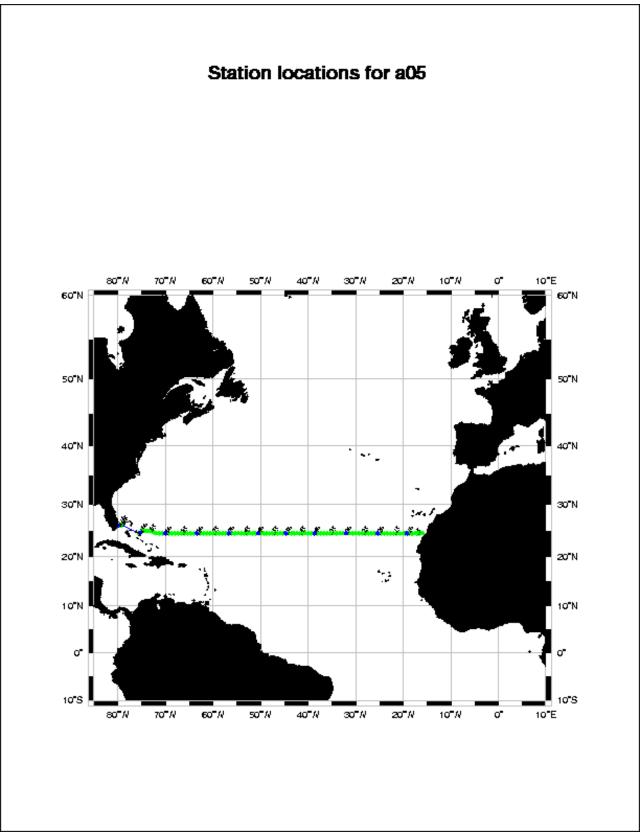
# WHP Cruise Summary Information

WOCE section designation Expedition designation (EXPOCODE) Chief Scientist(s) and their affiliation Dates Ship Ports of call Number of stations Geographic boundaries of the stations	29HE06_1-3 Gregorio Parril 1992.07.14 - 1 B.I.O. HESPÉR	992.08.15 RIDES ruz de Tenerife	to Las Palmas
Geographic boundaries of the stations	80°03.95"W	20°04.19 N 24°28.40"N	15°58.08"W
Floats and drifters deployed Moorings deployed or recovered	none none		
Contributing Authors (In order of appearance)	R. Millard M.J. Garcia A. Cruzado R. Molina J. Escánez W. Smethie F. Millero A.F. Ríos G. Rosón M. Garcia E. Alvárez Z.R. Velásquez J. García-Brau M.D. Gelado J.J. Hernández	n	

# WHP Cruise and Data Information

Instructions: Click on items below to locate primary reference(s) or use navigation tools above.

Cruise Summary Information	Hydrographic Measurements
Description of scientific program	CTD - general
	CTD - pressure
	CTD - temperature
Cruise track (figure)	CTD - conductivity/salinity
Description of stations	CTD - dissolved oxygen
Description of parameters sampled	
	Salinity
	Oxygen
	Nutrients
	CFCs
Principal Investigators for all measurements	
Cruise Participants	
	CO2 system parameters
Other incidents of note	Other parameters
	Acknowledgments
	References
	DQE Reports
	CTD



(Produced from .SUM files by WHPO)

WHP Ref. No.: A5 Last updated: 2 May 1994

## **REPORT OF THE CRUISE HE06**

#### 1.1. Cruise Narrative

1.1.1. Highlights

Expedition Designation:	HESPÉRIDES A-5 CRUISE 06 (HE06)
Chief Scientist:	Gregorio Parrilla, IEO
Ship:	B.I.O. Hespérides
Ports of Call:	Leg 1 Cádiz - Sta. Cruz de Tenerife. Leg 2 Sta. Cruz de Tfe Las Palmas de G.C. Leg 3 Las Palmas de G.C Miami
Cruise Dates:	Leg 1 July 14 to July 17, 1992 Leg 2 July 17 to July 18, 1992 Leg 3 July 19 to August 15, 1992

#### 1.1.2. Cruise summary

Cruise track is shown in fig. 1. Situation and date of stations are given in table I.

#### Sampling:

Water sampling included measurements of salinity both by CTD and bottle samples, CTD and bottle sample Oxygen determination, CTD temperature, nutrients (silicate, nitrate, nitrite and phosphate), CFC, pH, alkalinity, CO<sub>2</sub>, particulate matter, chlorophyll pigments, C14. Al. ACDP.

Type and Number of stations:

During the cruise 118 CTD/rosette stations were occupied using a 24 bottle rosette equipped with 10 or 12 liter in GO water sampling bottles; 6 test stations were made between Cadiz and Las Palmas de G.C., 101 on the A-5 section and 11 on the Strait of Florida Section. For navigation and placement of stations, GPS and dynamic positioning were used.

#### 1.1.3. List of Principal Investigators

Name	Responsibility	Affiliation
G. Parilla	CTD	IEO
H. Bryden	CTD	JRC
R. Molina	S	IEO
J. Escánez	O <sub>2</sub>	IEO
A. Cruzado	Nutrients	CEAB
W. Smethie	CFC	LDGO
A. Ríos	ph, Alk, CO <sub>2</sub>	IIM
F. Millero	ph, Alk, CO <sub>2</sub>	RSMAS
G. Rosón	Calcium	IIM
J. Garcia Braun	Chlorophyll	IEO
Z. Velásquez	Chlorophyll	CEAB
J. Hernández	Al	FCMLP
W. Broecker	C14	LDEO
M. García	ADCP	UPC

#### 1.1.4. Preliminary results

The ship departed from Cádiz on July 14, 1992 and 4 stations were made to test CTD and Rosette before arriving to Sta. Cruz de Tenerife on the 17th.

After the ship left Tenerife on the 18th and before arriving to L. Palmas the same day two more test stations were performed and the ACDP was checked.

During these stations several tests of a Falmouth Scientific Inst. CTD were also carried out.

The ship departed from L. Palmas in the early hours of the 20th to arrive to the first station of the section A-5 the same day. This section was finished, after 101 stations were made, at the Bahamas on August 14<sup>th</sup>. During the next day the Strait of Florida Section was completed and the cruise accomplished.

We carried 3CTDs, 2 belonging to IEO and 1 to WHOI. They are EG&G NBIS MARK III instruments equipped with Sensor Medics dissolved oxygen sensors and titanium pressure sensor (Millard et al 1991). All were calibrated at the WHOI facilities before the cruise. Because the delays inflicted by the hurricane Andrew on the equipment shipment from Miami to Woods Hole the post-cruise calibration were not performed on the CTDs until December. The conductivity and oxygen sensors were also calibrated at sea using the analysis of the water samples collected at each station. The depths of the sampling were based on the classical standard ones although they were varied on a station by station basis according to participants need to sample a particular layer provided there was no impairment of the in situ calibration activities.

# Table I

Station	Latitude	Longitude	Depth	Date	Time
1	24 29.97N	15 58.08W	51	07 20 92	17 23
2	24 29.96N	16 24.27W	120	07 20 92	20 07
3	24 29.95N	16 29.95W	570	07 20 92	21 31
4	24 30.18N	16 55.87W	1505	07 21 92	00 32
5	24 29.98N	17 04.93W	1895	07 21 92	05 47
6	24 29.72N	17 30.81W	2402	07 21 92	11 52
7	24 30.02N	18 00.04W	2555	07 21 92	16 02
8	24 29.43N	18 20.29W	2734	07 21 92	21 41
9	24 30.04N	18 45.04W	2944	07 22 92	02 22
10	24 30.08N	19 09.82W	3034	07 22 92	07 08
11	24 30.26N	19 35.04W	3378	07 22 92	22 25
12	24 30.20N	20 00.02W	3739	07 23 92	04 41
13	24 30.09N	20 40.01W	4162	07 23 92	11 12
14	24 30.00N	21 20.13W	4350	07 03 92	17 46
15	24 30.09N	21 59.07W	4673	07 04 92	01 00
16	24 29.85N	22 40.00W	4700	07 24 92	08 17
17	24 30.14N	23 20.32W	4991	07 04 92	15 22
18	24 30.04N	23 59.95W	5101	07 24 92	21 55
19	24 29.91N	24 40.21W	5197	07 05 92	04 23
20	24 29.90N	25 20.13W	5285	07 25 92	11 11
21	24 30.17N	25 59.92W	5347	07 25 92	17 40
22	24 30.17N	26 40.06W	4854	07 26 92	00 20
23	24 30.28N	27 19.65W	5536	07 26 92	06 51
24	24 30.00N	27 59.83W	5601	07 26 92	13 40
25	24 30.20N	28 39.39W	5655	07 26 92	20 15
26	24 30.16N	29 20.01W	5648	07 27 92	03 20
27	24 30.01N	29 59.90W	5408	07 27 92	09 57
28	24 30.01N	30 38.90W	5678	07 27 92	16 03
29	24 30.06N	31 20.27W	6080	07 27 92	22 45
30	24 30.17N	31 59.72W	5830	07 28 92	05 10
31	24 30.19N	32 39.57W	6320	07 28 92	12 05
32	24 29.95N	33 20.06W	6195	07 28 92	18 25
33	24 30.22N	33 59.85W	5650	07 29 92	01 24
34	24 30.27N	34 40.03W	5950	07 29 92	07 44
35	24 30.02N	35 19.85W	5035	07 29 92	14 22
36	24 30.10N	36 00.13W	5600	07 29 92	20 20
37	24 30.07N	36 39.91W	5020	07 30 92	02 55
38	24 30.06N	37 19.98W	5835	07 30 92	08 44
39	24 30.13N	38 00.05W	5567	07 30 92	15 38
40	24 30.14N	38 39.67W	4501	07 30 92	22 02
41	24 30.03N	39 19.93W	4370	07 31 92	03 39
42	24 30.15N	40 00.04W	5100	07 31 92	09 22

