50	5638	*	*	5/8/2012
66	-54.00	24.50	6226	*	*	5/8/2012
67	-54.67	24.50	6275	*	*	5/8/2012
68	-55.33	24.50	5614	*	*	6/8/2012
69	-56.00	24.50	6566	*	*	6/8/2012
70	-56.67	24.50	6024	*	*	6/8/2012
71	-57.34	24.49	6116	*	*	6/8/2012
72	-58.01	24.49	6209	*	*	7/8/2012
73	-58.67	24.51	6145	*	*	7/8/2012
74	-59.33	24.50	5903	*	*	7/8/2012
75	-60.00	24.50	6005	*	*	8/8/2012
76	-60.67	24.50	5867	*	*	8/8/2012
77	-61.33	24.50	5965	*	*	8/8/2012
78	-61.99	24.49	5827	*	*	8/8/2012
79	-62.66	24.50	5988	*	*	9/8/2012
80	-63.34	24.50	5928	*	*	9/8/2012
81	-64.00	24.50	5858	*	*	9/8/2012
82	-64.67	24.50	5791	*	*	10/8/2012
83	-65.33	24.49	5769	*	*	10/8/2012
84	-66.00	24.50	5832	*	*	10/8/2012
85	-66.66	24.51	5705	*	*	11/8/2012
86	-67.32	24.52	5734	*	*	11/8/2012
87	-68.00	24.50	5805	*	*	11/8/2012
88	-68.66	24.50	5784	*	*	11/8/2012
89	-69.33	24.50	5685	*	*	12/8/2012
90	-70.00	24.50	5626	*	*	12/8/2012
91	-70.66	24.49	5604	*	*	12/8/2012
92	-71.33	24.50	5582	*	*	12/8/2012
93	-72.00	24.50	5571	*	*	12/8/2012
94	-72.57	24.75	5559	*	*	13/8/2012
95	-73.17	24.99	5401	*	*	13/8/2012
96	-73.84	25.00	5288	*	*	13/8/2012
97	-74.33	25.01	4994	*	*	13/8/2012
98	-74.82	25.10	4730	*	*	14/8/2012
99	-75.46	24.55	3341	*	*	14/8/2012
100	-75.30	24.61	4831	*	*	14/8/2012
101	-75.52	24.50	1040	*	*	14/8/2012
102	-79.23	26.07	362	*	*	15/8/2012
103	-79.31	26.05	496	*	*	15/8/2012
104	-79.40	26.06	601	*	*	15/8/2012
105	-79.48	26.06	685	*	*	15/8/2012
106	-79.57	26.06	772	*	*	15/8/2012
107	-79.67	26.06	708	*	*	15/8/2012
108	-79.77	26.06	597	*	*	15/8/2012
109	-79.85	26.05	321	*	*	15/8/2012
110	-79.93	26.05	262	*	*	15/8/2012
111	-80.00	26.05	256	*	*	15/8/2012
112	-80.07	26.05	128	*	*	16/8/2012

4. DATA EVALUATION

The quality of the CO_2 data was rechecked in both CO_2 datasets and the consistency between them was also evaluated. To this end, final CO_2 data from the RSMAS group was obtained through the OUTPUT option of the WAVES search system and compared to the also final IIM CO_2 data in terms of C_T, A_T and pH. In the case of pH some calculations had to be done in order to work with comparable data: measured pH_{NBS15} from the IIM dataset was converted to the Sea Water Scale (SWS) and referred to 25°C, obtaining the variable pH_{SWS25}. This last parameter was calculated for the RSMAS dataset from C_T and A_T measurements with dissociation constants of Mehrbach *et al.*, (1973) refitted by Dickson and Millero, (1987) and boric acid constants from Dickson, (1990) using CO_2sys program (Pierrot et al., 2006) because no measured pH data was available in the final version of the RSMAS dataset obtained from GLODAP. Measured A_T values, for both cases, could be compared directly. For C_T, comparisons were performed directly, too, despite being a calculated parameter in the IIM dataset, as the change in scale was performed keeping invariable C_T. Thus, values did not need to be recalculated.

4.1. Linear correlations between RSMAS and IIM carbon datasets

As a first step, linear correlations were performed between C_T, A_T and pH from each dataset. Results are shown in Figure 3. The three carbon parameters showed good agreement. Regression coefficients and the coefficient of determination found were 0.99 (r^2=0.96) for C_T, 0.96 (r^2=0.98) for A_T and 0.99 (r^2=0.98) for pH_{SWS25}. All p-values were smaller than $2.2e^{-16}$. Averaged differences ± Standard deviation (IIM-RSMAS) were 1±11.5 µmol kg^{-1} for C_T, -2.3±6 µmol kg^{-1} for A_T, and 0.007±0.021 units for pH_{SWS25}.

