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CHEMICAL AND HYDROGRAPHIC PROFILES AND UNDERWAY MEASUREMENTS FROM THE EASTERN NORTH ATLANTIC DURING JULY AND AUGUST OF 1993

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NOTICE

LOCATION OF DATA FILES

Data files can be downloaded from AOML's web site (http://www.aoml.noaa.gov/ocd/oaces/data) or by anonymous ftp (ftp.aoml.noaa.gov) from the directory pub/ocd/carbon/pc/natl93. For help in downloading, contact either:

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KEY TO AFFILIATION ABBREVIATIONS

AOML	Atlantic Oceanographic and Meteorological Laboratory
CIMAS	Cooperative Institute for Marine and Atmospheric Studies
MBARI	Monterey Bay Aquarium Research Institute
NCAR	National Center for Atmospheric Research
PMEL	Pacific Marine Environmental Laboratory
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SIO	Scripps Institution of Oceanography
U. W.	University of Washington

KEY TO DATA TYPE ABBREVIATIONS

^{13}C	$^{13}C/^{12}C$ stable isotopic ratio of TCO_2
CFCs	Chlorofluorocarbons
fCO_2	Fugacity of Carbon Dioxide
O_2	Dissolved Oxygen
TAlk	Total Alkalinity
TCO_2	Total Carbon Dioxide

ABSTRACT

From July 4 to August 30, 1993, the National Oceanic and Atmospheric Administration's (NOAA) Ocean-Atmosphere Carbon Exchange Study (OACES) and Radiatively Important Trace Species (RITS) programs participated in an oceanographic research cruise aboard the NOAA ship MALCOLM BALDRIGE. The objectives of the OACES component were to determine the source and sink regions of CO_2 in the Equatorial and North Atlantic during the summer and to establish a baseline of total carbon inventory in the region. Data were collected from 5° S to Iceland along a nominal longitude of 20° W. This report presents only the OACES-related data from legs 1, 2A, and 2B, including hydrography, nutrients, carbon species, dissolved oxygen, total inorganic carbon, chlorofluorocarbons, total alkalinity, pH, and salinity. Included are contour plots of the various parameters and descriptions of the sampling techniques and analytical methods used in data collection.

KEY WORDS: alkalinity, carbon dioxide, CFC, chlorofluorocarbons, CO_2, CTD, dissolved inorganic carbon, fugacity, hydrography, North Atlantic, nutrients, oxygen, pH, salinity, sigma-theta, temperature.

1. INTRODUCTION

Human industrial and agricultural activity produces various gases such
carbon dioxide (CO_2), chlorofluorocarbons, nitrous oxide, and methane which enter t
atmosphere and absorb heat radiated by the earth's surface. This results in a n
warming of the atmosphere and creates the phenomenon commonly called t
"greenhouse effect." Only about half the anthropogenic carbon remains, howev
Many believe that the global ocean provides the primary sink for the "missing" C
The potential climatic impact of the increasing concentration of these gases requir
a thorough understanding of the absorption and storage properties of the oceans.

The National Oceanic and Atmospheric Administration's (NOAA) Ocea
Atmosphere Carbon Exchange Study (OACES) and Radiatively Important Tra
Species (RITS) programs participated in a multifaceted oceanographic research cru
conducted aboard the NOAA ship MALCOLM BALDRIGE from July 4 to August
1993. The objectives of the OACES component of the cruise were to determine t
source and sink regions of CO_2 in the Equatorial and North Atlantic during t
summer and to establish a baseline of total carbon inventory in the region in order
measure the uptake rate of atmospheric CO_2 in future cruises. The objective of t
RITS cruise was to evaluate the distribution and transport of tropospheric ozone a
ozone precursors in the North Atlantic and was performed in association with t
North Atlantic Regional Experiment (NARE), a component of the International Glo
Atmospheric Chemistry (IGAC) Project. This report presents only the OACES-rela
data from the cruise, including hydrography, nutrients, carbon species, dissol
oxygen (O_2), total inorganic carbon (TCO_2), chlorofluorocarbons (CFCs), total alkalin
(TAlk), pH, and salinity. Biological productivity data is covered in the report
Michisaki et al., (1995). The full chemical and hydrographic data set may
downloaded from the Atlantic Oceanographic and Meteorological Laboratory's (AOM
anonymous ftp site at ftp.aoml.noaa.gov (see Appendix B for further details).

Part 1 of this report contains a description of the study area and a map show
the cruise track. Part 2 describes the sampling techniques and analytical meth
used, and contains three subsections covering hydrographic methods, carb
parameters, and underway measurements. The first subsection includes CTD, salin
O_2, nutrients, and CFC analysis methods. Subsection two covers TAlk, pH, TCO_2, a
discrete fugacity of CO_2 (fCO_2). The last subsection describes underway fC
measurements. Acknowledgments and references are contained in Parts 3 an
respectively. Contour plots of each parameter and various other graphs appea
Appendix A. Appendix B gives the structure of the data file, the units used for e
parameter, and details on how to obtain the full data files.

1.1 DESCRIPTION OF THE STUDY AREA

This study comprised two consecutive research cruise legs during 1993, repeating a section carried out by R. V. OCEANUS cruise 202 during July and August of 1988. Leg 1 sailed from Fortaleza, Brazil on July 4, 1993 and, after a test station, proceeded to the first station at 5° S and 25° W. From there the ship steamed north along the 25° W line to approximately 6° N. The ship then turned NW and continued to 14° N and 29° W. At that point malfunctioning boilers and the previous shutdown of the reverse osmosis system made the production of fresh water impossible and forced a diversion to Cape Verde and subsequently to Madeira. The second leg was divided into two parts: Leg 2A and Leg 2B. Leg 2A included the stations missed in Leg 1 and departed Madeira on August 2. After occupying a station to test all over-the-side systems, the ship proceeded to 34° N and 21.2° W. There the ship turned W-SW and steamed to about 20° N and 29° W where it turned S, following the 29° W line to 16° N, occupying stations at 2° intervals. After moving S to a station at 15° N the ship reversed course and retraced its route, occupying stations at 2° intervals and returning to Madeira on August 16. Leg 2B left Madeira on August 17 and proceeded to an initial station at 35° N, 20.6° W. The ship then steamed northward along the 20° line to the final station at 63.2° N and arrived in Reykjavik, Iceland on August 30, 1993. The cruise tracks for Legs 1, 2A, and 2B are shown in Figure 1.

2. DATA COLLECTION AND ANALYTICAL METHODS

During July and August 1993, a total of 83 stations were occupied between Fortaleza, Brazil and Reykjavik, Iceland and 94 CTD casts were made. Thirty-nine CTD casts occurred during Leg 1, 22 during Leg 2A, and 33 during Leg 2B. The CTD instrumentation consisted of three Neil Brown Instruments™ Mark III systems, including pressure, temperature, and conductivity sensors, and a General Oceanics™ 24-bottle rosette. CTD data were recorded during the downcast and upcast, and discrete water samples were collected in 10-L Niskin™ bottles during the upcast. Samples were collected in the following order: CFCs, O_2, fCO_2, TCO_2, pH, TAlk, inorganic carbon-13 (^{13}C), nutrients, chlorophyll, phaeopigments, and salinity. CTD casts were taken to within 25 m of the bottom in most cases where instrument problems did not preclude this (see Figure 2 for bottle trip depths and positions). CTD data were acquired and processed at sea using the software package of Millard (1993). Salinities and sea surface temperatures were also measured continuously during the entire cruise by a thermosalinograph located at the bow intake at 5 m depth.