Station	Latitude	Longitude	Depth	Date	Time
43	24 30.15N	40 34.85W	4572	07 31 92	14 45
44	24 29.95N	41 10.08W	5200	07 31 92	19 57
45	24 30.17N	41 44.97W	4789	08 01 92	01 37
46	24 30.00N	42 19.82W	4000	08 01 92	06 53
47	24 30.08N	42 54.88W	3574	08 01 92	12 15
48	24 30.02N	43 29.73W	3797	08 01 92	16 35
49	24 30.02N	44 04.85W	4177	08 01 92	21 39
50	24 30.21N	44 40.07W	3000	08 02 92	02 37
51	24 30.01N	45 15.08W	3640	08 02 92	07 00
52	24 29.93N	45 49.79W	2778	08 02 92	11 34
53	24 29.95N	46 24.91W	3511	08 02 92	14 58
54	24 29.95N	47 00.00W	3707	08 02 92	20 40
55	24 30.08N	47 34.98W	3980	08 03 92	01 25
56	24 29.84N	48 09.84W	3894	08 03 92	06 24
57	24 29.99N	48 44.97W	4379	08 03 92	11 27
58	24 30.03N	49 19.94W	5135	08 03 92	16 53
59	24 30.07N	49 54.77W	4796	08 03 92	22 29
60	24 29.90N	50 29.74W	4994	08 04 92	03 51
61	24 30.00N	51 04.95W	5076	08 04 92	09 25
62	24 30.08N	51 39.87W	4810	08 04 92	15 32
63	24 30.02N	52 14.99W	4728	08 04 92	22 03
64	24 29.99N	52 50.00W	5100	08 05 92	03 27
65	24 30.06N	53 24.93W	5637	08 05 92	09 04
66	24 29.92N	53 59.61W	6140	08 05 92	15 18
67	24 29.96N	54 40.00W	6209	08 05 92	21 34
68	24 29.94N	55 19.80W	5540	08 06 92	03 46
69	24 29.95N	56 00.01W	6444	08 06 92	09 57
70	24 30.03N	56 40.03W	6180	08 06 92	16 42
71	24 29.88N	57 19.79W	6116	08 06 92	23 51
72	24 29.91N	58 00.05W	6123	08 07 92	06 30
73	24 29.94N	58 39.96W	6071	08 07 92	13 09
74	24 30.08N	59 19.49W	5827	08 07 92	19 48
75	24 30.06N	60 00.12W	5937	08 08 92	02 04
76	24 30.00N	60 39.92W	5794	08 08 92	08 29
77	24 30.17N	61 19.40W		08 08 92	14 56
78	24 29.93N	61 59.88W	5891	08 08 92	21 37
79	24 30.07N	62 39.90W	5909	08 09 92	03 51
80	24 29.95N	63 20.12W	5850	08 09 92	10 33
81	24 29.95N	63 59.90W	5771	08 09 92	16 43
82	24 29.93N	64 39.94W	5762	08 09 92	23 12
83	24 30.37N	65 20.39W	5642	08 10 92	10 25
84	24 29.96N	65 59.98W	5764	08 10 92	17 05
85	24 30.04N	66 39.93W	5647	08 10 92	22 58
86	24 29.98N	67 19.99W	5658	08 11 92	05 14

Station	Latitude	Longitude	Depth	Date	Time
87	24 30.01N	68 00.04W	5739	08 11 92	11 34
88	24 29.95N	68 39.93W	5712	08 11 92	17 32
89	24 29.92N	69 19.93W	5620	08 11 92	23 27
90	24 29.97N	70 00.00W	5561	08 12 92	05 20
91	24 29.87N	70 40.00W	5541	08 12 92	11 10
92	24 29.88N	71 19.92W	5519	08 12 92	16 50
93	24 30.00N	71 59.97W	5510	08 12 92	22 35
94	24 45.05N	72 35.94W	5497	08 13 92	04 10
95	24 59.80N	73 10.00W	5344	08 13 92	09 56
96	24 59.97N	73 49.95W	5242	08 13 92	15 38
97	25 00.00N	74 20.04W	4948	08 13 92	20 23
98	25 06.11N	74 49.77W	4702	08 14 92	01 47
99	24 32.77N	75 27.70W	3347	08 14 92	08 22
100	24 37.41N	75 19.12W	4800	08 14 92	11 45
101	24 30.00N	75 31.00W	930	08 14 92	16 03

Water samples were collected from 10 or 12 liters PVC Niskin GO bottles mounted on a GO Rosette Sampler. All the water sample conductivity and oxygen measurements were made in a constant temperature laboratory soon after each cast was completed. Descriptions of analytical techniques, precision and accuracy are given later in this report. Additional samples were also collected for the analysis of the other parameters listed above, description of which are presented in other sections of this report.

According to the WOCE Implementation Plan this line was located at 24°N. As two oceanographic sections had been made previously in 1957 and 1981) around 24.5°N (Roemmich and Wunsch, 1985) we asked the WOCEIPO to move the WOCE section A5 to this latitude, which was agreed to. With respect to the station separations and because we were constrained by ship time, we decided to use the following judgment: the first 6 stations were located at the 50, 100, 150, 1500, 2000 and 2500 isobaths (about 18nm separation). From there to the 4000m depth (stl2) the separation was about 23nm. From station 12 to the eastern limits of the Mid Atlantic Ridge we separated the stations by 36nm. Across the Ridge the separation was 32nm. From its western limits to the 5000 isobath near the Bahamas, stations were separated again 36nm. Stations close to the Bahamas were separated by less than 30nm. The stations across the Straits of Florida were occupied every 5nm.

Near to Bahamas we deviated the heading of the section slightly from the original plan in order to cross the continental slope perpendicular to the direction of the isobaths and to obtain a clear crossing of the Deep Western Boundary Current.

The ADCP and a thermosalinograph recorded continuous during the whole cruise. Wind information was recorded every hour.

At the end of the cruise the ship was checked for Tritium and C14 contamination by the Tritium laboratory of the University of Miami.

Vertical profiles for T, S and  $O_2$  together with a listing of this data for standard depths for each station are given in the Annex.

# 1.1.5. Incidences

During the test stations, there were problems with the rosette: several of the bottles were not triggered. The trouble had to do, probably, with too much friction on the bolts since this rosette had never been used before. After some lubrication the problem disappeared. There were some problems, during the test stations and some of the first stations of the A-5 section, with the portside winch. The oil of the hydraulic circuit became too hot causing the winch to lose power. After station 11 we switched to the other winch that worked from the stern.

On station 62, CTD # 1 stop sending conductivity data and it was replaced by CTD # 2 until station 74 when CTD# 1 was brought back, only for 7 stations since we started getting pressure spiking. From station 81 to 88 we used CTD #2 and from there on we used CTD# 1 after it was repaired on board.

On station 83 the wire was reterminated after cutting off 10 m of wire because of a faulty electrical contact. It was also reterminated after station 110 (in the Florida Strait) because of two-blocking the CTD on recovery at this station.

On station 61 the CTD hit the bottom because of a failure of the depth recorder.

The portable hydrophone-recording system for use with the pinger failed from the beginning and we were not able to repair it. We tried to use the EA500 SIMRAD echosounder of the ship, but there was not the necessary documentation on board so we could not effectively use the pinger at all. We decided to keep the CTD package between 50 or 100 m above the bottom when the floor was too rough and less that 50 m when it was flat.

The proposed Tritium and Helium survey by Dr. Z. Top could not be made since the equipment was lost during shipment from Miami and it never arrived to the ship.

Name	Responsibility	Affiliation
G. Parrilla	Chief Scientist	IEO
H. Bryden	Co-Chief Scientist	WHOI
J. Alonso	CTD Watch	IEO
E. Alvarez	CTD Watch/Thermosalingraph	PCM
B. Amengual	S, O <sub>2</sub>	IEO
G. Bond	CTD Watch/CTD Electronics	WHOI
J. Garcia-Braun	O <sub>2</sub> , Chlorophyll	IEO
J. Hernández	AI	FCMLP
A. Cantos	CTD Watch/ADCP	Ainco I

# 1.1.6. List of Participants

Name	Responsibility	Affiliation
A. Cruzado	Nutrients	CEAB
J. Escánez	O <sub>2</sub>	IEO
S. Fiol	CO <sub>2</sub>	U. La Coruña
M.J. García	CTD Watch/Data Processing	IEO
D. Gelado	AI	FCMLP
E. Gorman	CFC	LDGO
A. Lavín	CTD Watch/Data Processing	IEO
R. Millard	CTD Watch/CTD Programming	WHOI
R. Molina	CTD Watch/S	IEO
J. Molinero	Electronics	IEO
A. Osiroff	CTD Watch/ Data Processing	SHMA
A.F. Ríos	CO <sub>2</sub> /M.O.P.	IIM
G. Rosón	Calcium	IIM
P. Sánchez	CTD Watch/Data Processing	IEO
W. Smethie	CFC	LDGO
Z. Velasquez	Chlorophyll	CEAB
A. Fougere	Falmouth SI CTD	WHOI
C. Heuer	Tritium/Helium	RSMAS
G. Mathieu	CFC	LDGO

#### 1.1.7. Acronyms

IEO	Instituto Espanol de Oceanografia	
IIM	Instituto de Investigaciones Marinas	
CEAB	Centro de Estudios Avanzados Blanes	
FCMLP	Facultad de C. del Mar	
PCM	Programa Clima Maritimo	
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences	
WHOI	Woods Hole Oceanographic Institution	
LDGO	Lamont Doherty Geological Observatory	
SHMA	Servicio de Hidrografía Naval	
UPC	Unversidad Politecnica de Cataluna	
JRC	James Rennell Centre	

# 2. MEASUREMENT TECHNIQUE AND CALIBRATIONS

# 2.1. CTD measurements

(R. Millard and M.J. Garcia)

#### 2.1.1. Instrumentation, Calibrations and Standards

Two EG&G/NBIS Mark IIIb CTD underwater units each equipped with pressure, temperature, conductivity and polographic oxygen sensors were used throughout the cruise. The CTD instrument numbers are 1100 and 2326 and they belong to the Instituto Espanol de

Oceanografia (IEO). Each CTD is configured identically with the same data scan length, variables, and scanning rate of 31.25 Hz. (A detailed description of the Mark IIIb CTD can be found in Brown and Morrison, 1978.) Both instruments were modified at Woods Hole Oceanographic Institution (WHOI) to add a titanium pressure sensor with a separately digitized resistive temperature device (RTD). A third EG&G/NBIS Mark IIIb CTD was provided by WHOI (WHOI instrument No. 8) but was not used during this expedition. A General Oceanics (GO) rosette fitted with 24 10 liters Niskin bottles was used with the CTD for collecting water samples. The GO rosette bottles are mounted approximately 0.5 m above the CTD sensors.