4.2. Crossover analysis

Both datasets were gone through secondary quality control (2ndQC) procedures used in CARINA (CARbon IN the Atlantic) which involve crossovers analysis to quantify possible systematic biases (Key *et al.*, 2010; Tanhua *et al.*, 2010). Thus, both datasets were compared with different historical cruises that have taken place intersecting the 24.5°N section somewhere along its defined transect. Table 2 summarizes the list of selected cruises to carry out the 2ndQC.

Crossover analyses between both WOCE A05 carbon datasets (RSMAS and IIM) and each one of the other considered sections were carried comparing data values below 1500 dbar for stations that were located within two degrees of latitude. The following parameters were checked: A_T, C_T, and pH_{SWS25}. As a result of this analysis, a mean and standard deviation of the offset, defined as the difference between two cruises, was quantified in each comparison, for each of the given carbon parameters. Then, the offsets derived were used to calculate an additive adjustment for C_T, A_T, and pH data in both datasets using least square models. The corrections obtained are summarized in Table 3. Figure 4 shows the cruise to cruise offsets found for the IIM dataset and the final adjustment obtained, for each carbon parameter.

IIM-C_T data vs. RSMAS-C_T data

r² = 0.96
1±11.5 µmol kg-1

IIM-A_T data vs. RSMAS-A_T data

r² = 0.98
-2.3±6 µmol kg-1

IIM-pH_{SWS25} data vs. RSMAS-pH data

r² = 0.98
-0.007± 0.02 units
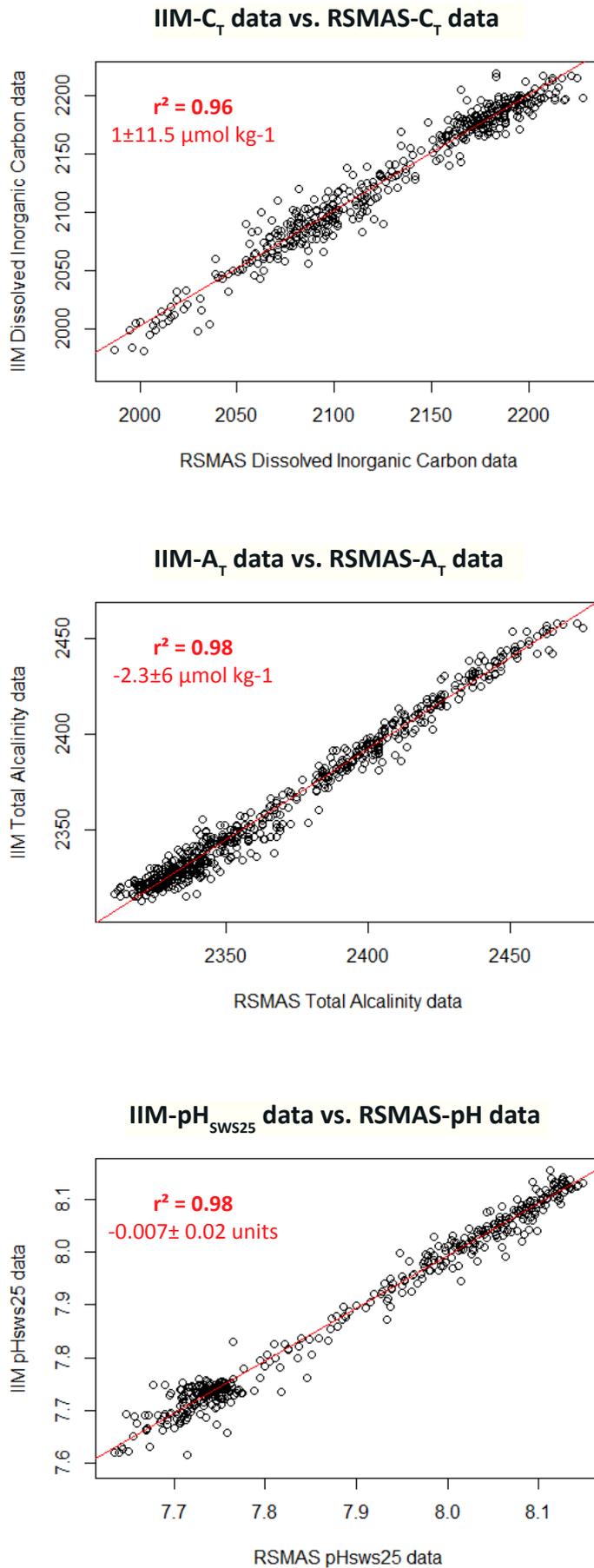
Fig 3. C_T (upper panel), A_T (middle panel) and pH_{SWS25} (lower panel) linear correlations between final RSMAS and IIM datasets for values obtained along the A05 section in 1992. Linear regression, coefficient of determination (r^2) for each parameter and the averaged difference ± standard deviation (IIM-RSMAS) found are shown in red.