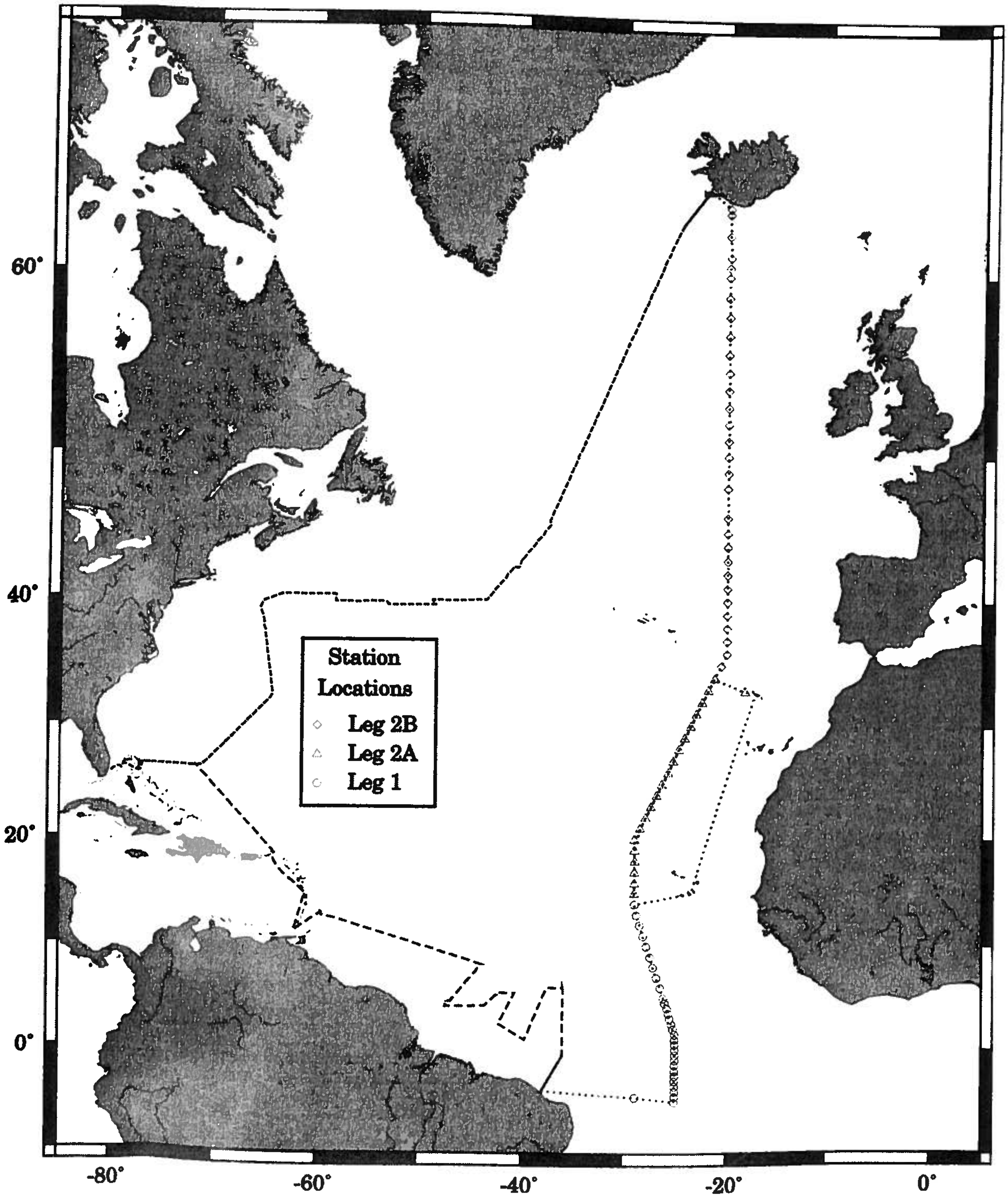

Figure 1: North Atlantic 1993 Cruise Track
Note: Only underway fCO_2 measurements were performed on Leg 0 and Leg1.

2.1 HYDROGRAPHIC METHODS

2.1.1 CTD and Hydrographic Operations

Several problems occurred with the three Neil Brown Instruments™ CTDs (serial numbers 1148, 2156, and 2769). These included a noisy conductivity sensor, sensor drift, unrealistically high temperature offsets on isolated casts, bottle mistrips, problems with the new software data acquisition package, and deck unit troubles. The latter required frequent swapping of deck units during the cruise. At the second Madeira inport (between Legs 2A and 2B), a "fourth" CTD was constructed from the three originals. Although it performed better, doubt was cast on the relevance of the pre-cruise pressure and temperature calibrations.

During post-cruise data reduction, these problems were dealt with on a cast by cast basis using various methods. For example, incorrect bottle depths were adjusted using a careful comparison of the bottle salinities (BOTS) and the CTD salinity profiles (CTDS), using knowledge of the history and trend of the BOTS-CTDS residuals. On several casts where the upcast bottle trip CTD values failed to be logged due to software problems, downcast values were matched to the nominal bottle trip depths and the BOTS-CTDS residuals were used to confirm the match. For the few stations exhibiting large temperature offsets, corrections were made based on interpolation over adjacent casts.

Despite the problems, a reasonably high quality CTD data set was obtained which will be useful for most scientific purposes. Studies which by their nature push the limit of CTD technology and accuracy (for example, fine structure studies or comparative studies of long term temporal changes in temperature and/or salinity based on detailed comparisons with the results of other cruises, etc.) will probably not be possible with this data set. Details can be found in Table 1.

Pre-cruise laboratory calibrations were performed on the pressure and temperature sensors. Typical laboratory accuracies are ±6.5 db for pressure and ±0.005 °C for temperature. The conductivity sensor was also calibrated in the laboratory, but due to the nature of the conductivity cell there is the possibility of at-sea calibration drift, so bottle salinities collected during each CTD upcast were used for the final calibration of the CTD salinities.

As explained above, it is not possible to quantitatively assess the accuracy of the temperature and pressure sensors as there was no post-cruise laboratory calibration available. However, comparisons with historical data and checks for internal consistency such as examination of the computed density profiles for each CTD cast did not raise any particular doubts about the pre-cruise calibration values. It is possible to quantitatively assess the accuracy of the conductivity sensor by comparison with the bottle salinities, which were accurate to within ±0.002. The average difference was 0.000 ±0.007 ($n = 1942$) after removing 9 outliers with difference greater than ±0.05.

Table 1: Range of salinity correction (results of polynomial):

CTD CASTS	ΔS (0 M)[1]	ΔS (DEEP)[2]	COMMENT
1-16	-0.001	0.006	
17	0.009	0.004	
18	-0.004	0.002	
19-22	0	0.007	
23	-0.083	-0.05	t=t-0.173[3]; computer restart
28	0.006	0.007	
29	0.001	0.013	
30	0.013	0.015	casts 28-32: changing deck units nearly every cast
31	0.005	0.008	
32	0.006	0.013	
33-34	0	0.003	
35	-0.343	-0.291	changed to CTD_1, 35 and 36
36	-0.3	-0.399	
37			(no cast 37; same location as 38) back to CTD_2 for cast 38
38-42	0.001	0.007	no cast 41; at-sea memory loss
43	0	0.009	
44-45	0.001	0.008	
46	0.021	0.024	switched to CTD_2..., 46-53
47	0.019	0.024	
48	-0.013	0.019	
49	-0.045	0.038	
50	-0.201	0.003	t=t-0.109[3]
51	-0.083	0.032	t=t-0.109[3]
52	-0.357	0.008	t=t-0.109[3]
53	-0.2	0.091	t=t-0.109[3]
54-57	0.002	0.007	switched to CTD_4 for duration
58	-0.041	0.009	
59-61	0.001	0.007	
62-65	0.003	0.009	
66	-0.01	-0.009	
67-70	0.004	0.01	
71	0.005	0.009	
72			(no 72; same location as 71)
73-79	0.005	0.009	(no 74)
80-81	0.01	0.012	
82-84	0.005	0.01	
85-86	0.005	0.008	
87	0.005	0.01	
88	0.015	0.013	

CTD CASTS	ΔS (0 M)[1]	ΔS (DEEP)[2]	COMMENT
89	0.007	0.009	
90-94	0.008	0.01	(no 93)

Comments:
1. Bottle - CTD salinity upcast values (surface)
2. Bottle - CTD salinity upcast values (deep water)
3. Temperature correction

Oxygen

Oxygen samples were collected in 150-mL ground-glass stoppered sample bottles and were analyzed using the method described by Carpenter, (1965), with computer-controlled colorimetric endpoint determination as described in Friederich, et al., (1984). Analyses of Niskin™ bottles tripped at the same depth were used to estimate the precision. The average deviation of analysis for these samples was 0.31 µmol/kg ±0.31 (n = 21). The average deviation is defined as $(\sum |x_1 - x_2|)/n$ where x_1 and x_2 are the measured oxygen concentrations for each value of duplicates and n is the number of duplicates.

Oxygen data were compared with data obtained on the Oceanus-202 cruise (Doney and Bullister, 1992; Tsuchiya et al., 1992) in order to discern any large scale offsets with historical deep water observations. These comparisons led to the conclusion that the North Atlantic 1993 O_2 values were systematically lower by 7.5 µmol/kg than the Oceanus-202 data for the entire cruise. This offset has been observed on other cruises run by NOAA/AOML and we recommend adding 7.5 µmol/kg to all oxygen values in this report. Note that the O_2 data in this report has not been adjusted.

Salinity

Salinity samples were collected in 200-mL bottles. New caps were used for each sample. Bottle salinities were analyzed using a Guildline™ 8400B Autosal standardized with Wormley standard water batch #119 in a temperature controlled van. Conductivity ratios were converted to salinities conforming to the PSS78 standard. Analyses of Niskin™ bottles tripped at the same depth were used to estimate the precision. The average deviation (as defined in the oxygen section above) of analysis for these samples was 0.001 ±0.001 (n = 36).

Temperature, Density and Depth

Depth, potential temperature and density (σ_θ, σ_2, and σ_4) values were calculated using standard Woods Hole Oceanographic Institute (WHOI) hydrographic subroutines. Depth was calculated from pressure using methods based on Saunders and Fofonoff, (1976); density was determined using the calculations presented in F. Millero and A. Poisson, (1981); and potential temperature referenced to zero pressure (theta) is calculated by integrating the adiabatic lapse rate using a fourth-order Runge-Kutta algorithm.

2.1.2 Nutrient Analysis

For Leg 1, two independent groups analyzed nutrients. The AOML nutrient group continued for the entire cruise, while the U. W. group's data is for Leg 1 only. Contour plots of nutrient concentrations are presented in two forms: a combination of AOML and U. W. data that uses U. W. data for Leg 1 and AOML data for Legs 2A and 2B, and all AOML data (see Figures A-9 – A-14). Figures A-26, A-27, and A-28 show a comparison between the two sets of nutrient data.