Titanium pressure sensors were manufactured by Paine Instrument and were installed with a separate pressure-temperature sensor in both CTDs prior to the cruise. The pressure data has a resolution of 0.1 decibars and an overall accuracy of + 2.0 decibars for CTD# 1100 and + 5.0 decibars for CTD # 2326. The pre-cruise pressure calibration was used for CTD # 1100 while a combination of pre and post cruise pressure calibration was used to process CTD # 2326. The Titanium pressure transducer processing methods follow Millard, et. al (1993). Pressure is calibrated across the pressure sensor's range in the laboratory before and after the cruise. These calibrations are carried out at both room temperature and at the ice point.

The temperature sensor is Rosemount platinum # 171. The fast response temperature thermistor normally employed in the Mark IIIb has been removed. The temperature resolution is  $0.0005^{\circ}$ C and the accuracy is better than  $\pm 0.0015^{\circ}$ C (Millard & Yang (1993)) over the range 0 to  $30.0^{\circ}$ C. Temperature was calibrated in the laboratory before and after the cruise with the CTD instrument fully immersed as described by Millard & Yang (1993). A large (0.01 to  $0.015^{\circ}$ C) shift of temperature in the same direction was observed to occur with both CTD's 1100 and 2326. This shift was traced to a faulty pre-cruise laboratory temperature standardization. The conductivity sensor is a 3 centimeter alumina cell manufactured by EG&G/NBIS. The resolution of conductivity is 0.001 Ms/cm and the accuracy is directly tied to the water sample salinity accuracy discussed elsewhere in this report. The overall accuracy of the CTD conductivity calibrated to the rosette water bottle salinities is believed to be better than  $\pm 0.0025$  psu.

The CTD oxygen is measured with a polographic sensor manufactured by Sensormedics. The CTD oxygens are calibrated to shipboard Winkler oxygens.

# 2.1.2. CTD data collection and processing

The CTD data logging and processing was accomplished on two MSDOS PCs. The data logging was handled on an IBM compatible 80386 system with an 80387 math coprocessor. The EG&G data logging program CTDACQ was used to record down and up profiles, separately on disk together with a rosette bottle file. The CTD data was edited to flag spurious data using the EG&G program CTDPOST. The remainder of the CTD postprocessing was performed using the WHOI PC-based CTD processing system as described by Millard and Yang (1993). The post-processing was performed on an IBM compatible 80486 system with a 600 Mbyte optical disk (Sony SMO-C501) used for data archiving.

# 2.1.3. CTD calibration constants

The standard Alumina conductivity cell materials expansion factors: Alpha = -6.5 E-6, Beta = 1.5 E-8 were applied to CTD #1100 and CTD #2326. When the pre-cruise pressure calibration was applied to CTD 2326 data, a Beta = -1.5 E-8 was required to produce a salinity without a depth dependence; but a combination of pre/post-cruise pressure calibration allowed the use of the standard Beta value. The combined pressure calibration was used to process all CTD #2326 data because it produced CTD salinities free of depth dependence and yielded the pressure bias observed at sea.

# 2.1.3.1.Pre and post-cruise Laboratory calibrations polynomial coefficients

$$Eng = E+Dr+Cr^2$$

(where r is the measured raw CTD data value and Eng is the standard engineering unit of the variable).

The coefficients for each sensor are:

a) Pressure: (Loading/unloading)

CTD #1100<br/>E= -1.075;D= .108604;C=0.593893 E-9 pre-cruiseCTD #2326<br/>E= 0.15;D= .104831;C= -0.799383 E-9 (pre-cruise)E= -12.5;D= .105437;C= -0.752607 E-9 (post-cruise)E= -6.3;D= .105127;C= -0.752607 E-9 (pre/post cruise combined)

b) Temperature: (post-cruise)

CTD #1100 (2<sup>nd</sup> order fit, stand. dev. = 0.00035) E= -0.4055; D= 0.499576 E-3; C= 0.13946 E-11 : Lag= 0.225 s

CTD #2326 (1<sup>st</sup> order fit, stand. dev. = 0.0006) E= 0.0026; D= 0.499889 E-3; Lag= 0.250 s

c) Conductivity:

For CTD #2326 and CTD #1100 conductivity calibrations the post-cruise temperatures were used. For CTD #2326 the data was pressure averaged again after the cruise using the combined pre/post-cruise pressure calibrations while CTD 1100 used the pre-cruise pressure calibration. The conductivity (salinity) calibration was examined closely at the change of instruments during the cruise (i.e. instrument swap outs at stations 62 - 63, 73 - 74, 80 - 81, 88 - 89) and no shifts were found that were not arguably due to oceanic variability.

# CTD #1100

This CTD required some fine-tuning of conductivity slope calibrations.

#### Bias, E= -0.0116 for all the stations

Stations	Slope D=
1 – 62	0.1000 453 E-2
74 (fit to itself)	0.1000 565 E-2
75	0.1000 512 E-2
76	0.1000 510 E-2
77	0.1000 508 E-2
78	0.1000 506 E-2
79	0.1000 505 E-2
80	0.1000 503 E-2
89 – 91	0.1000 500 E-2
92 – 101 (fit to sta. 93 – 95)	0.1000 483 E-2

Stations 96, 97 and 98 salinities are low compared to the water samples, but we believe that water sample salinities are suspect for these stations.

#### CTD #2326

For this CTD, there is significant down-up hysteresis in one of the salinity sensors (P, T, or C: mostly likely Conductivity). The up-profile salinity is .005 - .007 fresher than the corresponding down-profile at a given potential temperature. Of course, at the bottom of the profile the salinity agrees but by 2.5°C (3500 dbars) on the 6000 dbar profiles a .005 psu discrepancy exists. A program was written to extract and create down-profile conductivity calibration data and we have to refit CTD #2326 conductivities below 2500 dbars.

		Sta	ation		Slope, D=
63	(Fit	to	down	profile	0.1000 2693 E-2
64	cond	lucti	vity)		0.1000 1727 E-2
65					0.1000 1699 E-2
66					0.1000 1671 E-2
67					0.1000 1642 E-2
68					0.1000 1614 E-2
69					0.1000 1585 E-2
70					0.1000 1557 E-2
71					0.1000 1529 E-2
72					0.1000 1500 E-2
73					0.1000 1472 E-2
81 –	88 B	ias,	E= 0.01	121	0.999936 E-3
				(0	1-27-93 calibration)

Stations 63 – 73, bias; E= 0.0083

Final CTD data edit:

Two mean profiles were created. One for the West African Basin and a second for the North American Basin, by averaging all deep BIO Hésperides stations on pressure surfaces. These mean profiles have been used to screen the individual casts of each

basin for question able temperature, salinity and oxygen data, comparing individual profiles to respective mean profile.

Two edit criteria were used to flag questionable data:

- 1) Temperature, Salinity and Oxygen variations whose difference from the mean profile exceeding 5.5 standard deviations;
- 2) Stability parameter exceeding –1.0E-5 per meter.

A list of stations with bad or questionable data at the surface is given below:

	1	2
W African B.		2, 5, 10, 18, 19, 20,
	44, 47	22, 23, 27, 28, 29, 31,
		33, 34, 36, 37, 38, 42,
		43, 45, 46, 48, 50, 51,
		52, 53
N American B.	57, 74, 76, 81	55, 56, 58, 59, 60, 61,
		62, 68, 69, 70, 72, 77,
		78, 79, 80, 82, 85, 86,
		87

- 1. Stations with bad or too low surface salinities.
- 2. Stations with questionable surface salinities.

# d) Oxygen

The oxygen parameters were adjusted as shown on tables II and III. The header abbreviations denote the following:

- STA= First and last station numbers of the group used for calibration.
- BIAS, SLOPE, PCOR, TCOR, WT, LAG and Edit factor are parameters of the fit as described by Millard and Yang (1993).
- STD DEV= Standard deviation of the fit after some outlying water sample observations are discarded.
- OBS= Number of water sample observations used for the calibration.

# Table IICoefficients for Oxygen Calibrations

STN	BIAS	SLOPE	PCOR	TCOR	WT	LAG
1-11	.029	.1104e-02	.1664e-03	2783e-1	.7510e+00	.7560e+01
12-14	.049	.1139e-02	.1461e-03	2990e-1	.7500e+00	.7500e+01
15-19	.031		.1504e-03	2939e-1	.8219e+00	.4167e+01
15	"	.1129e-02	"	"	"	"
16	"	.1156e-02	"	"	"	"
17	"	.1158e-02	"	"	"	"
18	"	.1170e-02	"	"	"	"
19	"	.1182e-02	"	"	"	"

STN	BIAS	SLOPE	PCOR	TCOR	WT	LAG
20-22	.024	.1197e-02	.1517e-03	3090e-1	.7408e+00	.7299e+01
23-31	.032	.1205e-02	.1491e-03	3033e-1	.7934e+00	.3211e+01
32-40	.024	.1228e-02	.1501e-03	2926e-1	.9210e+00	.7833e+01
41-43	.015	.1233e-02	.1553e-03	2998e-1	.7740e+00	.7000e+01
44-46	.006	.1229e-02	.1616e-03	3065e-1	.6702e+00	.1623e+02
47-50	.000	.1235e-02	.1673e-03	3092e-1	.5287e+00	.2187e+02
51-55	.012	.1226e-02	.1590e-03	2953e-1	.8080e+00	.7340e+01
56-62	.032	.1216e-02	.1499e-03	2906e-1	.8221e+00	.1549e+02
63-71	036	.1256e-02	.1683e-03	3041e-1	.7448e+00	.4612e+01
70	"	.1269e-02	"	"	"	"
72-73	047	.1338e-02	.1686e-03	3241e-1	.6362e+00	.2927e+01
74-80	.027	.1201e-02	.1515e-03	2865e-1	.8869e+00	.1027e+02
81-83	053	.1276e-02	.1788e-03	3177e-1	.6312e+00	.3351e+01
84-87	030	.1284e-02	.1645e-03	3047e-1	.8147e+00	.1998e+00
88	"	.1320e-02	"	"	"	"
89-101	.039	.1200e-02	.1459e-03	2779e-1	.9109e+00	.1390e+02