Table 2. Selected cruises to perform the crossover analysis in 1992 WOCE A05 carbon datasets, following CARINA secondary Quality Control (2nQC) procedures.

CARINA Cruise ID	New Expocode	Synonyms (includes old expocode)	Ship	Cruise Name	Chief Scientist	Carbon P.I.
32	06MT20040311	06MT20040311	Meteor	M60-5	D.Wallace	D.Wallace
63	29HE20030408	29HE091; FICARAM VI	Hesperides	FICARAM VI	A.FRios	A.F.Rios, R.Wanninkhof
68	316N20030922	316N20030922	Knorr	North Atlantic	J. Swift	-
69	316N20031023	316N20031023	Knorr	North Atlantic	J. Swift	-
85	33RO19980123	33RO19980123	-	-	-	-
86	33RO20030604	33RO2003060	Ronald H. Brown	Atlantic Ocean	-	-
172	74DI19980423	74DI233	Discovery	-	Smythe-Wright	M.Alvarez, I.S.Aristegui
173	74DI20040404	74DI20040404	Discovery	Atlantic zonal section at 24.5N	S. Cunningham	U. Schuster

http://carina.geomar.de/cruises/list

GLODAP Cruise ID	New Expocode	Synonyms (includes old expocode)	Ship	Cruise Name	Chief Scientist	Carbon P.I.
9	29HE06_1-3	29HE06_1-3 (A05)	BIO Hesperides		G. Parrilla	F.Millero, A.F.Rios
25	316N151_3	316N151_3 (A20)	RV Knorr		R.Pickart	F.Millero, C.Sabine, D.Wallace
26	316N151_4	316N151_4 (A22)	RV Knorr		T.Joyce	F.Millero, C.Sabine, D.Wallace
23	OACES93, 3175MB93	3175MB93, OACES93 (A16Na, AR21),NATL-93	Baldridge	OACES 93	R.Wanninkhof	F.Millero, R.Feely
45	TTO-NAS	316N19810401(L1), 316N19810416(L2), 316N19810516(L3), 316N19810721(L4), 316N19810619(L5), 316N19810821(L6), 316N19810923(L7)	RV Knorr	ANAS	P.Brewer(L1), J.Sarmiento(L2), L.Armi(L3), W.Broecker(L4), T.Takahashi(L5), W.Jenkins(L6), P.Brewer(L7)	P.Brewer, T.Takahashi
46	TTO-TAS	316N198212_1(L1), 316N198212_2(L2), 316N198301(L3)	RV Knorr	ATAS	J.Sarmiento(L1), C.Rooth(L2), T.Takahashi(L3)	T.Takahashi

http://cdiac.ornl.gov/oceans/glodap/AtlTable1.html

Table 3. Corrective adjustments found following CARINA second quality control procedures for C_T, A_T and pH in each (RSMAS, IIM) carbon dataset studied.