2.1.2A AOML Nutrients

Dissolved Nutrients

Dissolved nutrient samples were collected in aged 60-mL linear polyethylene bottles after three complete seawater rinses and were stored in the dark at 4 °C until analysis was completed (within 24 hours of sample collection). Concentrations of dissolved inorganic nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), and silicate (SiO_4), reported in µmol/kg, were determined using an ALPKEM™ RFA/2 Auto-Analyzer in a temperature controlled van. The water used for the preparation of standards, determination of blank, and wash between samples was filtered Gulf Stream seawater obtained from the surface waters of the Straits of Florida. At each station a 7-point standard curve was run prior to sample analysis.

Nitrite and Nitrate

The automated colorimetric procedure and methodologies used in the analysis of nitrite and nitrate are essentially those described by Armstrong et al., (1967), with slight modifications described in Atlas et al., (1971). Standardizations were performed prior to each sample run with working solutions prepared aboard ship each day from pre-weighed "Baker Analyzed" reagent grade standards. Nitrite (NO_2) was determined by diazotizing with sulfanilamide and coupling with N-l napthylethelendiamine dihydrochloride (NEDA) to form an azo dye. The color produced is proportional to the nitrite concentration.

Samples for nitrite+nitrate (NO_2+NO_3) analysis were passed through a copperized cadmium column, which reduces nitrate to nitrite, and the resulting nitrite concentration was then determined as described above. Nitrate is the difference between nitrite+nitrate and nitrite. The detection limits for nitrite and nitrate were 0.1 µmol/kg and 0.4 µmol/kg respectively. Analyses of Niskin™ bottles tripped at the same depth were used to estimate the precision. The average deviation (as defined in the oxygen section above) of analysis for these samples was 0.066 µmol/kg ±0.099 (n = 26).

Phosphate

The automated procedure for the determination of phosphate in seawater is described by Murphy and Riley, (1962), with modifications by Grasshoff, (1965). Phosphate was determined by the reaction with an acidic molybdate solution. The phosphomolybdic acid which formed was subsequently reduced with ascorbic acid. The resulting molybdenum blue complex is proportional to the phosphate concentration in the sample. The detection limit for phosphate was 0.08 µmol/kg. Analyses of Niskin™ bottles tripped at the same depth were used to estimate the precision. The average deviation (as defined in the oxygen section above) of analysis for these samples was 0.005 µmol/kg ±0.007 (n = 26).

Silicate

The analytical procedures and methodologies used in the analysis of silicate are those described by Armstrong et al., (1967), with modifications described in Atlas et al., (1971). Silicate was determined from the reduction of silicomolybdate in acidic solution to molybdenum blue by stannous chloride. The color produced is proportional to the concentration of silicate in the sample. The detection limit for silicate was 0.4 µmol/kg. Analyses of Niskin™ bottles tripped at the same depth were used to estimate the precision. The average deviation (as defined in the oxygen section above) of analysis for these samples was 0.029 µmol/kg ± 0.056 (n = 26).

2.1.2B University of Washington Nutrients

Four nutrients (phosphate, silicate, nitrate, and nitrite) were analyzed using an ALPKEM™ RFA/2 rapid flow analyzer. The methodologies used are found in Whitledge, et al. (1981) and adapted to the RFA/2 as indicated by the AlpKem method number listed below. Primary standards were prepared in deionized water; working standards were prepared in low nutrient seawater. At each station fresh running standards were prepared, and a five point standard curve (adjusted to cover the entire ranges of the nutrients) was run prior to sample analysis. A calibration standard was analyzed at the end of each sample run. This allowed for regular monitoring of the response, drift, and linearity of each chemistry.

Phosphate

Phosphate is converted to phosphomolybdic acid and reduced with ascorbic acid to form phosphomolybdous acid in a reaction stream heated to 37 °C. The analytical precision as determined by replicate measurements (usually 4-6 samples) from 9 different depths was 0.025 µmol/kg (1.09%). (ALPKEM Method # A303-S200-11)

Silicate

Silicate is converted to silicomolybdic acid and reduced with stannous chloride to form silcomolybdous acid. The analytical precision as determined by replicate measurements (usually 4-6 samples) from 9 different depths was 0.20 µmol/kg (0.63%). (ALPKEM Method # A303-S220-11)

Nitrite

Nitrite is diazotized with sulfanilamide and coupled with NEDA to form a red azo dye. The analytical precision as determined by replicate measurements (usually 4-6 samples) from 9 different depths was 0.01 µmol/kg (1%). (ALPKEM Method # A303-S180-07)

Nitrate + Nitrite

Nitrate+nitrite is measured by reducing nitrate to nitrite in a copperized Cd coil and then measuring for nitrite. Nitrate is the difference between nitrate+nitrite and the independently measured nitrite. The analytical precision as determined by replicate measurements (usually 4-6 samples) from 9 different depths was 0.07 µmol/kg (0.24%). (AlpKem Method # A303-S170-22)

2.1.3 CFC Analysis

Specially designed 10-L water sample bottles were used on the cruise to reduce CFC contamination. These bottles have the same outer dimensions as standard 10-L Niskin™ bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing normally used to close Niskin™ bottles.

Water samples for CFC analysis were the first samples collected from the 10-L bottles. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 10-L bottles into 100-mL precision glass syringes equipped with 2-way metal stopcocks. The syringes were immersed in a holding tank of clean surface seawater until analyses. To reduce the possibility of contamination from high levels of CFCs frequently present in the air inside research vessels, the CFC extraction/analysis system and syringe holding tank were housed in a modified 20' laboratory van on the deck of the ship.

For air sampling, a ~100 meter length of 3/8" OD Dekoron™ tubing was run from the CFC lab van to the bow of the ship. Air was sucked through this line into the CFC van using an Air Cadet™ pump. The air was compressed in the pump, with the downstream pressure held at about 1.5 atm using a back pressure regulator. A tee allowed a flow (~100 mL/min) of the compressed air to be directed to the gas sample valves, while the bulk flow of the air (>7 L/min) was vented through the back pressure regulator.

Concentrations of CFC-11 and CFC-12 in air samples, seawater and gas standards on the cruise were measured by shipboard electron capture gas chromatography (EC-GC), using techniques similar to those described by Bullister and Weiss (1988). For seawater analyses, a ~30-mL aliquot of seawater from the glass syringe was transferred into the glass sparging chamber. The dissolved CFCs in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 minutes at ~70 mL/min. Water vapor was removed from the purge gas while passing through a short tube of magnesium perchlorate desiccant. The sample gases were concentrated on a cold-trap consisting of a 3" section of 1/8" stainless steel tubing packed with Porapak N (60-80 mesh) immersed in a bath of isopropanol held at -20 °C. After 4 minutes of purging the seawater sample, the sparging chamber was closed and the trap isolated. The cold isopropanol in the bath was forced away from the trap which was heated electrically to 125 °C. The sample gases held in the trap were then injected onto a precolumn (12" of 1/8" OD stainless steel tubing packed with 80-100 mesh Porasil C, held at 90 °C), for the initial separation of the CFCs and other rapidly eluting gases from more slowly eluting compounds. The CFCs then passed into the main analytical column (10', 1/8" stainless steel tubing packed with Porasil C 80-100 mesh, held at 90 °C), and then into the EC detector.

The CFC analytical system was calibrated frequently using standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column and EC detector were similar to those used for analyzing water samples. Two sizes of gas sample loops were present in the analytical system. Multiple injections of these loop volumes could be done to allow the system to be calibrated over a relatively wide range of CFC concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard and blank samples was about 12 minutes.

Concentrations of CFC-11 and CFC-12 in air, seawater samples and gas standards are reported relative to the SIO93 calibration scale (Cunnold, et. al., 1994). CFC concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts-per-trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles of CFC per kg seawater (pmol/kg). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a CFC working standard (PMEL cylinder 32386) into the analytical instrument. The concentrations of CFC-11 and CFC-12 in this working standard were calibrated versus a secondary CFC standard (9944) before the cruise and a primary standard (36743) (Bullister, 1984) after the cruise. No measurable drift between the working standards could be detected during this interval. Full range calibration curves were run 10 times during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 1 to 2 hours) to monitor short term changes in detector sensitivity.

Extremely low (<0.01 pmol/kg) CFC concentrations were measured in deep water (>2000 meters) from about 30°N to 5°N along the section, as expected from CFC measurements made during the earlier occupation of this section in 1988 (Doney and Bullister, 1992), and from other transient tracer studies made in this region of the eastern North Atlantic. Based on the median of CFC concentration measurements in the deep water of this region, which is believed to be nearly CFC-free, a blank correction of 0.007 pmol/kg for CFC-11 and 0.003 pmol/kg for CFC-12 have been applied to the data set. For very low concentration water samples, subtraction of the water sample CFC blank from the measured CFC water sample concentration yields a small negative reported value.

On this expedition, we estimate precisions (1 standard deviation) of about 1% or 0.005 pmol/kg (whichever is greater) for dissolved CFC-11 measurements and 2% or 0.005 pmol/kg for CFC-12 (see listing of replicate samples given in Tables 2 and 3).