 Table III
 Statistics of Adjustments for Oxygen Calibrations

STN	STD DEV	OBS	STN	STD DEV	OBS
1-11	.7188e-01	59 of 59	47-50	.5274e-01	84 of 91
12-14	.4233e-01	46 of 60	51-55	.5526e-01	83 of 100
15-19			56-62	.3870e-01	116 of 131
15	.6791e-01	19 of 21			
16	.1566e+00	18 of 20	63-71	.5401e-01	176 of 189
17	.5021e-01	19 of 21	70	.7953e-01	22 of 23
18	.3341e+00	21 of 21			
19	.5171e-01	21 of 22	72-73	.8711e-01	45 of 45
20-22	.56355e-01	62 of 67	74-80	.6576e-01	159 of 161
23-31	.6148e-01	189 of 203	81-83	.6388e-01	64 of 66
32-40	.5958e-01	150 of 170	84-87	.7946e-01	72 of 72
			88	.8969e-01	24 of 24
41-43	.7023e-01	68 of 69			
			89-101	.5241e-01	213 of 229
44-46	.4442e-01	68 of 69			

#### Notes to these tables

- Parameters obtained from stations 7 to 9 apply to stations 1 11.
- Stations 15 to 19 were fit fixing parameters of 15 21 except slope.
- Stations 32 to 39 calibrations applied to stations 32 to 40.
- Station 70 calibrated as group 63 71 except slope
- Station 88 calibrated as 84 87 except slope
- Station 89 to 101. Sta. 96 and 98 are excluded in setting calibration parameters. When they were included WT was negative.

Figure 2 shows the histograms for salinity and oxygen differences between CTD and bottle samples deeper than 2500 db.

The mean and standard error for the first one are 1.9 E-4 and 1.3 E-4 respectively. For oxygen, they are 1.1 E-4 and 2 E-3.

# 2.2. Salinity

(R. Molina)

For the salinity measurements the recommendations given in the training Course Notes (Ocean Scientific Int., Funchal, July 1991) were followed. The water sample salinities were measured with a Guildline Autosal Model 8400A salinometer. The manufacturer claims a precision of 0.0002 and an accuracy of 0.003 when the instrument is operated at a temperature between  $+4^{\circ}$  and  $-2^{\circ}C$  of ambient temperature. All the salinity measurements were made in a temperature controlled laboratory about 1° to 3°C below that of the salinometer water bath.

Two different batches of standard water were used: batch P120 (April 6, 1992) with 50 ampoules and 20 ampoules from batch P117 (July 10, 1991). After the salinometer was standardized with water from the first batch, 8 samples from an ampoule of the second batch were measured, and the labelled value of 34.994 was obtained within  $2x10^{-5}$ . On the average, the salinometer was standardized every 31 samples.

Water samples were collected from the Niskin bottles in Ocean Scientific International glass bottles and the measurements were made within the 24 hours after the station was finished. In total 2294 samples were measured.

In determining the conductivity ratio, three measurements were made from every sample providing the differences were smaller than  $2x10^{-5}$ . If not, more measurements were made until three consecutive values exhibited differences smaller than  $2x10^{-5}$ .

Sta.	Depth	Bottle no.	No. of Samples	Standard dev.
50	2500	02, 3, 4, 5, 6, 7	6	± 3.6x10 <sup>-4</sup>
64	2532	6	8	± 1.3x10 <sup>-4</sup>
72	249	16	8	± 2.1x10 <sup>-4</sup>

In 3 stations, samples were replicated with the following results:

During one day when the air conditioning of the laboratory broke down, salinity measurements for stations 2 to 3 were made with the laboratory temperature 0.3°C above the salinometer bath temperature.

#### 2.3. Oxygen

(J. Escánez)

Oxygen determinations were carried out following the Winkler method and using the reagents prepared according to Carpenter (1965). We used the modified Carpenter's equation as given by Culberson et al (1991). The endpoint of titration was determined visually using starch as indicator.

Reagents were dispensed with all glass and teflon dispensers "Dispensette" from Brand GMBH and Co. (0-2 ml capacity) with certified accuracy of  $\pm$  0.6% and a coefficient of cariation of  $\pm$  0.1%. The tips of the dispensers were lengthened up to 6 cm with thin plastic tubing to avoid the precipitation of manganese hydroxide in the neck of sample flasks.

Titration was done with a Metrohm Dosimat E.412 automatic burette using Potassium lodate "pro.anlaysi" Merck (Lot N° 150 BZ 252853. Assay 99.95 - 100.05%) at a concentration of 0.0100 N.

Standards and blanks were dispensed with class "A" calibrated hand pipets with certified accuracy of  $\pm$  0.02 ml for 10 ml pipets and  $\pm$  0,006 ml for 1 ml pipets.

In total, 2338 samples were taken (Table IV). In order to assess good quality results, calibration sets were run through 7 stations. Inter-sample calibrations were run on 3 stations by taking 1 sample from 6 Niskin bottles triggered at the same depth, while on 4 stations intra-samples calibrations were performed taking 6 samples of 2 Niskin bottles triggered at the maximum and minimum  $O_2$  layers respectively. Values are shown in Tables V and VI.

Analysts	Station Casts	Stations Analyzed	No. of Samples Analyzed
J.G. Braun	36	11	234
B. Amengual	38	20	446
J. Escánez	38	81	1658

# Table IVDistribution of Casts/Analysts

#### Table VCalibrations between Casts

STN	DEPTH	BOTTLE NO.	O <sub>2</sub> (ml/l) Mean	O <sub>2</sub> (ml/l) Std. Dev.
1	40 m	12, 13, 14, 15, 17	X= 5.711	sd=± 0.009
1	40 m	1, 2, 3, 4, 5, 6	X= 4.661	sd= ± 0.031
50	2500 m	2,3,4,5,6,7	X= 5.655	sd= ± 0.005
107	378 m	3,4,5,6,7,8	X= 2.998	sd= ± 0.005

#### Table VI Calibrations within Casts (Maximum and Minimum)

STN	BOTTLE NO.	MAX/MIN O <sub>2</sub>	O <sub>2</sub> (ml/l) Mean	O <sub>2</sub> (ml/l) Std. Dev.
14	1	Max	X= 5.601	sd= ± 0.015
14	10	Min	X= 2.575	sd= ± 0.003

STN	BOTTLE NO.	MAX/MIN O <sub>2</sub>	O <sub>2</sub> (ml/l) Mean	O <sub>2</sub> (ml/l) Std. Dev.
32	8	Max	X= 5.622	sd= ± 0.002
32	12	Min	X= 3.294	sd= ± 0.014
67	6	Max	X= 5.907	sd= ± 0.009
67	12	Min	X= 3.513	sd= ± 0.002
89	5	Max	X= 6.193	sd= ± 0.003
89	11	Min	X= 3.469	sd= ± 0.005

#### 2.4. Nutrients

(A. Cruzado)

Analyses were performed on board with a four channel SKALAR segmented flow autoanalyzer. Samples were collected in 150 ml acid-rinsed polythene flasks directly from the Niskin bottles, following the protocol established by the WOCE Hydrographic Programme. Analyses were carried out immediately without any treatment of the samples. When necessary, samples were kept in the cold room (unfrozen and never for more than 10 hours) without additives.

The analytical techniques followed were those described by Whitledge et al. (1981) with minor modifications to adapt them to the particular conditions of the instrument used and concentration ranges observed. Primary standards were prepared at the beginning and in the middle of the cruise prepared every two days and preserved with some drops of chloroform in the fridge. Running standards were interleaved with unknown samples in order to provide a measure of analytical stability. Whenever changes in sensitivity (particularly in the case of nitrate) were noticed, these standards allowed for a correction to be applied.

All concentrations were referred to double distilled water prepared by reverse osmosis through milliRo, dionization through Milli-Q and distillation. No sea water sample has ever given a concentration negative with respect to this double distilled water. Phosphate analysis corrected for the change in absorbance due to the salinity effect. Surface seawater was used as carrier and, except for silicate, it always showed the minimum concentrations in the water column.

Silicate concentrations below the surface were often found to be lower than the surface values and very close to the values given by double distilled water. Replicate samples were analysed at various depths both from the same and from different Niskin bottles. A comparison of all the primary and secondary standards used during the cruise is underway and may introduce some small corrections to the results. A statistical assessment of such analyses is being prepared. Some nutrient diagrams are shown in figure 3.

#### Addendum to the Report on Cruise HE06 (A-5, WOCE 1992). Nutrients (A. Cruzado)

During the HE06 cruise (July/August 1992) along the WOCE line A-5, dissolved inorganic nutrients (orthophosphate, nitrate+nitrite, nitrite, and orthosilicate) were collected and analyzed on board the R/V Hesperides using a continuous flow analyzer by Antonio

Cruzado (Centro de Estudios Avanzados de Blanes, Spain) following methods adapted from Withledge et al. (1981). These methods were used in the fifth 1989/1990 ICES international inter-comparison exercise for nutrients in seawater (Aminot and Kirkwood, 1995). Three different quality control procedures were applied to the A5 nutrient data. First, spurious chemical data were flagged according to WOCE quality control codes. These are data values shown to be analytically incorrect ("Bad"). Second, the A5 chemical data were compared to the August 1992, Trident cruise on the RV Baldrige between Abaco Island, the Bermuda Rise and the Mid-Atlantic Ridge (Garcia, 1996). This provided a mean to compare the two cruises in the western basin only. Third, the A5 data were compared to historical oceanographic data collected since the GEOSECS program (Table 1). The long-term precision of the A5 chemical data was estimated following the method of Saunders (1986). Potential temperature (Fofonoff and Millard, 1983) was fitted to the nutrient data from the HE06 and AT109 cruises by linear least-squares for water with temperatures less than or equal to 1.8°C and 2.1°C in the western (45-75 W) and eastern (20-44 W) Atlantic basins, respectively (Garcia, 1996). The standard deviation of the measured values for each chemical variable from the expected values calculated from the coefficients of the regression lines for stations in the western and eastern basins are shown in Table 2. Chemical data points which deviated significantly (more than 5 SD from the mean) were flagged as questionable. No quality control was applied to the nitrite data.