|	Adjustments		
	AT	CT	pH$_{sws25}$
RSMAS	2.6	0.4	0.011
IIM	4.0	1.0	0.009
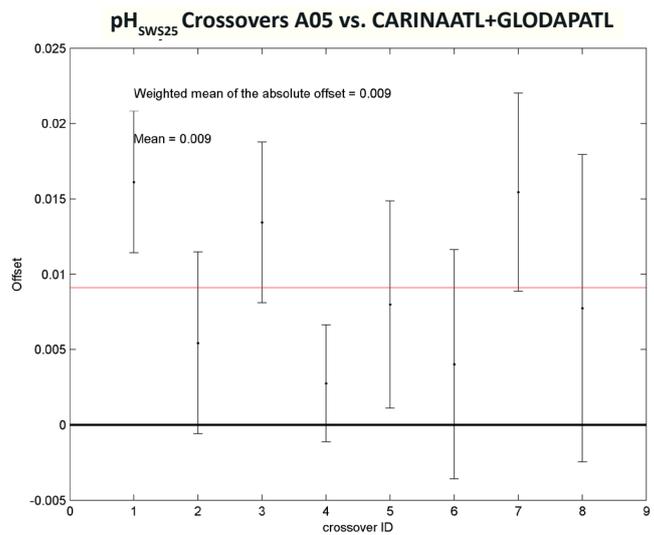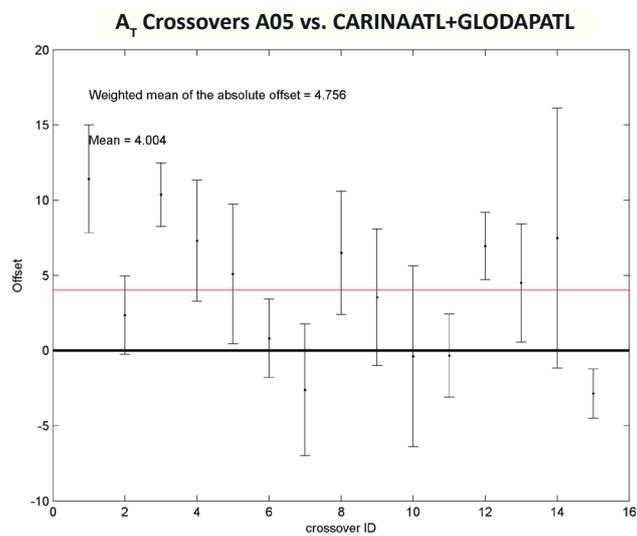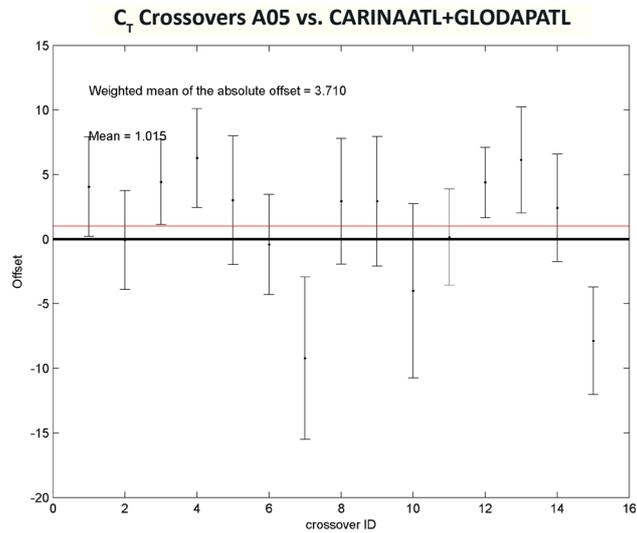
Fig. 4. C_T (upper panel), A_T (middle panel) and pH_{SWS25} (lower panel) crossover analysis results for the IIM CO_2 database. Mean and standard deviation of the offset between cruises (black) and corrective adjustment found for each parameter studied using least square models (red line).

In the first work where the IIM dataset was gone under quality control, no adjustments where proposed for any of the parameters studied (Wanninkhof *et al.*, 2003). GLODAP procedures recommended an offset of 4 µmol kg^{-1} for C_T and 6 µmol kg^{-1} for AT to take into consideration a change in measured data and no tips or bias thresholds were proposed in the case of pH. Thus, the dataset was considered to be inside quality requirements of GLODAP and no adjustments were proposed. Following CARINA procedures, offsets of 4 µmol kg^{-1} for C_T, 6 µmol kg^{-1} for A_T and 0.005 units for pH_{SWS25} are suggested to be applied as the best adjustment (Key *et al.*, 2010). In the case of the IIM dataset, the measured data were biased by 4.0 µmol kg^{-1} for A_T and by 0.009 units for pH_{SWS25}. The C_T calculated from the two previous parameters with dissociation constants of Mehrbach *et al.*, (1973) refitted by Dickson and Millero, (1987) and boric acid constants from Dickson, (1990) had an offset of 1.0 µmol kg^{-1}. From these results, it can be concluded that both quality control procedures were consistent for IIM C_T and A_T. Nevertheless, taking into account the recommended minimum offsets to adjust carbon data in CARINA, pH_{SWS25} measurements should be improved.

In this context, it should be taken into consideration that, over the last few years ocean CO_2 research, this has evolved from classical studies based only on CO_2 inventories and transports estimations, where the amount of C_T data and its accuracy were the most critical considerations, to a wider range of research topics that are focused in other CO_2 variables, such as pH or carbonate saturation levels. In this sense, following the CARINA advice, the IIM measured pH should be adjusted to reduce the offset of 0.009 units that almost doubles the recommended threshold and could lead to errors if data are used in works where pH changes are evaluated. Furthermore, as not all A_T titrations performed during the cruise were calibrated with CRMs (Rosón *et al.*, 2003), we have considered better to apply also the adjustment to A_T data in order to reduce the bias and avoid new bias in the original calculated C_T, that showed to have accurate levels according to crossovers, due to a reduction of pH values without changing alkalinity. Consequently, A_T and pH_{SWS25} data were bias-adjusted and C_T was calculated again with the same dissociation constants used previously, obtaining a 2ndQC IIM dataset (IIM_{QCed}). The offsets of the new dataset were reduced to zero for the three CO_2 parameters. Adjustments found for RSMAS dataset ($A_T \approx 2.7$ µmol kg^{-1}, $C_T \approx 0.4$ µmol kg^{-1} and $pH_{SWS25} = 0.011$ units) were inside the limits permitted in CARINA for A_T and C_T although not for pH.