A number of water samples (~70 out of a total of ~1700) had clearly anomalous CFC-11 and/or CFC-12 concentrations relative to adjacent samples. At Station 44, a significant number of water samples had elevated levels of CFC-12, believed to be due to release of CFC-12 from the ship's air conditioning system. Other anomalous samples appeared to occur more or less randomly during the cruise, and were not clearly associated with other features in the water column (e.g. elevated oxygen concentrations, salinity or temperature features, etc.). This suggests that the high values were due to individual, isolated low-level CFC contamination events. These samples are included in this report and are given a quality flag of either 3 (questionable measurement) or 4 (bad measurement). A total of 7 analyses of CFC-11 were assigned a flag of 3 and 9 analyses of CFC-12 were assigned a flag of 3. A total of 27 analyses of CFC-11 were assigned a flag of 4 and 69 CFC-12 samples assigned a flag of 4.

Table 2: NA93 Replicate dissolved CFC-11 analyses (in pmol/kg)

Station	Sample	Replicate Number 1	2	3
1	413	0.018	0.028	
1	419	0.125	0.123	
1	420	0.116	0.388	
1	422	0.917	0.799	
1	424	1.736	1.709	
2	1304	0.014	0.043	
2	1308	-0.00	0.008	
2	1318	1.752	1.678	
3	1505	0.000	0.004	
3	1524	1.771	1.749	
4	1705	0.008	0.012	
4	1709	0.051	0.041	
4	1713	0.019	0.021	0.020
6	2304	0.031	0.017	
6	2312	0.030	0.024	
7	2424	1.743	1.790	
9	3107	0.011	0.010	
9	3124	1.759	1.767	
12	3706	0.033	0.036	
12	3724	1.754	1.744	
14	4507	0.054	0.053	
14	4518	1.277	1.268	
14	4524	1.739	1.737	
16	4808	0.012	0.016	
16	4824	1.690	1.613	
17	4918	1.144	1.134	
18	5709	0.028	0.026	
18	5724	1.649	1.674	
19	5807	0.001	0.005	
20	6008	0.013	0.011	
20	6023	1.657	1.677	
22	6604	0.018	0.005	
22	6606	0.019	0.004	
22	6819	1.469	1.474	
23	7118	0.710	0.701	
23	7123	1.666	1.689	1.633
24	7618	0.675	0.669	
24	7619	0.882	0.885	
25	7812	0.007	0.002	
25	7818	0.775	0.775	
25	7823	1.638	1.681	
26	8018	0.775	0.778	
26	8023	1.814	1.794	
27	8603	0.003	-0.00	0.011
27	8814	0.030	0.044	
28	9117	0.522	0.528	0.518
28	9118	0.752	0.758	0.761
28	9401	0.004	0.006	
28	9418	0.772	0.780	
29	9711	0.096	0.084	
29	9715	0.669	0.682	
30	10322	2.019	2.051	
31	10516	0.191	0.184	
31	10523	1.862	1.855	
32	11010	0.639	0.621	
32	11018	2.604	2.590	
33	11409	0.134	0.138	
33	11412	0.562	0.572	
33	11418	2.454	2.454	
34	12110	0.244	0.248	
34	12121	2.467	2.429	
35	12710	0.355	0.347	
35	12721	2.251	2.235	
35	12722	2.122	2.128	
36	13006	0.001	0.004	
36	13024	2.138	2.135	
37	13608	0.011	0.004	
37	13613	0.152	0.153	
37	13619	2.338	2.335	
38	13902	-0.001	0.010	
38	13915	0.967	0.964	
38	13923	2.096	2.043	
39	14415	1.616	1.655	
39	14421	2.108	2.129	
40	14908	-0.002	-0.00	
44	16801	0.007	0.002	
44	16805	-0.006	0.000	
45	17002	-0.006	-0.00	
45	17010	0.001	-0.00	
46	17205	-0.001	0.000	

Station	Sample	Replicate Number		
		1	2	3
47	17703	0.000	-0.005	
47	17710	0.001	-0.004	
48	18302	-0.002	-0.004	
48	18303	-0.002	-0.003	
48	18314	0.553	0.558	
48	18316	1.889	1.873	
49	18618	2.388	2.409	
49	18622	2.153	2.168	
50	19103	-0.002	0.000	0.001
50	19112	0.179	0.174	
51	19604	0.000	0.001	
51	19611	0.218	0.216	
51	19613	0.758	0.763	
51	19615	2.060	2.066	
52	19805	0.006	0.010	
52	19821	2.412	2.478	
53	20405	0.004	0.002	
53	20409	0.228	0.225	
53	20421	2.748	2.661	
54	20605	0.019	0.020	
54	20610	0.471	0.480	
56	21609	0.546	0.534	
56	21622	2.883	2.836	
60	22716	3.218	3.218	
61	23109	1.633	1.646	

Station	Sample	Replicate Number		
		1	2	3
63	23304	0.208	0.208	
63	23322	3.245	3.230	
64	23909	1.745	1.766	
64	23915	2.800	2.783	
64	23920	3.145	3.144	
65	24206	0.636	0.641	
65	24210	2.017	2.010	
66	24717	3.361	3.337	
68	25322	3.340	3.303	
69	25417	3.393	3.424	
69	25422	3.085	3.064	
71	25722	3.234	3.243	
71	25724	3.102	3.116	
72	26223	2.973	3.002	
74	26821	3.684	3.748	
75	27305	2.335	2.302	
75	27315	3.447	3.571	
78	28308	2.198	2.188	
78	28314	3.438	3.788	
78	28320	3.810	3.644	
80	28718	3.587	3.581	
81	28814	3.917	3.916	
81	28820	3.859	3.890	
81	28823	3.779	3.790	
83	29108	4.030	3.981	

Table 3: NA93 Replicate dissolved CFC-11 analyses (in pmol/kg)

Station	Sample	Replicate Number			
		1	2	3	4
1	413	0.010	0.012		
1	419	0.076	0.077		
1	422	0.448	0.424		
1	424	0.976	0.978		
2	1308	-0.003	0.003		
2	1313	0.440	0.441		
2	1318	0.980	0.943		
3	1505	0.004	0.000		
4	1705	0.010	0.006		
4	1709	0.021	0.017	0.022	

Station	Sample	Replicate Number			
		1	2	3	4
4	1713	0.010	0.010	0.012	
4	1724	0.933	0.933		
6	2304	0.011	0.038		
6	2312	0.014	0.010		
9	3107	0.006	0.004		
9	3124	0.985	0.988		
12	3706	0.023	0.030		
12	3724	0.973	0.990		
14	4507	0.029	0.034		
14	4518	0.695	0.644		

Station	Sample	Replicate Number			
		1	2	3	4
14	4524	0.967	0.970		
16	4808	0.008	0.017		
16	4824	0.943	0.906		
17	4918	0.601	0.602		
18	5709	0.015	0.025		
18	5724	0.946	0.963		
20	6023	0.917	0.972		
22	6606	0.004	0.005		
23	7123	1.032	0.967		
24	7618	0.393	0.366		
24	7619	0.471	0.478		
25	7812	0.000	-0.001		
25	7818	0.432	0.427		
25	7823	0.915	0.942		
26	8018	0.421	0.418		
26	8023	1.014	1.020		
27	8814	0.027	0.025		
28	9117	0.302	0.302	0.306	
28	9118	0.416	0.414	0.403	
28	9401	0.015	0.014		
28	9418	0.433	0.432		
29	9711	0.056	0.062		
29	9715	0.379	0.397		
30	10322	1.109	1.132		
31	10516	0.118	0.118		
32	11010	0.329	0.325		
32	11018	1.365	1.368		
33	11408	0.054	0.064		
33	11418	1.287	1.331		
34	12110	0.149	0.149		
34	12121	1.348	1.347		
35	12710	0.210	0.200		
35	12721	1.219	1.238		
35	12722	1.195	1.187		
36	13006	-0.003	0.005		
36	13024	1.177	1.175		
37	13608	0.001	0.003		
37	13613	0.077	0.076		
37	13619	1.271	1.271	1.248	1.268
38	13902	0.003	0.003		

Station	Sample	Replicate Number			
		1	2	3	4
38	13915	0.496	0.518		
38	13923	1.148	1.120		
39	14415	0.816	0.869		
39	14421	1.170	1.205		
40	14908	0.000	0.002		
44	16805	0.003	-0.002		
45	17002	-0.003	-0.003		
45	17010	-0.003	0.000		
46	17205	0.000	0.000		
47	17703	-0.001	-0.003		
47	17710	-0.003	-0.005		
48	18302	0.004	0.000		
48	18303	-0.002	-0.001		
48	18316	0.936	0.992		
49	18618	1.234	1.252		
49	18622	1.156	1.164		
50	19103	-0.001	-0.002	-0.002	
50	19112	0.095	0.086		
51	19604	0.001	0.000		
51	19611	0.107	0.117		
51	19613	0.376	0.398		
51	19615	1.053	1.050		
52	19805	0.000	0.006		
52	19821	1.322	1.353		
53	20405	0.004	0.007		
53	20409	0.128	0.130		
53	20421	1.443	1.400		
54	20605	0.011	0.015		
54	20610	0.249	0.227		
56	21609	0.271	0.280		
56	21622	1.527	1.479		
60	22716	1.586	1.635		
61	23109	0.793	0.769		
63	23322	1.627	1.640		
64	23909	0.780	0.813		
64	23915	1.353	1.312		
64	23920	1.537	1.534		
65	24206	0.327	0.324		
65	24210	0.932	0.935		
66	24702	0.024	0.019		