Cruise/Leg	Ship	Cruise dates	Institution
AT109-II	Atlantis II	August-September, 1981	WHOI
AT109-I	Atlantis II	June-July, 1981	WHOI
Trident	Baldridge	August, 1992	LDEO
EN129	Endeavor	April, 1985	WHOI
GEOSECS	Knorr	July, 1972-April, 1973	SIO
TTO-NAS	Knorr	April-October, 1981	SIO
TTO-TAS	Knorr	December-February, 1983	SIO
KN104	Knorr	July-August, 1983	WHOI
OC133-II	Oceanus	January, 1983	WHOI
OC202	Oceanus	July-September, 1988	SIO

**Table 1**Historical data (1972-92) used in this work

Table 2Estimates of precision (1 SD) of the AT109-II and HE06 chemical data.<br/>Numbers in parenthesis indicates the number of data points in the<br/>calculation described in the text above (Garcia, 1996).

Cruise	Phosphate	N+N	Silicate	Oxygen
Western Atlantic (75-45 W)				
AT109-II	0.04 (81)	0.5 (83)	1.8 (83)	2.2 (86)
HE06	0.08 (58)	0.3 (79)	1.9 (82)	1.4 (83)
Eastern Atlar	ntic (20-44 W)			
AT109-II	0.03 (65)	0.2 (64)	0.6 (64)	1.9 (74)
HE06	0.08 (62)	0.2 (88)	0.9 (94)	1.6 (99)

#### 2.5. CFC-11 and CFC-12 (W. Smethie)

The objective of the CFC measurement program on this cruise was to measure the distribution of CFC-11 and CFC-12 in the thermocline along 24°N in the Atlantic and in recently ventilated components of North Atlantic Deep Water, including the Deep Western Boundary Current, spreading southward in the western North Atlantic.

The CFC measurements were made on board with a CFC analysis system interfaced to a gas chromatograph with an electron capture detector. This method is described in Smethie et al. (1988) and is similar to the Bullister and Weiss (1988) technique.

One difference for this cruise was the use of a Porasil B precolumn and a SP21000 main column instead of Porasil B for both columns. This combination allowed CFC-113 and carbon tetrachloride to be detected as well as CFC-11 and CFC-12. However carbon tetrachloride and CFC-113 were not measured on every station because of the longer analysis time required. The purpose of these measurements was to obtain preliminary information on the distribution of these substances in the ocean and they are not of the same quality as the CFC-11 and CFC-12 measurements.

Some problems were encountered. A set of new syringes had a low level CFC-11 contamination (0.02 – 0.04 pmol/kg). Blanks for these syringes were determined and monitored by analyzing zero CFC water from the deep eastern basin or by comparison to duplicate samples collected in old syringes which were not contaminated. These blanks decreased during the cruise. There was a high (20-30% of surface water concentration) and variable CFC-113 system blank and the Niskin bottles became severely contaminated with CFC-113 at station 75, probably due to a fire control exercise by ship's personnel, and remained contaminated for the remainder of the cruise.

The general sampling strategy was to sample every other station which resulted in approximately 60 nm spacing. Every station was sampled near the western boundary. Generally 10 or 11 samples were taken between the surface and 1000 m along the entire section. In the eastern basin the deep water contained no CFCs, but samples were collected to determine Niskin bottle/sampling blanks and syringe blanks. In the western basin, CFCs were detected throughout the water column. Vertical spacing varied between 150 and 400 m with more closely spaced samples at about 1500 m and 3500-4000m to resolve CFC maxima at these levels. A section was also taken across Florida Strait with approximately 5 nm horizontal resolution and 50-100 m vertical resolution. A total of about 1100 water samples, not including duplicates, were analyzed.

In the figure 4, shown are vertical profiles of preliminary shipboard values of F-11.

# 2.6. pH, Alkalinity, CO<sub>2</sub>

These measurements were carried on board by two independent groups.

2.6.1. CO<sub>2</sub> (F. Millero)

The total alkalinity, TA, total carbonate, TCO<sub>2</sub> and pH were determined from titrations of seawater collected at 31 stations. The titrators were calibrated with Dickson standard before and during the cruise. The results agree to  $\pm$ 7 µmol Kg-1. The pH was determined from the initial emf reading relative to TRIS buffers. The results for Dickson samples agree with laboratory spectroscopic measurements to  $\pm$ 0.005m ptl.

The values of the partial pressure of carbon dioxide,  $pCO_2$ , were calculated from the TA and  $TCO_2$  are higher than the atmospheric values.

In figure 5 some preliminary results are shown.

# 2.6.2. pH and CO<sub>2</sub>

(A.F. Ríos)

Direct pH measurements were made on the NBS scale for all stations (1 to 112 inclusive and at all levels, about 2400 samples total). The samples, kept in a 50 ml plastic bottles and perfectly closed, were introduced into a combined glass electrode associated to a thermocompensater. Measurements were referred to  $15^{\circ}$ C according to the variation of pH with temperature (Pérez and Fraga, 1987a). The accuracy of measurement is 0.1% of the total inorganic carbon (Zirino, 1985), i.e. ±0.004 units, but in samples taken in very homogenous water columns it is possible to detect differences less than this value.

Alkalinity measurements were made by titration of about 250 ml of a seawater sample with HCl O, <sup>13</sup>N, with potentiometric detection of the endpoint (Pérez and Fraga, 1987b). Stations 1 to 101 were sampled at all levels (about 2300 samples). Reproducibility was tested by sampling a 25 l storage bottle and was found to be less than 0.1%.

Total inorganic carbon and carbon dioxide pressure was determined indirectly from the pH and alkalinity according to methods described by Pérez and Fraga (1987b).

Some preliminary results are shown in figure 6.

# 2.7. Particulate Organic Matter

(A.F. Ríos)

Two liters of seawater at levels (10, 15, 50, 100, 200 and 400 m) on 25 stations were filtered through a glass fiber filter (Whatman GF/F of 25 mm diameter) in order to determine the particulate carbon and nitrogen using a 2400 Perkin Elmer Elemental Analyzer.

To determine particulate phosphorous, samples of one liter of seawater retained I filters (Millipore AAWPO2500) were taken at the same stations and levels as before. These samples will be oxydized with percloric-sulphuric acid (Ríos and Fraga, 1987) and later determination of phosphate will be carried out by the method described by Grasshoff et al. (1983).

Carbohydrates will be determined by the technique of Antron reagent (Rios, 1992) from samples of one liter of seawater retained in filters (Millipore AAWP02500) taken at these same stations and levels.

# 2.8. Calcium

(G. Rosón)

The 450 samples analysed for this parameter were taken on 20 stations at all levels.

The method used for determining calcium is a volumetric titration of about 130 g of seawater with potentiometric detection of end point by calcium selective electrode, using EGTA (ethyleneglycol-bis) (B-aminoethyleter), N, N, N1, N1, tetraacetic acid) as titrant (0.18 M) and 25 ml of borax (0.1 M) as buffer (Rosón and Pérez, 1990; Rosón, 1992). The reproducibility of the method, made on a 25 l storage bottle, was 0.07% for 70 samples.

#### 2.9. Carbon-14

(W. Smethie for W. Broecker)

Carbon-14 samples were collected in the thermocline at a few select stations. These samples will be analyzed by accelerator mass spectrometry. This is part of a larger program to collect samples over the entire North Atlantic from ships of opportunity during the next few years. The objective is to determine the distribution of bomb carbon-14 in the thermocline and compare this distribution to the distributions measured in 1981 on the TTO program and 1972 on the GEOSECS program. The evolving bomb carbon-14 distribution will be used to investigate circulation and mixing in the thermocline and uptake of carbon dioxide by the ocean.

Samples were collected at stations 13, 24, 35, 53, 66, 81, and 92. In general 8 samples were collected at each station, one in the surface mixed layer and seven at the following sigma-theta surfaces: 26.2, 26.4, 26.6, 26.8, 27.0, 27.2, and 27.4. Samples were also collected at stations 103 (one in the oxygen maximum) and 107 (six throughout the water column) in the Straits of Florida and at test station (ten samples) just west of the Strait of Gibraltar. A total of 71 samples were collected.

#### 2.10. ADCP

(M. Garcia)

The ADCP model used was a RD-VMO 150. The selected sampling intervals were 180 s, 40 depth bins of 8 m length. The profiler was recording continuously during the whole cruise and the data was recorded on diskettes.

#### 2.11. Thermosalinograph

(E. Alvárez)

During W.O.C.E. A-5 section, temperature and salinity were measured across the Atlantic Ocean surface using a Seabird thermosalinometer (serial number 626a). Data acquisition

began on station number one and finished close to Miami harbor. The time step between each acquisition was three minutes. The obtained data were stored in groups of files, each group corresponding to one navigation day. Water conductivity was recorded from the third navigation day on. Two electricity failures (during the second and fourth days) and at least one water flux stoppage (during the fourth day) interrupted the continuous time series.

# 2.12. Chlorophyll Pigments and Primary Production

Two kinds of analysis have been undertaken for pigment studies. One was based on spectrophotometric equations with readings of absorbances at 664, 645, 630 and 750 nm. In the other smaller volumes of seawater were used for analysis of chlorophyll and phaeopigments based on fluorescence readings before and after acidification of the sample.

# 2.12.1.Chlorophyll Pigments

(Z.R. Velásquez)

Water samples were taken at several depths (0-250m) on all stations of the WOCE A-5 section from NW Africa to the Bahamas.