5. RESULTS

5.1. *Carbon species distribution along A05 section*

In figures 5, 6, 7 and 8, IIM and IIM$_{QCed}$ distributions of C$_T$, A$_T$ and pH$_{SWS25}$ fields along the WOCE A05 section at 24.5°N in 1992 are presented.

Figure 5 shows the distribution of C$_T$ (µmol kg^{-1}) along the WOCE A05 section of the IIM (original and QCed) data. In general, the C$_T$ concentrations are greater in the east than in the west and increase from the surface towards the bottom. There is a strong vertical gradient in the upper layers, from the surface (2010-2090 µmol kg^{-1}) to 1000 dbar (2180-2210 µmol kg^{-1}), where a first relative maximum across the entire section is appreciated, because of the presence of Antarctic Intermediate Water (AAIW), that is more intensified in the eastern basin due to a signal associated with the Mediterranean outflow. Below that level, values turn back to 2170-2190 µmol kg^{-1} and increase slowly with depth, reaching the same values than in the shallower maximum near the bottom. This deep smoother gradient is due to Upper and Lower North Atlantic Deep Water (NADW) presence, which while spreading to the south occupy largely the section almost until the bottom, crossing amid Antarctic waters. Included within them, Labrador Sea Water (LSW) signal is easily identified around ~1200-2300 dbar, which has greater presence on the western boundary and arrives until half of the eastern basin getting mixed on its way with Antarctic water and so increasing its carbon concentration gradually. Below, LSW pattern can be described accurately, showing how different vertical boundaries appear going down until ~5000 dbar, about each ten degrees of latitude along the entire western basin, clearly lagged below the main core of LSW while it moves on and changes its carbon concentration. The limit of the lower NADW is situated just on the top of the Mid Atlantic Ridge and from there on, a more homogeneous water in concentration (2190-2200 µmol kg^{-1}) fills the rest of the eastern basin. Near the bottom the C$_T$ exhibits the highest concentrations, more intensified in the west (>2200 µmol kg^{-1}) associated with Antarctic Bottom Water (AABW).

Figure 6 shows the distribution of A$_T$ concentrations (µmol kg^{-1}) along WOCE A05 section of IIM (original and QCed) data. Opposite to the C$_T$ field, the highest concentrations are found at the surface (2420-2450 µmol kg^{-1}) and decrease rapidly down to ~800-1000 dbar increasing then again in deep waters. A$_T$ concentrations are higher in the east than in the west and the lowest values (2310-2320 µmol kg^{-1}) are distributed in good agreement with the C$_T$ relative minimum that denotes LSW presence. A$_T$ minimum starts at the western boundary ranging in depth between ~1000 and 4000 dbar for about five degrees of latitude to the right, then narrows forming an horizontal band that extends from ~1000 to 2000 dbar and continues far away almost to the first half of the eastern basin. This low concentration (2320 µmol kg^{-1}) band seems to be coated with a second continuousone (2330 µmol kg^{-1}) that narrows too, and spreads to the other margin, finally connecting to a low concentration signal coming from the east. The lower limit of NADW (2340 µmol kg^{-1}) crossing the entire section is deeper in the western basin and swallower afterward the Mid Atlantic Ridge. In the western basin high values (> 2340 µmol kg^{-1}) are found close to the bottom, where AABW extends. In the eastern basin those A$_T$ concentrations have a wider distribution, between 3000 dbar and the bottom.