Station	Sample	Replicate Number			
		1	2	3	4
66	24717	1.713	1.697		
68	25322	1.726	1.723		
69	25417	1.722	1.771		
69	25422	1.578	1.587		
71	25722	1.654	1.682		
71	25724	1.622	1.626		
72	26223	1.572	1.576		
74	26821	1.902	1.940		
75	27305	1.139	1.120		

Station	Sample	Replicate Number			
		1	2	3	4
75	27315	1.744	1.807		
78	28308	1.069	1.059		
78	28314	1.737	1.973		
78	28320	1.868	1.894		
80	28718	1.838	1.836		
81	28814	2.056	2.010		
81	28820	2.003	2.004		
81	28823	1.968	1.980		
83	29108	2.091	2.054		

Table 4: NA93 CFC air measurements for Leg 1

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
5-Jul-93	1624	04 10.6 S	033 19.6	261.5	514.6
5-Jul-93	1708	04 10.6 S	033 19.6	261.9	515.3
5-Jul-93	1722	04 10.6 S	033 19.6	260.2	515.7
8-Jul-93	606	04 03.3 S	024 59.5	-9	-9
8-Jul-93	1158	03 42.9 S	025 00.1	262.7	509.7
8-Jul-93	1211	03 42.9 S	025 00.1	262.6	508
8-Jul-93	1226	03 42.9 S	025 00.1	262.6	507.6
8-Jul-93	1239	03 42.9 S	025 00.1	263.6	509
9-Jul-93	712	03 42.9 S	025 00.1	262.3	510.8
9-Jul-93	725	03 42.9 S	025 00.1	262.7	510
9-Jul-93	754	02 10.9 S	025 00.4	263.4	510.3
9-Jul-93	809	02 10.9 S	025 00.4	264.1	510.3
9-Jul-93	824	02 10.9 S	025 00.4	263.1	509.4
10-Jul-9	2246	01 08.6 S	025 00.8	263.4	508
10-Jul-9	2258	01 08.6 S	025 00.8	263.5	504.9
10-Jul-9	2312	01 08.6 S	025 00.8	263.3	506.3
12-Jul-9	1450	04 48.8	026 04.5	264.7	-9
12-Jul-9	1504	04 48.8	026 04.5	264.5	511.2
12-Jul-9	1517	04 48.8	026 04.5	-9	-9
13-Jul-9	144	04 48.8	026 04.5	-9	-9
13-Jul-9	157	04 48.8	026 04.5	-9	-9
13-Jul-9	210	04 48.8	026 04.5	-9	-9
13-Jul-9	2112	09 00.0	027 00.0	261.2	507.7
13-Jul-9	2125	09 00.0	027 00.0	261.3	504.8
13-Jul-9	2141	09 00.0	027 00.0	260.7	503
13-Jul-9	2160	09 00.0	027 00.0	264.4	512
14-Jul-9	1811	10 46.4	028 03.1	264.3	513
14-Jul-9	1825	10 46.4	028 03.1	264.1	515

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
14-Jul-9	1838	10 46.4	028 03.1	263.9	514.9
14-Jul-9	1852	10 46.4	028 03.1	264.9	514.6
15-Jul-9	1200	11 52.1	028 27.9	267.9	-9
15-Jul-9	1227	11 52.1	028 27.9	265.9	521.4
15-Jul-9	1252	11 52.1	028 27.9	268.8	521.4
15-Jul-9	1318	11 52.1	028 27.9	266.5	518.4
17-Jul-9	122	15 00.3	028 17.0	265.7	517.6
17-Jul-9	135	15 00.3	028 17.0	268.3	515.7
17-Jul-9	155	15 00.3	028 17.0	266.7	517.5
17-Jul-9	209	15 00.3	028 17.0	268.8	516.9
17-Jul-9	1645	16 45.1	025 19.7	267	523.8
17-Jul-9	1659	16 45.1	025 19.7	266.5	521.2
17-Jul-9	1725	16 45.1	025 19.7	267.6	521.9
17-Jul-9	1741	16 45.1	025 19.7	267	-9

Table 5: NA93 CFC air measurements for Leg 2

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
2-Aug-93	928	33 45.9	020 31.7	266.8	515.2
2-Aug-93	940	33 45.9	020 31.7	267.1	519
2-Aug-93	953	33 45.9	020 31.7	267.7	520.8
3-Aug-93	1233	32 00.0	022 24.2	266.6	517.1
3-Aug-93	1259	32 00.0	022 24.2	267.5	514.9
4-Aug-93	354	29 44.1	023 41.6	264.2	515.8
4-Aug-93	408	29 44.1	023 41.6	264.6	513.1
4-Aug-93	422	29 44.1	023 41.6	265	512.6
5-Aug-93	858	25 59.2	025 46.5	264.9	521.3
5-Aug-93	911	25 59.2	025 46.5	266.5	524.1
5-Aug-93	923	25 59.2	025 46.5	266.4	521.8
6-Aug-93	1447	21 50.6	028 01.4	264.5	519.9
6-Aug-93	1460	21 50.6	028 01.4	265.9	519
6-Aug-93	1513	21 50.6	028 01.4	264.8	519.8
8-Aug-93	1044	19 58.7	029 02.2	267.5	519.3
8-Aug-93	1056	19 58.7	029 02.2	268.6	519.3
8-Aug-93	1108	19 58.7	029 02.2	266.9	520.6
9-Aug-93	1717	14 59.2	029 00.2	262.4	523.6
9-Aug-93	1742	14 59.2	029 00.2	264.1	512.8
11-Aug-9	1333	23 00.0	027 26.1	267.7	524.3
11-Aug-9	1345	23 00.0	027 26.1	270.2	524.2
11-Aug-9	1358	23 00.0	027 26.1	267.5	523.5
12-Aug-9	1407	26 38.7	025 26.5	265.9	523
12-Aug-9	1420	26 38.7	025 26.5	266.5	524.2

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
12-Aug-9	1433	26 38.7	025 26.5	266	524
13-Aug-9	11	27 38.6	024 53.0	271.7	521
13-Aug-9	24	27 38.6	024 53.0	269.7	517.4
13-Aug-9	37	27 38.6	024 53.0	270	516.7
13-Aug-9	1225	28 59.7	024 07.5	266.3	521
13-Aug-9	1238	28 59.7	024 07.5	266.5	518.2
13-Aug-9	1251	28 59.7	024 07.5	266.4	521.2
20-Aug-9	2203	41 00.0	020 00.0	271.2	523.6
20-Aug-9	2215	41 00.0	020 00.0	269	530.1
22-Aug-9	2042	45 58.0	020 00.0	266.2	521.1
22-Aug-9	2055	45 58.0	020 00.0	267	524.9
22-Aug-9	2108	45 58.0	020 00.0	265.1	515.6
25-Aug-9	750	52 00.0	020 00.0	266.2	516.6
25-Aug-9	803	52 00.0	020 00.0	267.4	523.7
25-Aug-9	815	52 00.0	020 00.0	272.7	514.8
29-Aug-9	51	62 59.2	019 59.9	265.3	517.5
29-Aug-9	104	62 59.2	019 59.9	266.5	518.7
29-Aug-9	117	62 59.2	019 59.9	267.3	518.5

Table 6: NA93 CFC Air values (interpolated to station locations)

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
2-Aug-93	928	33 45.9	020 31.7	266.8	515.2
2-Aug-93	940	33 45.9	020 31.7	267.1	519
2-Aug-93	953	33 45.9	020 31.7	267.7	520.8
3-Aug-93	1233	32 00.0	022 24.2	266.6	517.1
3-Aug-93	1259	32 00.0	022 24.2	267.5	514.9
4-Aug-93	354	29 44.1	023 41.6	264.2	515.8
4-Aug-93	408	29 44.1	023 41.6	264.6	513.1
4-Aug-93	422	29 44.1	023 41.6	265	512.6
5-Aug-93	858	25 59.2	025 46.5	264.9	521.3
5-Aug-93	911	25 59.2	025 46.5	266.5	524.1
5-Aug-93	923	25 59.2	025 46.5	266.4	521.8
6-Aug-93	1447	21 50.6	028 01.4	264.5	519.9
6-Aug-93	1460	21 50.6	028 01.4	265.9	519
6-Aug-93	1513	21 50.6	028 01.4	264.8	519.8
8-Aug-93	1044	19 58.7	029 02.2	267.5	519.3
8-Aug-93	1056	19 58.7	029 02.2	268.6	519.3
8-Aug-93	1108	19 58.7	029 02.2	266.9	520.6
9-Aug-93	1717	14 59.2	029 00.2	262.4	523.6
9-Aug-93	1742	14 59.2	029 00.2	264.1	512.8
11-Aug-9	1333	23 00.0	027 26.1	267.7	524.3