The phytoplanktonic pigments were determined on board immediately after sampling by the spectrophotometric technique described by Jeffrey and Humphrey (1975). About 3.3 liters of seawater were filtered under vacuum through 4.7 cm Whatman GF/F filters. After extraction during a minimum of 24 hours with 5 ml (90%) acetone in the dark at 0°C, the resulting suspension was centrifuged at 3000 rpm for 30 minutes.

The absorbances at 664, 645 and 630 nm, required for the computation of the concentrations of Chlorophyll A, B and C, were determined in the supernatant (5 ml), allowance being made for the eventual presence of turbidity by measuring also the absorbance at 750 nm. All absorbance measurements were done with a LBK spectrophotometer linked to a computer.

The following formula was used for the computation of the pigment concentration in the supernatant in  $\mu$ g/l.

(Chlorophyll (µg/l) =OD\* Vac / Vsw

OD (a) = 11.85*(D664-D750)-1.54*	(D645-D750)-0.08*(D630-D750)
OD (b) = 21.03*(D645-D750)-5.43*	(D664-D750)-2.26*(D630-D750)
OD (c) = 24.52*(D645-D750)-1.67*	(D664-D750)-7.66*(D645-D750)

where Vac = volume of acetone (in ml); Vsw = volume of seawater (in l); Dxxx = optical density at wavelength xxx and 1 cm optical path

Pheopigments were determined by acidifying the extracts with two drops of 10% HCl and reading at the same wavelengths.

Samples of water at the same level were preserved with Lugol (Potassium lodate/lodine solution buffered with sodium acetate) for further phytoplankton analysis with an Olympus inverted microscope to which a computer/video digitizing system has been adapted.

In the figure 7 vertical profiles of total chlorophyll for stations 1 through 60 are shown.

# 2.12.2.Chlorophyll Pigments and Primary Production

(J. García-Braun)

Water samples were taken for pigment analysis at several depths (mainly, 0 - 200 m) on 90 stations for a total of 1152 analyses for chlorophyll and phaeophytin.

With respect to the pigment distribution in the water column, ours main objectives were: to obtain the vertical distribution of chlorophyll a, based on fluorescence readings, calibrated against spectrophotometer following SCOR-UNESCO (1966) and the vertical distribution of chlorophyll and phaeophytin, based on fluorescence readings, before and after acidification, according to equations by Lorenzen (1966); and to estimate the pigments biomass including size classes, evaluating picoplankton less than 2 microns and populations bigger than 2 microns.

Two samples of 1 liter sea water for each depth were filtered through Whatman GF/F filters. Pigments were extracted in 10 ml of 90% acetone during about 12 hours in the dark at 0°C. The fluorescence measurements (before and after acidification with two drops of 10% CIH) were used to calculate the pigments according with the following equations:

Chlorophyll a =  $11.64 e_{663} - 2.16 e_{645} + 10 e_{630}$ 

where  $e_{663}$ ,  $e_{645}$  and  $e_{630}$  are the absorbances at 663, 645 and 630 nm after substration of the absorbance at 750 nm, using 1 cm spectrophotometer cell. If the obtained value is multiplied by the extract volume in ml and divided by the volume of seawater filtered in liters, the amount of chlorophyll a in mg/m3 is obtained.

The equation proposed by SCOR-UNESCO (1966) was used to calibrate the Fluorometer Turner Design in which all the readings of Fluorescence were made during the cruise. Concentrations of chlorophyll a and phaeophytin a were also calculated following the equations given by Lorenzen (1966).

Vertical profiles of chlorophyll and phaeophytin for several stations are shown in figure 8.

# 2.12.2.1. Primary Production

(J. García-Braun)

Water samples for primary production experiments were taken at several depths in the photic zone, representing approximately 100%, 25%, 10% and 1% of surface light. The standard C14 method proposed by Steeman Nielsen (1952) was used with some

modifications. The incubations were done in incubators under artificial light during 2-3 hours. The selected stations (11 stations and 99 samples) were chosen in order to make the incubations in early hours during the morning.

For each depth, samples of 100 cc of seawater were inoculated with 4  $\mu$  Ci of C14 bicarbonate. After incubation one sample was passed through Nucleopore filter (2 micron pore size) and the other sample through Whatman GF/F filters. A separate sample was incubated in the dark in order to substract the incorporated radioactivity with respect to the light bottles. The filters were preserved in the deep freeze for future readings of counts per minute in a Liquid Scintillation Counter.

#### 2.13. Aluminum

(M.D. Gelado and J.J. Hernández)

A voltametric method was used for aluminum determination during WOCE-AS Cruise.

The procedure is based on complexation of aluminum with 1,2-dihydroxyanthraquinone-3suplhonic acid (DASA) and measurement of reduction current of this complex using high speed cathodic stripping voltametry (HSCSV). Reduced AI-DASA complex produces an intensity of faradaic current proportional to dissolved AI concentration. The free DASA ligand has a cathodic peak at - 0.63 V while AI-DASA peak is more negative at -1.1 V (Ag/CIAg).

Optimal experimental parameters include an accumulation potential of -0.95 V during 45 s, DASA concentration 2x10<sup>-6</sup> M and staircase scan mode to 30 V/s speed. Samples are buffered at 7.1 pH using N, N1bis(2-hydroxyethyl)-2-aminoethane suphonic acid(BES). The method (Gelado-Caballero, 1992) is specially adapted for on board determinations.

The electrochemical system has been designed to measure the instantaneous currents at short times with a low noise level (Hernandez-Brito et al., 1990). Thus, the analytical time required for each sample is substantially reduced, allowing an increase of the number of measurements in situ. A PAR303A electrochemical cell with hanging mercury drop electrode (HMDE) was connected to a specially made computer-controlled potentiostat.

The detection limit was 1.75 nM for 30 s adsorption time. The deviation was less than 3% for a 19 nM AI concentration based on repetitions for 7 seawater samples.

In total 1000 samples were taken in 52 stations. In most of the stations, except in those close to the African coast, maximum was detected at the surface layers. Below a minimum at intermediate depths the dissolved AI concentrations increased with depth.

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# 3 References

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# DQE of CTD data for the 6<sup>th</sup> cruise of the r/v "Hesperides", WOCE section A5 across the North Mid-latitude Atlantic.

Eugene Morozov

Data quality of 2-db CTD temperature, salinity and oxygen profiles and reference rosette samples were examined. Vertical distributions and theta-salinity curves were compared for individual stations using the data of up and down CTD casts and rosette probes. Data of several neighboring stations were compared.

Questionable data in \*.hy2 file were marked in QUALT2 word.

The calibration of upcast CTDSAL and CTDOXY data seem to be worse than downcast data.

There were two data sets for WCT files. One for the eastern part of the section the (station numbers 49 and less) and the western part (stations 50-112). The data sets came different sources so I analyzed them separately.

Listing of results from the comparison of salinity and oxygen data. Only those stations are listed which have data remarks.

Station	Pressure	Remarks	
9	585 db	OXYGEN is low (2.61) compared with upcast CTDOXY	
		(3.94) and downcast CTDOXY (3.06). Downcast CTDOXY	
		seems reasonable. I flag both OXYGEN and upcast	
		CTDOXY 4 -Bad. Upcast CTDTEMP is wrong (3.943)	
11	3045 db	OXYGEN (5.59) is high compared with upcast CTDOXY	
		(5.45) and downcast CTDOXY (5.44), flag 4.	
	3372 db	SALNTY is 0.02 PSU higher that CTD upcast and	
		downcast, the flag is 4 - SALNTY - Bad	
12	•	sequence of samples is given in .hy2 file. It is not in	
		with pressure. It causes difficulties to work with such a file.	
	Some of samples correspond to negative pressure, they sh		
	removed from the file. Enormous differences (over 2.3 PSU) are found between SALNTY a CTDSAL at several levels.		
		em are flagged 4 - Bad, some not.	
	I flag bad S		
		367 db	
		401 db.	
	454 db SALNTY (35.750) and upcast CTDSAL (35.846) both are Ba They do not match with downcast CTDSAL (35.720).		
	Similar prob	plems with oxygen at the same levels:	

#### Eastern part

Station	Pressure	Remarks
12	I flag OXYC	GEN 4 - Bad at levels: 343 db
		367 db
		401 db
		454 db
	I flag upcas	t CTDOXY 4 - Bad at levels: 78 db
		343 db
		367 db
		401 db
13	2025 db	SALNTY (35.050) is high compared with 35.039 upcast
		and 35.041 downcast CTDSAL, flag 4.
	2533 db	SALNTY (34.989) is high compared with 34.982 upcast
		and 34.979 downcast CTDSAL, flag 4.
	3053 db	SALNTY (34.946) is high compared with 34.940 upcast
		and 34.941 downcast CTDSAL, flag 3.
	4078 db	SALNTY (34.894) is low compared with 34.896 upcast and
4.4		34.896 downcast CTDSAL, flag 3, these are very deep waters.
14		are lower than upcast CTDSAL by at least 0.01 for the
		on, better for downcast CTDSAL.
	0	3 for the whole station SALNTYes
	403 db	SALNTY (35.789) is high compared with 35.742 upcast and
	4070 db	35.734 downcast CTDSAL, flag 4.
	4070 00	SALNTY (34.884) is low compared with 34.898 upcast and 34.899 downcast CTDSAL, flag 4.
	4377 db	SALNTY (34.881) is low compared with 34.894 upcast and
	4377 05	34.894 downcast CTDSAL, flag 4.
15	65 db	There is a strange 20 m thick layer of low salinity water. It
10		is temperature compensated and even the oxygen is
		slightly less. It seems true because it is supported by
		bottle measurements although there are differences
		between CTDSAL and SALNTY. They can be explained
		by high salinity gradient. There is no such a layer on
		neighboring stations.
		ake out where this freshened water could appear from in the
		e Canary Basin.
	1515 db	There are differences between SALNTY (35.170) and
		downcast CTDSAL (35.157). Upcast CTDSAL matches well
		with SALNTY (35.172). I don't flag anything questionable
		and attribute these differences to tidal internal waves which
		are extremely large here.
	4646 db	SALNTY (34.901) is high compared with upcast 34.892
16	760 46	and downcast CTDSAL 34.892 flag 4.
16	762 db	SALNTY (35.223) is high compared with upcast CTDSAL
	4734 db	35.212 and downcast CTDSAL 35.198, flag 4.
	4734 00	SALNTY (34.905) is high compared with upcast CTDSAL 34.890 and downcast CTDSAL 34.890 , flag 4.
		34.030 and downlast of DOAL 34.030, 11ay 4.