Figure 7 shows the distribution of pH_{SWS25} along WOCE A05 section of the IIM (original and QCed) data. Large-scale pH distribution is well described, where higher values (8-8.1 pH units) are found at the surface and decrease quickly with depth, according to the previously described increasing C_T and decreasing A_T strong gradients from the upper layers, until a pH minimum zone. Then, rises a little and decreases again until the bottom. The pH minimum zone (7.65-7.7 pH units), associated to the presence of AAIW, is situated around ~1000 dbar where is enhanced its presence in the eastern margin. Within the NADW, the LSW pH signal is less evident than in the C_T or A_T fields because the non-saline dependence of pH. The full distribution of deep waters shows a relatively low pH signal that appears to decrease gradually by the mixing of water masses from west to east. Near the bottom, AABW, with a clear relative pH minimum, is well identified.
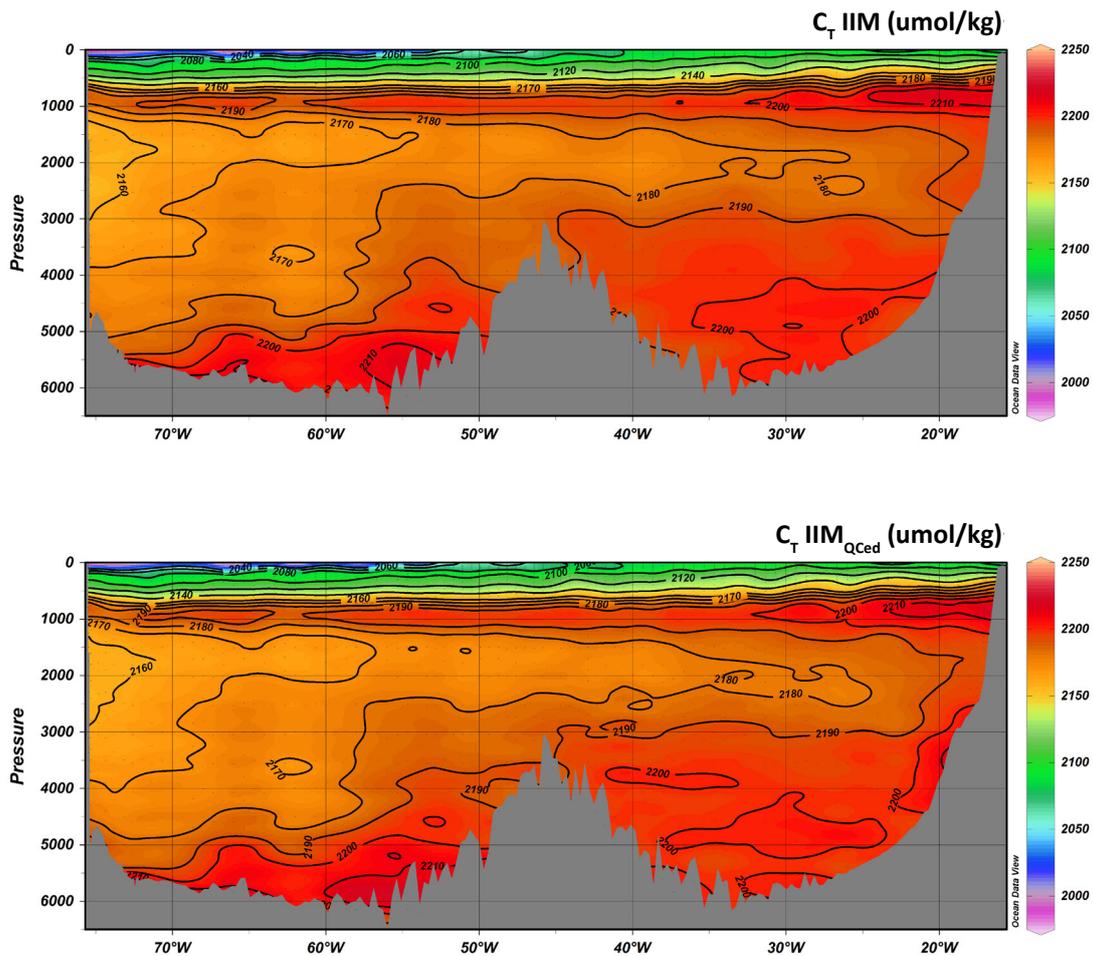