Date	Time	Latitude	Longitude	F11(PPT)	F12(PPT)
11-Aug-9	1345	23 00.0	027 26.1	270.2	524.2
11-Aug-9	1358	23 00.0	027 26.1	267.5	523.5
12-Aug-9	1407	26 38.7	025 26.5	265.9	523
12-Aug-9	1420	26 38.7	025 26.5	266.5	524.2
12-Aug-9	1433	26 38.7	025 26.5	266	524
13-Aug-9	11	27 38.6	024 53.0	271.7	521
13-Aug-9	24	27 38.6	024 53.0	269.7	517.4
13-Aug-9	37	27 38.6	024 53.0	270	516.7
13-Aug-9	1225	28 59.7	024 07.5	266.3	521
13-Aug-9	1238	28 59.7	024 07.5	266.5	518.2
13-Aug-9	1251	28 59.7	024 07.5	266.4	521.2
20-Aug-9	2203	41 00.0	020 00.0	271.2	523.6
20-Aug-9	2215	41 00.0	020 00.0	269	530.1
22-Aug-9	2042	45 58.0	020 00.0	266.2	521.1
22-Aug-9	2055	45 58.0	020 00.0	267	524.9
22-Aug-9	2108	45 58.0	020 00.0	265.1	515.6
25-Aug-9	750	52 00.0	020 00.0	266.2	516.6
25-Aug-9	803	52 00.0	020 00.0	267.4	523.7
25-Aug-9	815	52 00.0	020 00.0	272.7	514.8
29-Aug-9	51	62 59.2	019 59.9	265.3	517.5
29-Aug-9	104	62 59.2	019 59.9	266.5	518.7
29-Aug-9	117	62 59.2	019 59.9	267.3	518.5

2.2 CARBON PARAMETERS

2.2.1 Total Dissolved Inorganic CO_2 (TCO_2)

Sampling

Samples were drawn from 10-L Niskin™ bottles into 0.5-L Pyrex™ bottles using Tygon™ tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5 mL headspace volume. 0.2 mL of saturated mercuric chloride ($HgCl_2$) solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L™ grease. The samples were stored at room temperature in the dark for a maximum of two days.

Analysis

The TCO_2 analyses were performed by extracting the inorganic carbon in a seawater sample by acidification and subsequent displacement of the gaseous CO_2 into a coulometer cell. Two coulometers were used on the cruise. Both were equipped with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson of Brookhaven National Laboratory (BNL). The first system, "AOML-1" was previously used on the NOAA S-Atl-91 and EqPac-92 cruises (Forde et al., 1994; Lantry et al., 1995). The second system, "AOML-2", was brought into service in February 1993 and this was its first use at sea.

For analysis on the SOMMA system, a 0.5 L sample bottle was inserted in a water bath at 20 °C. Water from the bottle was displaced by pressurization into a thermostated pipette using a (700 parts per million by volume (ppm) CO_2 in air) gas. The sample was injected into an extraction chamber which contained 1 mL 10% H_3PO_4 solution previously stripped of CO_2. The evolved CO_2 gas from the sample was run through a condenser and a magnesium perchlorate drying column to dry the gas stream, and through an ORBO-53™ tube to remove volatile acids, using a carrier stream of CO_2-free ultra high purity nitrogen. In the coulometer cell the CO_2 is absorbed by a proprietary solution procured from Utopia Instrument Company (UIC). This solution changes color from blue to colorless by addition of the (acid) CO_2 gas. A photodiode detects the color change and causes a current to pass through the cell with electrolytic production of hydroxide ions at the cathode. The titration current is turned off when the solution reaches the original color. The current passed through the cell is measured by a counter and is directly proportional to the amount of CO_2 injected. The details of the system can be found in Johnson, (1992) and Johnson et al., (1993). The coulometer cell solution was replaced after 30 mg of carbon was titrated or when the coulometer runs were less then 9 minutes. This typically was after 18-20 hours of continuous use. Typical sample titration times were 9 to 16 minutes.

Both coulometers were calibrated by injecting aliquots of pure CO_2 using an 8-port valve with two sample loops. The CO_2 gas volumes bracketed the amount of CO_2 extracted from the water samples for the two AOML systems. The gas loops were calibrated at BNL. Liquid certified reference materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO) were run on each cell. The results were close to the values determined manometrically by Keeling at SIO as shown below.

Av. value of CRMs run on AOML-1: 2033.46 μmol/kg ± 1.15 n = 55

Av. value of CRMs run on AOML-2: 2032.86 μmol/kg ± 0.96 n = 51

The manometric value (SIO reference material batch #16) was 2034.54 μmol/kg ± 0.91 n = 9.

Note: Only the first replicate of the analyses, which were run early in coulometer cells, were used for the averages.

Replicate seawater samples were taken from the deepest Niskin™ sample and run at different times during the cell. The first replicate was used at the start of the cell with fresh coulometer solution, the second at the end of the cell after about 30 mg of C were titrated, while the third analysis was performed using a new coulometer cell solution. No systematic difference between the replicates was observed. As example, the replicate samples run on SOMMA AOML-1 had an average absolute difference from the mean of 1 µmol/kg with a standard deviation of 1.9 µmol/kg for 40 sets of triplicates. The deviation is very similar to that observed for the CRMs and suggest no strong dependency of results with amount of carbon titrated for a particular cell.

The data of the two instruments were normalized using the averages of the reference material for the cruise. The following corrections were applied to the data: AOML-1, + 1.08 µmol/kg; AOML-2, + 1.68 µmol/kg.

Calculations

The instruments were calibrated three times during each cell solution with a set of CO_2 gas loop injections. Calculation of the amount of CO_2 injected was according to the Department of Energy (DOE) CO_2 handbook (DOE, 1994). The gas loops yielded a calibration factor for the instrument defined as:

$$\text{Cal. factor} = \frac{\text{calculated moles of } CO_2 \text{ injected from gas loop}}{\text{actual moles of } CO_2 \text{ injected}} \tag{1}$$

The concentration of CO_2 ($[CO_2]$) in the samples was determined according to:

$$[CO_2] = \text{Cal. factor} * \frac{(\text{Counts} - \text{Blank} * \text{Run Time}) * K \ \mu\text{mol/count}}{\text{pipette volume} * \text{density of sample}} \tag{2}$$

where "Counts" is the instrument reading at the end of the analysis, "Blank" is the counts/minute determined from blank runs performed at least once for each cell of the solution, "Run Time" is the length of coulometric titration (in minutes), and K is the conversion factor from counts to µmol which is dependent on the slope and intercept relation between instrument response and charge. For a unit with slope of 1 and intercept of 0, the constant is $2.0728 * 10^{-4}$ µmol/count.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes prior to, during, and after the cruise. The weights with the appropriate densities were used to determine the volume of the syringes and pipette. Calculation of pipette volumes, density, and final CO_2 concentration were performed according to procedures outlined in the DOE CO_2 handbook (DOE, 1994).

and run at different times during the cell. The first replicate was used at the start of the cell with fresh coulometer solution, the second at the end of the cell after about 30 mg of C were titrated, while the third analysis was performed using a new coulometer cell solution. No systematic difference between the replicates was observed. As example, the replicate samples run on SOMMA AOML-1 had an average absolute difference from the mean of 1 µmol/kg with a standard deviation of 1.9 µmol/kg for 40 sets of triplicates. The deviation is very similar to that observed for the CRMs and suggest no strong dependency of results with amount of carbon titrated for a particular cell.

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Calculations

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$$Cal.\ factor = \frac{calculated\ moles\ of\ CO_2\ injected\ from\ gas\ loop}{actual\ moles\ of\ CO_2\ injected} \tag{1}$$

The concentration of CO_2 ($[CO_2]$) in the samples was determined according to:

$$[CO_2] = Cal.\ factor * \frac{(Counts - Blank * Run\ Time) * K\ \mu mol/count}{pipette\ volume * density\ of\ sample} \tag{2}$$

where "Counts" is the instrument reading at the end of the analysis, "Blank" is the counts/minute determined from blank runs performed at least once for each cell of the solution, "Run Time" is the length of coulometric titration (in minutes), and K is the conversion factor from counts to µmol which is dependent on the slope and intercept relation between instrument response and charge. For a unit with slope of 1 and intercept of 0, the constant is $2.0728 * 10^{-4}$ µmol/count.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes prior to, during, and after the cruise. The weights with the appropriate densities were used to determine the volume of the syringes and pipette. Calculation of pipette volumes, density, and final CO_2 concentration were performed according to procedures outlined in the DOE CO_2 handbook (DOE, 1994).

Based on weighings of distilled water aliquots the volume of the AOML-1 pipette was 28.715 mL (20 °C, 1 atm) with a standard deviation of 0.013 mL. The pipette volume of AOML-2 was 27.177 mL with a standard deviation of 0.014 mL. Assuming that the standard deviation represents the uncertainty in the delivery to the extraction chamber this accounts for approximately 90% of the variance in the CRM value.

All TCO_2 values are corrected for dilution by 0.2 mL of mercuric chloride solution assuming the solution is saturated with atmospheric CO_2 levels and total water volume in the sampling bottles is 540 mL. The correction factor used is 1.00037. This is in addition to the correction to the CRM values for AOML-1 of + 1.08 µmol/kg and for AOML-2 of + 1.68 µmol/kg as listed above.