Station	Pressure	Remarks
16	CTDOXY de	owncast calibration is wrong below 1500 db. The values are
	higher that	OXYGEN and measurements on neighboring stations.
	4734 db	OXYGEN (5.59) is low compared with upcast CTDOXY
		5.79 and downcast CTDOXY 5.78, flag 4.
18	1316 db	SALNTY (35.158) is very low compared with upcast
		CTDSAL 35.220 and downcast CTDSAL 35.216, flag 4.
19	3553 db	OXYGEN (5.68) is high compared with upcast CTDOXY
		5.61 and downcast CTDOXY 5.60, flag 3.
	4066 db	SALNTY (34.896) is low compared with upcast CTDSAL
		34.899 and downcast CTDSAL 34.900, flag 4.
21	204 db	SALNTY (36.663) does not match with upcast CTDSAL
		(36.645)
		both 3 - Qble. There is a large salinity gradient at this
		ut nevertheless the discrepancy is very large and they both
		lowncast CTDSAL (36.507).
22	4069 db	SALNTY (34.891) is low compared with upcast CTDSAL
		34.901 and downcast CTDSAL 34.902, flag 4.
24		a wonderful Meddy around 1200 db and CTDSAL is
		by originators. It is absolutely true.
	1517 db	SALNTY (35.120) is high compared with upcast CTDSAL
		35.118 and downcast CTDSAL 35.117, I don't flag these
		differences as questionable they must be accounted for
	5663 db	internal waves. OXYGEN (5.61) is low compared with upcast CTDOXY
	5005 UD	(5.68) and downcast CTDOXY (5.68), flag 4.
25	3107 db	OXYGEN (5.70) is high compared with upcast CTDOXY
25	5107 05	(5.65) and downcast CTDOXY (5.65), flag 3.
27	5472 db	SALNTY (34.890) is high compared with upcast CTDSAL
21	0472 00	(34.887) and downcast CTDSAL (34.888), I flag SALNTY 3.
28	2526 db	SALNTY (35.056) is high compared with upcast CTDSAL
	2020 00	(34.985) and downcast CTDSAL (34.991). Originators flag
		upcast CTDSAL Qble, I flag SALNTY 4.
	4067 db	SALNTY (34.908) is high compared with upcast CTDSAL
		(34.900) and downcast CTDSAL (34.902), I flag SALNTY 4.
	4581 db	SALNTY (34.894) is high compared with upcast CTDSAL
		(34.891) and downcast CTDSAL (34.892), I flag SALNTY 3.
	5092 db	SALNTY (34.890) is high compared with upcast CTDSAL
		(34.886) and downcast CTDSAL (34.888), I flag SALNTY 3.
28	5718 db	SALNTY (34.888) is high compared with upcast CTDSAL
		(34.886) and downcast CTDSAL (34.886), I flag SALNTY 3.
29	1213 db	OXYGEN (4.36) is high compared with upcast CTDOXY
	ļ	(4.15) and downcast CTDOXY (4.12), flag 4.
	2430 db	OXYGEN (5.48) is low compared with upcast CTDOXY
		(5.58) and downcast CTDOXY (5.58), flag 4.
Station	Pressure	Remarks

30	5613 db	SALNTY (34.887) is high compared with upcast CTDSAL
		(34.884) and downcast CTDSAL (34.885), I flag SALNTY 3.
	5924 db	SALNTY (34.886) is high compared with upcast CTDSAL
		(34.884) and downcast CTDSAL (34.884), I flag SALNTY 3.
31	1517 db	SALNTY (35.165) is high compared with upcast CTDSAL
		(35.163) and downcast CTDSAL (35.154), I do not flag
		these data questionable as I think that the differences are
		caused by internal waves.
Station	s 30, 31, 32.	Calibration of downcast CTDOXY is wrong in the interval
2000-5	500. CTDOX	Y is lower than bottle measurements
33	809 db	OXYGEN (3.65) is high compared with upcast
		CTDOXY(3.42) and downcast CTDOXY (3.35), flag - 4.
34	3556 db	OXYGEN (5.73) is high compared with upcast CTDOXY
		(5.62) and downcast CTDOXY (5.61), flag 4.
	4066 db	OXYGEN (5.72) is high compared with upcast CTDOXY
		(5.66) and downcast CTDOXY (5.65), flag 4.
	4572 db	SALNTY (34.898) is high compared with upcast CTDSAL
		(34.891) and downcast CTDSAL (34.892), I flag SALNTY 4.
	5091 db	SALNTY (34.879) is low compared with upcast CTDSAL
		(34.884) and downcast CTDSAL (34.885), I flag SALNTY 4.
35	3555 db	SALNTY (34.912) is low compared with upcast CTDSAL
		(34.914) and downcast CTDSAL (34.916), I flag SALNTY 3.
	4068 db	SALNTY (34.895) is low compared with upcast CTDSAL
		(34.899) and downcast CTDSAL (34.899), I flag SALNTY 4.
	4581 db	SALNTY (34.888) is low compared with upcast CTDSAL
		(34.892) and downcast CTDSAL (34.893), I flag SALNTY 4.
Station	s 35, 36. Ca	libration of downcast CTDOXY is wrong in the interval 2500-
4500.	CTDOXY is	lower than bottle measurements and measurements on
neighbo	oring stations	
37	4068 db	SALNTY (34.902) is low compared with upcast CTDSAL
		(34.903) and downcast CTDSAL (34.905), I flag SALNTY 3.
38	3001 db	SALNTY (34.973) is high compared with upcast CTDSAL
38	3001 db	
		SALNTY (34.973) is high compared with upcast CTDSAL
Station 1500 d	  s 37, 38.  Ca  b.  CTDOXY	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on
Station 1500 d neighbo	s 37, 38. Ca b. CTDOXY oring stations	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on .
Station 1500 d neighbo Station	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on ion of downcast CTDOXY is wrong in the interval 1800-2800.
Station 1500 d neighbo Station CTDO	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat XY is higher t	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on .
Station 1500 d neighbo Station	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat XY is higher t s.	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on ion of downcast CTDOXY is wrong in the interval 1800-2800. han bottle measurements and measurements on neighboring
Station 1500 d neighbo Station CTDO	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat XY is higher t	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on ion of downcast CTDOXY is wrong in the interval 1800-2800. han bottle measurements and measurements on neighboring SALNTY (34.887) is low compared with upcast CTDSAL
Station 1500 d neighbo Station CTDO stations	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat XY is higher t s.	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on ion of downcast CTDOXY is wrong in the interval 1800-2800. han bottle measurements and measurements on neighboring SALNTY (34.887) is low compared with upcast CTDSAL (34.889) and downcast CTDSAL (34.890), I flag SALNTY 3.
Station 1500 d neighbo Station CTDO stations	s 37, 38. Ca lb. CTDOXY oring stations 40. Calibrat XY is higher t s.	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4. libration of downcast CTDOXY is wrong in the interval below is higher than bottle measurements and measurements on ion of downcast CTDOXY is wrong in the interval 1800-2800. han bottle measurements and measurements on neighboring SALNTY (34.887) is low compared with upcast CTDSAL

# Western part

Salinity and oxygen are examined separately because there were many problems with CTDOXY calibration.

# Salinity

Station	Pressure	Remarks
58	2535 db	SALNTY (34.980) is high compared with upcast CTDSAL
		(34.960) and downcast CTDSAL (34.962), I flag SALNTY 4.
64	Some bad	CTDSAL measurements are flagged 3 -Qble. They are
	really bad.	
67	5012 db	SALNTY (34.846) is low compared with upcast CTDSAL
		(34.855) and downcast CTDSAL (34.855), I flag SALNTY 4.
75	4579 db	SALNTY (34.886) is low compared with upcast CTDSAL
		(34.889) and downcast CTDSAL (34.890), I flag SALNTY 3.
	5609 db	SALNTY (34.842) is low compared with upcast CTDSAL
		(34.844) and downcast CTDSAL (34.845), I flag SALNTY 3.
83	1703 db	SALNTY (35.000) is low compared with upcast CTDSAL
		(35.030) and downcast CTDSAL (35.030), I flag SALNTY 4.
89	There is great difference between SALNTY and upcast and downcast	
	CTDSAL in	the upper 80 db layer. Bottle samples taken at 11; 28; 53;
	77 dbars	