Fig 5. Dissolved inorganic carbon (C_T) concentration along A05 section in 1992: IIM (upper panel) and IIM$_{QCed}$ (lower panel) data.
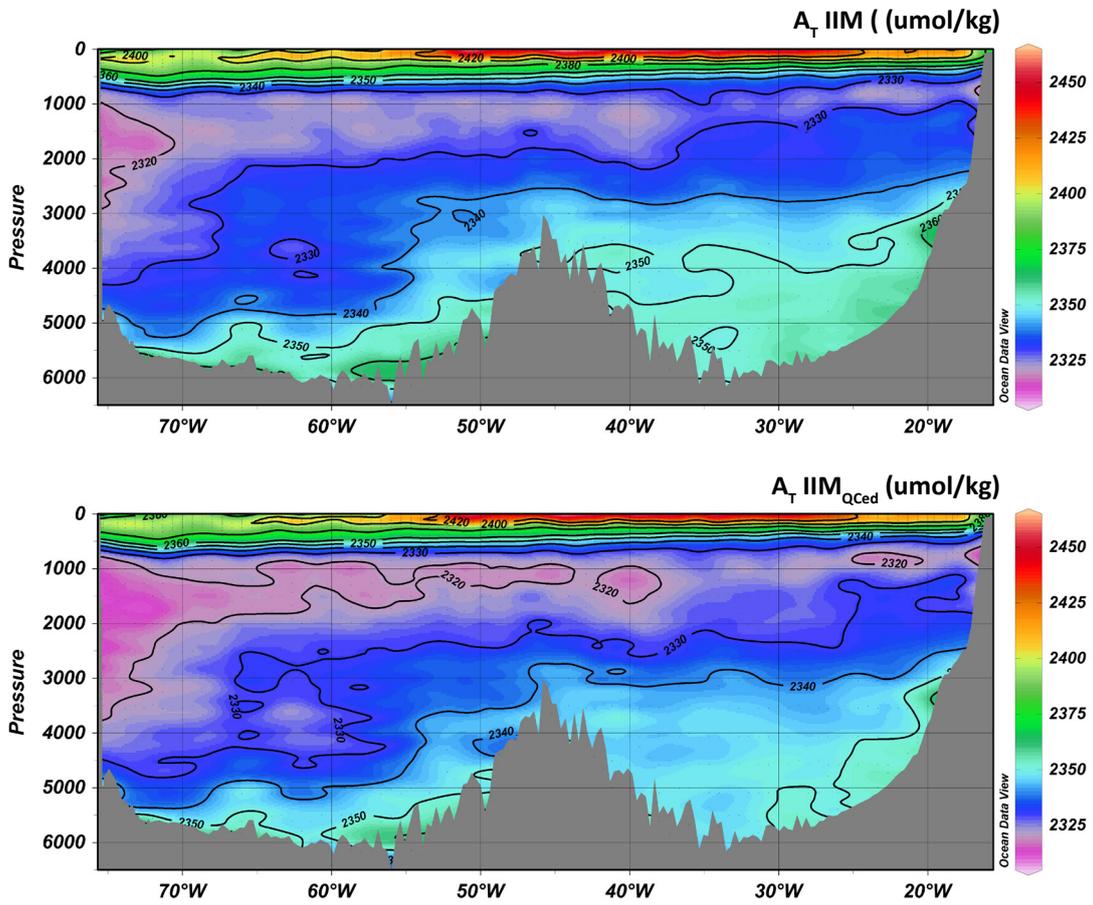
Fig 6. Total alkalinity (A$_T$) concentration along A05 section in 1992: IIM (upper panel) and IIM$_{QCed}$ (lower panel) fields.
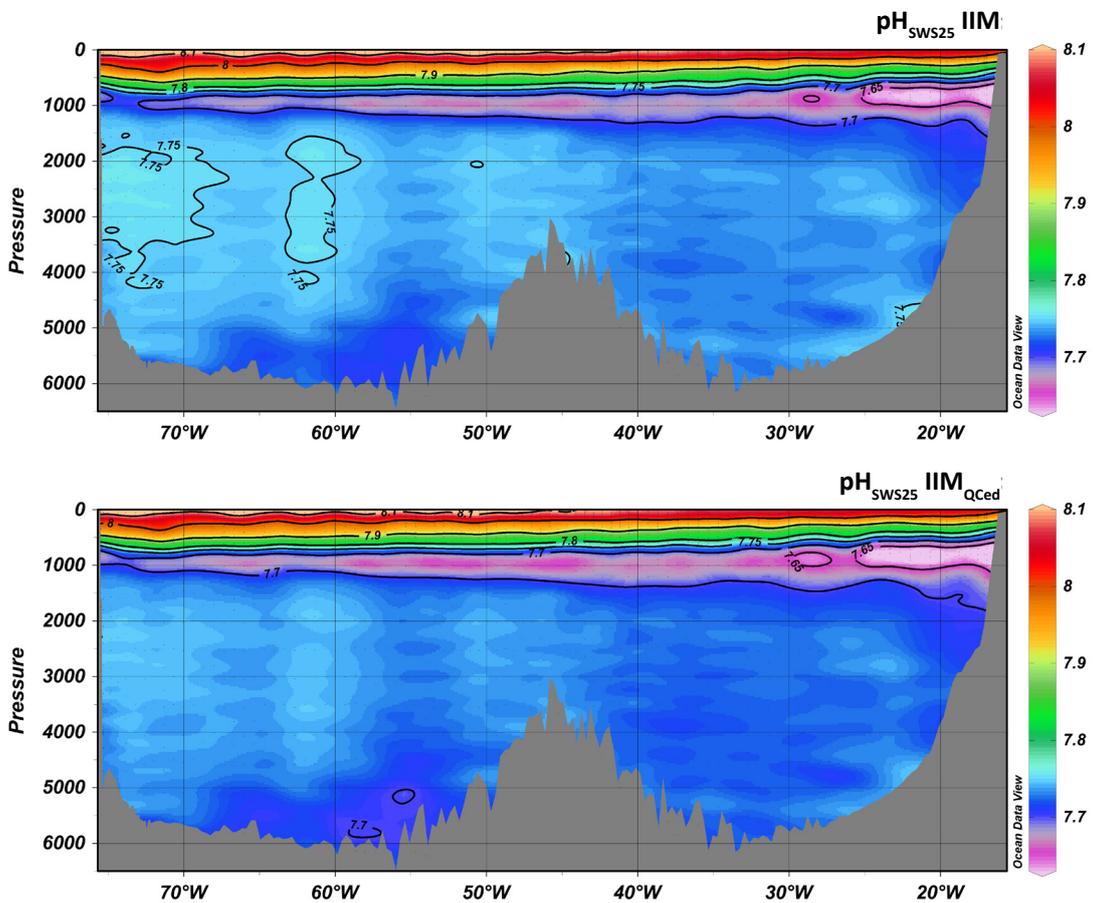

Fig 7 . Fields of pH distributions in the seawater scale and referred to 25ºC (pHSWS25) along A05 section in 1992: IIM (upper panel) and IIM$_{QCed}$ (lower panel) data.