2.2.2 Discrete Fugacity of CO_2 (fCO_2)[1]

Sampling

Samples were drawn from 10-L Niskin™ bottles into 500 mL Pyrex™ volumetric flasks using Tygon™ tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. Five mL of water was withdrawn with a pipette to create a small expansion volume. 0.2 mL of saturated $HgCl_2$ solution was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner. The samples were stored upside down at room temperature for a maximum of one day.

Analyzer description

The discrete fCO_2 system is patterned after the setup described in Chipman, et al., (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen, et al., (1995). The major difference between the systems is that our system uses a LI-COR™ model 6262 non-dispersive infrared (IR) analyzer, while the system of Chipman, et al. (1993) utilizes a gas chromatograph with a flame ionization detector and a methanizer that quantitatively converts CO_2 into CH_4 for analysis.

Samples collected in 500-mL volumetric flasks are brought to a temperature of 20.00 ±0.02 °C, by first inserting the flasks upside down in a pre-bath at 19-21 °C, and subsequently in a Neslab™ model RT-220 controlled temperature bath for equilibration and analysis. A 60-mL headspace is created in the sample flask by displacing the water using a compressed standard gas with a CO_2 mixing ratio close to the fCO_2 of the water. The headspace is circulated in a closed loop through the infrared analyzer which measures CO_2 and water vapor levels in the sample cell. The headspaces of two flasks are equilibrated simultaneously in two separate channels.

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[1] The fugacity of CO_2 (fCO_2) is the partial pressure of CO_2 corrected for non-ideality of CO_2 in air. At ambient temperature, $fCO_2 \approx 0.995 * pCO_2$.

While headspace from the flask in the first channel goes through the IR analyzer, the headspace of the flask in the second channel is recirculated in a closed loop. After the first sample is analyzed a valve is switched to put the second channel in line with the analyzer. The samples are equilibrated till the running mean of twenty consecutive 1-second readings from the analyzer differ by less than 0.1 ppm, which on average takes about 10 minutes. An expandable volume consisting of a balloon keeps the content of flasks at room pressure.

In order to maintain measurement precision, a set of six gas standards is run through the system after every 8 to 12 seawater samples. The standards have mixing ratios of 201.4, 354.1, 517.0, 804.5, 1012.2, and 1515 ppm which bracket the fCO_2 at 20 °C (fCO_2(20)) values observed in the water column.

The determination of fCO_2(20) in water from the headspace measurement involves several steps. The IR detector response for the standards is normalized for temperature, the IR analyzer voltage output for samples is normalized to 1 atm pressure, and the IR detector response is corrected for the influence of water vapor. The sample values are converted to a mixing ratio based on the compressed gas standards. The mixing ratio in the headspace is converted to fugacity and corrected to fugacity of CO_2 in the water sample prior to equilibration by accounting for change in total CO_2 in water during the equilibration process (for details see Wanninkhof and Thoning, (1993)). The change in fCO_2(20) caused by the change in TCO_2 is calculated using the constraint that TAlk remains constant during exchange of CO_2 gas between the headspace and the water. The calculation is outlined in the appendix of Peng et al., (1987).

Relative errors for fCO_2 analysis for the North Atlantic 1993 cruise were determined from duplicates taken from the same Niskin™ bottle (Table 7). The deviation is defined as: (difference in duplicates/(2*mean)*100) and is expressed both in parts per million by volume (ppm) and in percent.

Table 7: fCO_2 Measurement Error

						Deviation	
Leg	Sta.	Sample	Pressure	Temp	fCO_2	ppm	%
1	2	1302	3152.4	2.40	749.1	0.9	0.11
1	2	1303	2600.8	2.69	762.2	2.4	0.32
1	6	2303	4651.3	0.46	961.3	4.5	0.47
1	16	4824	0.2	27.14	263.9	0.6	0.22
1	19	5803	3803.2	2.07	764.2	4.3	0.56
1	29	9721	20.5	26.86	266.0	1.8	0.68
1	29	9722	0	27.13	272.5	0.9	0.32
1	30	10303	5000.8	1.82	772.2	1.5	0.20
2A	32	11010	1000.4	9.09	687.7	0.9	0.13
2A	32	11023	0	22.03	331.2	0.2	0.06

						Deviation	
Leg	Sta.	Sample	Pressure	Temp	fCO_2	ppm	%
2A	40	14903	3999.1	2.04	759.2	1.1	0.15
2A	40	14923	19.7	24.37	296.5	0.5	0.17
2A	44	16822	3	24.45	304.2	0.2	0.06
2A	48	18320	99.7	19.87	332.6	1.7	0.52
2B	57	21703	4010.7	2.20	758.0	1.1	0.15
2B	57	21704	3507.7	2.35	753.6	0.8	0.11
2B	59	22522	19.2	19.87	341.3	0.2	0.05
2B	61	23122	25.2	19.77	340.5	0.1	0.02
2B	76	27503	1196.1	4.62	770.8	0.2	0.03
2B	76	27517	250.1	9.43	599.0	0.6	0.10
						average %	0.22

2.2.3 Total Alkalinity and pH

pH Measurements

The pH measurements of seawater were made using the spectrophotometric techniques of Clayton and Byrne (1993). The pH of samples using the m-cresol purple (mCP) is determined from:

$$pH = pK_{ind} + \log [(R - 0.0069) / (2.222 - 0.133\,R)] \qquad (3)$$

where K_{ind} is the dissociation constant for the indicator and R (A_{578}/A_{434}) is the ratio of the absorbance of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm. The pH of the samples is perturbed by the addition of an indicator. The magnitude of this perturbation is a function of the difference between the seawater acidity and indicator acidity; therefore this correction was quantified for each batch of dye solution. To a sample of seawater (~30 mL), a normal volume of mCP (0.080 mL, in this case) was added and the absorbance ratio was measured. From a second addition of mCP and absorbance ratio measurement, the change in absorbance ratio per mL of added indicator (ΔR) was calculated. From a series of such measurements over a range of seawater pH, ΔR was described as a linear function of the value of the absorbance ratio (R_m) measured subsequent to the initial addition of the indicator (i.e. $R = 0.02959 - 0.1288\ R_m$). In the course of routine seawater pH analyses, this correction was applied to every measured absorbance ratio (R_m); i.e. the corrected absorbance ratio is calculated as

$$R = R_m + (0.02959 - 0.1288\,R_m) \qquad (4)$$

Clayton and Byrne (1993) calibrated the m-cresol purple indicator using TRIS buffers (Ramette et al., 1977) and the pH equations of Dickson (1993). They found that

$$pK_{ind} = 1245.69 / T + 3.8275 + (2.11 \times 10^{-3}) (35 - S) \qquad (5)$$

where T is temperature in Kelvin and is valid from 293.15 to 303.15 K and S = 30 to 37. The values of pH calculated from equations (3) and (5) are on the total scale in units of mol/(kg-soln). The total proton scale (Hansson, 1973) defines pH in terms of the sum of the concentrations of free hydrogen ion, $[H^+]$, and bisulfate, $[HSO_4^-]$

$$pH_T = -log[H^+]_T = -log\{[H^+] + [HSO_4^-]\} = -log\{[H^+](1 + [SO_4^{2-}] / K_{HSO4})\} \qquad (6)$$

where the concentration of total sulfate, $[SO_4^{2-}] = 0.0282 \times 35 / S$ and K_{HSO4} is the dissociation constant for the bisulfate in seawater (Dickson, 1990a).

We have redetermined the value of pK_{ind} from 273.15 to 313.15 K using a 0.04 M TRIS buffer (Ramette et al., 1977). The pH of the TRIS buffer was determined from the emf measurements made with the H_2,Pt | AgCl,Ag electrode system (Millero et al., 1993a). At 25 °C the buffer had a pH of 8.076 and yielded spectrophotometric values of pH that were in excellent agreement (~0.0001) with those found using equations (3) and (5). Our results from 273.15 to 313.15 K (0 to 40°C) were fitted to the equation (S = 35)

$$pK_{ind} = 35.913 - 216.404 / T - 10.9913 \log (T) \qquad (7)$$

with the standard error of 0.001 in pK_{ind} where the constants are on the total proton scale {mol/(kg-H_2O)}. The use of equation (3) and (7) from 0 to 40 °C makes the assumption that R is independent of the temperature.

The values of pH calculated from equation (3) and (7) are on the total scale in units of mol/(kg-H_2O). The conversion of the pH_T {mol/(kg-H_2O)} to the seawater pH_{SWS} {mol/(kg-soln)} can be made using (Dickson and Riley, 1979; Dickson and Millero, 1987):

$$pH_{SWS} = pH_T - log\{(1 + [SO_4^{2-}] / K_{HSO4} + [F^-] / K_{HF}) / (1 + [SO_4^{2-}] / K_{HSO4})\}$$

$$- \log (1 - 1.005 \times 10^{-3} S) \qquad (8)$$

where the total concentration of fluoride, $[F^-] = 0.000067 \times 35 / S$, and K_{HF} is the dissociation constant for hydrogen fluoride (Dickson and Riley, 1979). The seawater pH_{SWS} scale was used here since the carbonate constants used are on this scale (Dickson and Millero, 1987; Millero et al., 1993b).