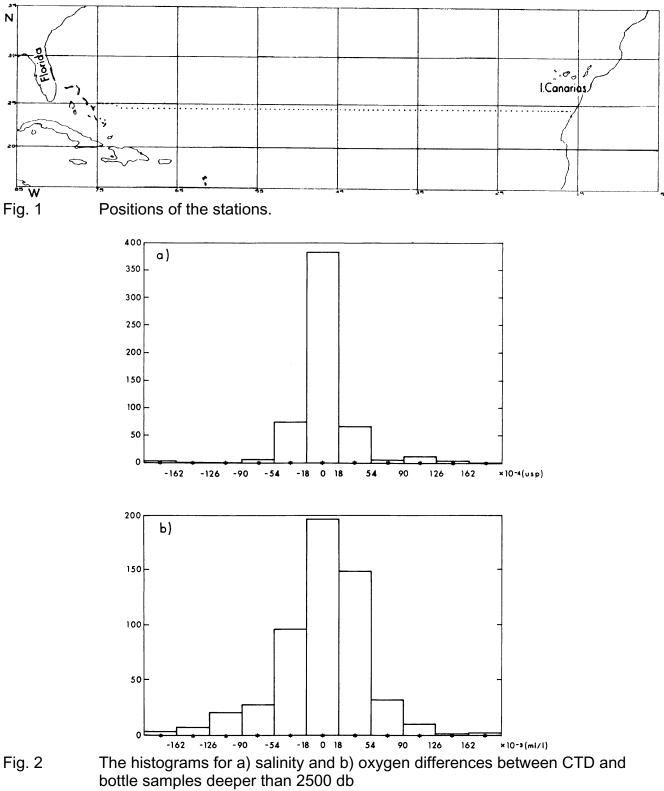
### Oxygen

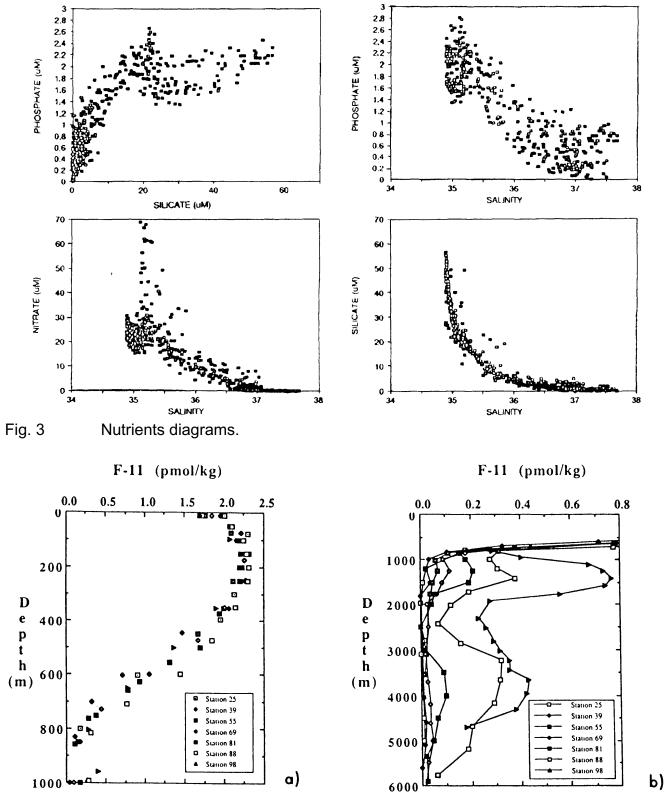
There are problems with calibration of CTD oxygen sensor for many of the stations. Some CTD casts contain data that are definitely bad and they are not flagged bad at all.

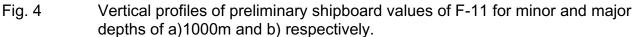
Station	Pressure	Remarks
52	2002 db	OXYGEN (5.65) is high compared with upcast CTDOXY
		(5.60) and downcast CTDOXY (5.57), flag - 4.
53	1518 db	OXYGEN (5.27) is high compared with upcast CTDOXY
		(5.14)and downcast CTDOXY (5.14), flag - 4.
55	3973 db	OXYGEN (5.84) is low compared with upcast CTDOXY
		(5.87) and downcast CTDOXY (5.88), flag - 4.
58	5157 db	OXYGEN (5.75) is low compared with upcast CTDOXY
		(5.80) and downcast CTDOXY (5.82), flag - 4.
63	4306 db	OXYGEN (5.85) is high compared with upcast CTDOXY
		(5.79) and downcast CTDOXY (5.80), flag - 4.
68	3564 db	OXYGEN (5.96) is high compared with upcast CTDOXY
		(5.87) and downcast CTDOXY (5.87), flag - 4.
	CTDOXY c	alibration is wrong below 2500 db. CTD measurements are
	less than bo	ottle.
69		alibration is wrong below 5000 db. CTD measurements are
	less than bo	ottle OXYGEN approximately by 0.02ml/l.

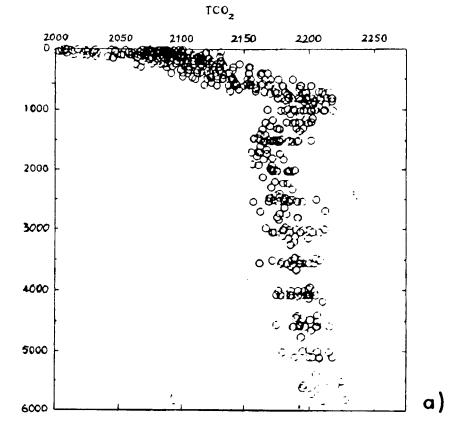
Station	Pressure	Remarks	
70	2505 db	OXYGEN (5.72) is low compared with upcast CTDOXY	
		(5.80) and downcast CTDOXY (5.80), flag - 4.	
Almost	Almost all CTDOXY measurements to the west of station 70 are noisy. Many of		
	them have wrong CTDOXY calibration mostly in deep waters.		
73	CTDOXY calibration is wrong below 1500 db. CTD measurements a		
	less than bottle OXYGEN approximately by 0.02ml/l.		
74	CTDOXY calibration is wrong below 5000 db. CTD measurements a		
	greater thar	n bottle OXYGEN approximately by 0.02ml/l.	
84	CTDOXY ca	alibration is wrong below 1500 db. CTD measurements are	
	less than bo	ottle OXYGEN approximately by 0.02ml/l.	
85		alibration is wrong in the interval 2500-4000 db. CTD	
		ents are lower than bottle OXYGEN approximately by	
	0.02ml/l.		
86		alibration is wrong below 1500 db. CTD measurements are	
		pottle OXYGEN approximately by 0.02ml/l.	
87		alibration is wrong below 1500 db. CTD measurements are	
		pottle OXYGEN approximately by 0.02ml/l.	
88		alibration is wrong below 1500 db. CTD measurements are	
	lower than bottle OXYGEN approximately by 0.02ml/l.		
89	4003 db	OXYGEN (6.06) is high compared with upcast CTDOXY	
	-	(6.17) and downcast CTDOXY (6.15), flag - 4.	
		tion is better but problems below 5000 db. CTDOXY is	
	higher than		
95	5408 db	OXYGEN (6.03) is high compared with upcast CTDOXY	
		(5.97) and downcast CTDOXY (5.94), flag - 4.	
97	1904 db	OXYGEN (5.80) is low compared with upcast CTDOXY	
		(6.01) and downcast CTDOXY (5.99), flag - 4.	
99 CTDOXY calibration is wrong below 2500 db. CTD me			
	lower than bottle OXYGEN approximately by 0.02ml/l.		
107		ple 15 OXYGEN is bad, flag - 4.	
		ple 14 OXYGEN is bad, flag - 4.	
109-111		s are not deep. CTDOXY calibration is bad in the entire	
	depth.		

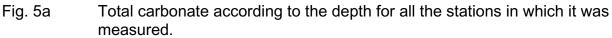
#### **FIGURES**











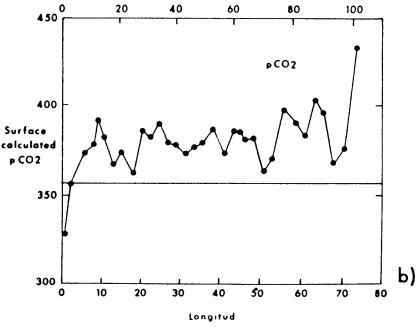
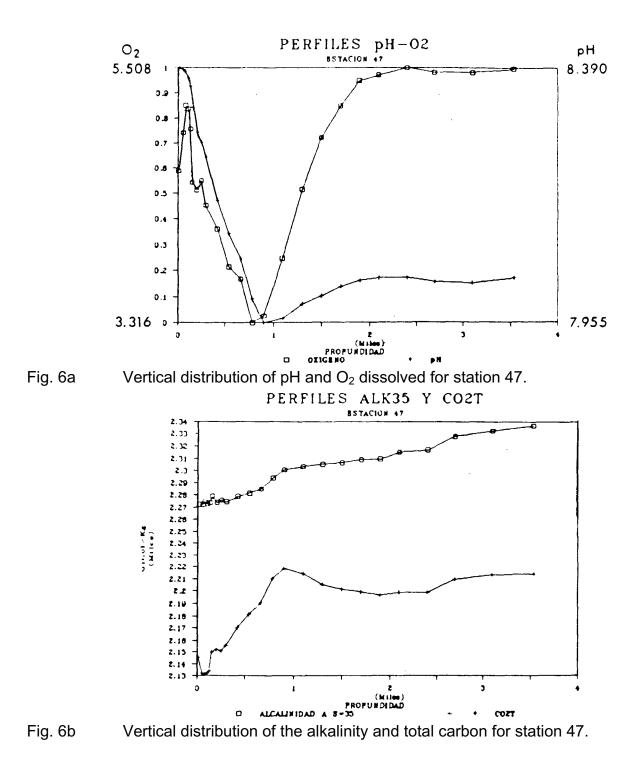
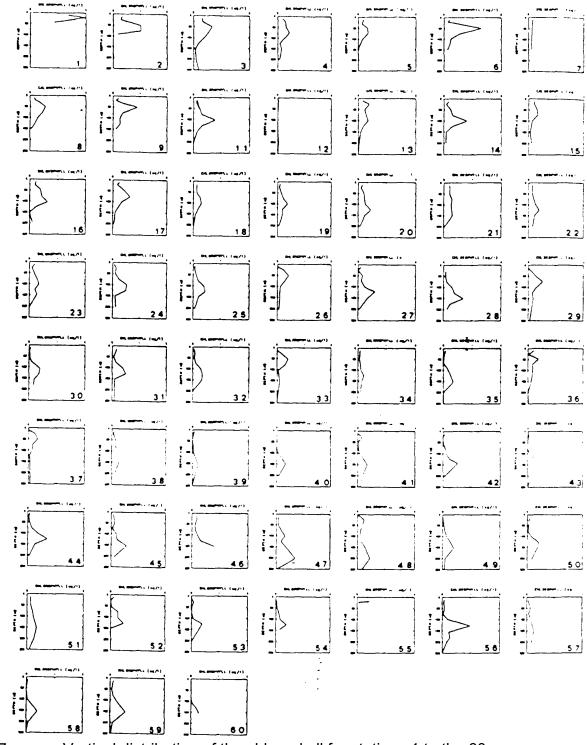


Fig. 5b

Calculated pressure of CO<sub>2</sub> throughout the passage of the cruise.







Vertical distribution of the chlorophyll for stations 1 to the 60.