5.2.   CO₂ variables along the Florida Strait

The IIM dataset and its quality controlled version also include the sampling of ten stations in the Florida Strait, as an exclusive feature. They are enumerated in Table 1 and located in a narrow track between -79.23°W and -80.07°W at 26°N, northernmost than the main section. The region was not covered in the RSMAS dataset and no public carbon data are available in the zone for the 1992 occupation. The Florida Current is composed of wind-driven circulation and the upper layer of the Atlantic Meridional Overturning Circulation (AMOC) that plays an important role in the heat budget of the North Atlantic region. The AMOC supplies the warm waters of the Gulf Stream system, that at this latitude is confined to this shallow (<800m) and narrow (<100km) channel. Thus, transports measurements in the Florida Strait, in terms of heat and mass, are supposed to be important for understanding global climate and a number of observational programs have been developed during extended periods of time to record its high frequency variability (Baringer and Larsen, 2001). Likewise, carbon transport measurements in Florida Strait are of major importance to correctly understand how the North Atlantic works in its CO_2 sink role. As first described in Rosón *et al.*, (2003), the C_{ANT} transport at 24.5°N is northward and mainly takes place in the first 1000m (94%), dominated by the flux of the Florida Current.

Figure 8 shows the C_T, A_T, and pH_{SWS25} IIM_{QCed} profiles in Florida Strait. The most significant feature is that there exists a very strong horizontal gradient in the three carbon species fields below the first 100m, due to the tilting down of the values isolines of all the parameters towards the east. As described in Rosón *et al.,* (2003), the jet of maximum geostrophic velocity is located near the surface very close to the western margin, resulting in the shallowing of the isopycnals towards the west, bringing older waters near the surface and giving rise to a very strong horizontal gradient in all physical and chemical properties. Furthermore, observed ranges in C_T and A_T concentrations and pH_{SWS25} values are wide and, from the surface to the bottom, are distributed in a relatively short depth compared to the main section. So, the vertical chemical gradient is also very strong in the Florida Strait. All together, these two pronounced spatial gradients make the zone to be highly heterogeneous in terms of the CO_2 system properties. Then, accurate and well distributed measurements are important to correctly describe the Florida Strait inorganic carbon dynamics. The distribution of some CO_2 variables and C_{ANT} estimates in the region were presented in Rosón *et al.*, (2003). As showed in figure 8, C_T and pH_{SWS25} present very similar distribution fields but with opposite trends: while C_T concentration is the lowest at the surface and increases progressively towards the bottom, pH reaches its lowest values there and shows the highest levels at the surface. A_T field shows a similar pattern to the ones of C_T and pH_{SWS25}, decreasing towards the bottom and influenced by a salinity maximum around ~200 dbar (data not shown) that interrupts the A_T gradient.
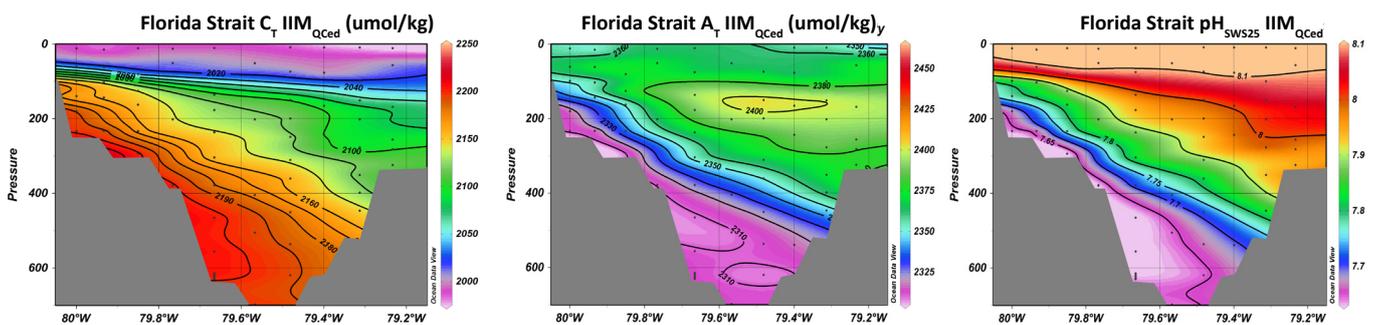

Fig 8. Dissolved inorganic carbon (C$_T$, left panel), total alkalinity (A$_T$, middle panel) and pH (pH$_{SWS25}$, right panel) distibutions of the IIM$_{QCed}$ data along the Florida Strait.

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