The absorbance measurements were made using a HP™ Diode Array 8452 A spectrophotometer. The temperature was controlled to 20 °C with an Endocal™ RTE 8DD refrigerated circulating temperature bath that regulates the temperature to ±0.01

°C. The temperature was measured using a Guildline™ 9540 digital platinum resistance thermometer.

Total Alkalinity Measurements, TAlk

TITRATION SYSTEM

The titration systems used to determine TAlk consisted of a Metrohm™ 665 Dosimat titrator and an Orion™ 720A pH meter that is controlled by a personal computer (Millero et al., 1993c). Both the acid titrant in a water-jacketed burette and the seawater sample in a water-jacketed cell were controlled to a constant temperature of 25 ±0.1 °C with a Neslab™ constant temperature bath. The plexiglass water jacketed cells used during the cruise were similar to those used by Bradshaw and Brewer (1988) except a larger volume (about 200 mL) was used to increase the precision. This cell had a fill and drain valve, which increased the reproducibility of the cell volume.

A GWBASIC™ program used to run the titration records the volume of the added acid and the emf of the electrodes using RS232 interfaces. The titration is made by adding HCl to seawater past the carbonic acid end point. A typical titration records the emf reading after the readings become stable (±0.09 mV) and adds enough acid to change the voltage to a pre-assigned increment (13 mV). In contrast to the delivery of a fixed volume increment of acid, this method gives data points in the range of a rapid increase in the emf near the endpoint. A full titration (25 points) takes about 20 minutes. Using three systems a 24-bottle station cast was completed in 3.5 hours.

ELECTRODES

The electrodes used to measure the emf of the sample during a titration consisted of a ROSS™ glass pH electrode and an Orion™ double junction Ag, AgCl reference electrode.

STANDARD ACIDS

The HCl used throughout the cruise was made, standardized, and stored in 500 mL glass bottles in the laboratory for use at sea. The 0.2526 M HCl solutions were made from 1 M Mallinckrodt™ standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater (~0.7 M). The acid was standardized using a coulometric technique by Millero's group (RSMAS) and Dickson's group (Taylor and Smith, 1959; Marinenko and Taylor, 1968). Both results agree to ±0.0001 N.

VOLUME OF THE CELLS

The volumes of the cells were determined in the laboratory by making weight titrations of Gulf stream seawater (S ~ 36). The TAlk of this water was determined by making a number of titrations. The volume was determined by comparing the values of TAlk obtained for Gulf stream seawater with open (weighed amount of seawater) and closed cells (V_{cell} = Talk × V_{HCl}(open) / V_{HCl}(closed)). The density of seawater at the temperature of the measurement (25 °C) was calculated from the international equation of state of seawater (Millero and Poisson, 1981). The nominal volume of all cells is approximately 200 mL. If the cells were modified during the cruise, adjustments were made to the volumes using the daily titrations on low nutrient surface seawater and CRMs.

VOLUME OF TITRANT

The volume of HCl delivered to the cell is traditionally assumed to have small uncertainties (Dickson, 1981) and equated to the digital output of the titrator. Calibrations of the burettes of the Dosimats were done with Milli-Q™ water at 25 °C. Since the titration systems are calibrated using standard solutions, this error in the accuracy of volume delivery will be partially canceled and included in the value of cell volumes assigned.

EVALUATION OF THE CARBONATE PARAMETERS

The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, $pH_{equiv} = 4.5$, according to the exact definition of total alkalinity (Dickson, 1981)

$$\begin{aligned} TAlk &= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] \\ &\quad + [SiO(OH)_3^-] + [HS^-] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \end{aligned} \tag{9}$$

At any point of the titration, the total alkalinity of seawater can be calculated from the equation

$$\begin{aligned} (V_0 \times TAlk - V \times N) / (V_0 + V) &= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] \\ &\quad + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [HS^-] + [NH_3] - [H^+] \\ &\quad - [HSO_4^-] - [HF] - [H_3PO_4] \end{aligned} \tag{10}$$

where V_0 is the initial volume of the cell or the sample to be titrated, N is the normality of acid titrant, and V is the volume of acid added. In the calculation all the volumes are converted to mass using the known densities of the solutions.

A FORTRAN computer program has been developed to calculate the carbonate parameters (pH_{sw}, E*, TAlk, TCO_2, and pK_1) in Na_2CO_3, TRIS, and seawater solutions. The program is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982) and Dickson (DOE, 1991). The fitting is performed using the STEPIT routine (J.P. Chandler, Oklahoma State University, Stillwater, OK 74074). The STEPIT software package minimizes the sum of squares of residuals by adjusting the parameters E*, TAlk, TCO_2 and pK_1. The computer program is based on equation (10) and assumes that nutrients such as phosphate, silicate and ammonia are negligible. This assumption is valid only for surface waters. Neglecting the concentration of nutrients in the seawater sample does not affect the accuracy of TAlk, but does affect the carbonate alkalinity.

The pH and pK of the acids used in the program are on the seawater scale, $[H^+]_{sw} = [H^+] + [HSO_4^-] + [HF]$ (Dickson, 1984). The dissociation constants used in the program were taken from Dickson and Millero (1987) for carbonic acid, from Dickson (1990a) for boric acid, from Dickson and Riley (1979) for HF, from Dickson (1990b) for HSO_4^- and from Millero (1995) for water. The program requires as input the concentration of acid, volume of the cell, salinity, temperature, measured emf (E), and volume of HCl (V_{HCl}). To obtain a reliable TAlk from a full titration at least 25 data points are collected (9 data points between pH=3.0 to 4.5). The precision of the fit is less than 0.4 µmol/kg when pK_1 is allowed to vary and 1.5 µmol/kg when pK_1 is fixed. Our titration program has been compared to the titration programs used by others (Johansson and Wedborg, 1982; Bradshaw et al.,1981; Bradshaw and Brewer, 1988) and the values of TAlk agree to within ±1 µmol/kg. The performance of our three titration systems has been monitored by titrating CRM Batch #16 that have a known TCO_2 and constant TAlk. The precision of the values of TAlk on these CRMs was ±2 µmol/kg throughout this cruise. All measured values of TAlk were normalized to the CRM value (2303 µmol/kg) obtained in the laboratory.

2.3 UNDERWAY MEASUREMENT METHODS

2.3.1 Underway fCO_2 Measurements

Underway fCO_2 measurements were performed quasi-continuously whenever the MALCOLM BALDRIGE was out at sea, and out of territorial waters if no science clearance was obtained. The survey department of the BALDRIGE maintained the instrument during the cruise. The data shown here include the transects from Miami to Fortaleza (Leg 0) and from Iceland to Miami (Leg 3).

System description and procedures

The underway system used during the cruise is described in detail in Wanninkhof and Thoning, (1993). The shipboard automated underway fCO_2 system runs on an hourly cycle during which three gas standards, a headspace sample from the equilibrator, and an ambient air sample are analyzed using a LI-COR™ infrared analyzer.

The IR analyzer/detector's voltage output is measured once per second with a Keithley™ (model 195 A) digital multimeter, 1-minute averages are calculated and stored on the hard disk of an MS-DOS™ computer. The mass flow controllers (MFCs) connected to the reference and sample inlet of the IR, the mass flow meter's (MFM's) measurement of the intake rate of ambient air and recirculation rate of the headspace of the equilibrator, the back pressure in the air and equilibrated air lines, and two thermistors readings of the water temperature in the equilibrator are all logged at 1-

minute intervals as well.

Compressed gas standards with nominal mixing ratios of 300, 350, and 400 ppm flow through the IR analyzer for 5 minutes each hour at 75 mL/min for calibration. The 300 ppm standard flows continuously at 50 mL/min through the reference side of the IR analyzer (detector) as well. All reference tanks undergo a pre- and post-cruise calibration at NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) against standards certified by the World Meteorological Organization (WMO).

The equilibrator, which was designed by R. Weiss of SIO, is made from a large (58 cm H x 23 cm ID) Plexiglas™ chamber. The equilibrator has a shower head in the top through which surface seawater is forced at a rate of 15-20 L/min. The water spray through the 16 L head space and the turbulence created by the jets impinging on the surface of 8 L of water, cause the gases in water and headspace to equilibrate. A drain 20 cm from the bottom of the equilibrator discharges excess water from the system over the side of the ship. Air in the equilibrator head space is circulated with an AIR CADET™ pump (model 7530-40) at 6 L/min in a closed loop through a MFM and back pressure regulator. During 23 minutes of each hour, 75 mL/min is teed off upstream of the back pressure regulator through a MFC and into the 12 mL sample cell of a LI-COR™ (model 6251) non-dispersive infrared (IR) analyzer. The air removed from the equilibrator through the IR analyzer is replaced with ambient air through an intake/vent line that runs to the outside of the ship. The introduction of the ambient air into the equilibrator chamber during sampling of the headspace results in an error in the determination of the equilibrated head space composition which is a function of water flow rate. Tests performed during the cruise showed that an appreciable bias (≈ 1 µatm towards ambient air values) could be introduced when water flow rates were greater than 20 L/min. The headspace equilibration time, as determined by return to equilibrium after perturbation by adding nitrogen to the head space, is approximately 2.5 minutes. The vent line on the equilibrator is necessary to assure that the pressure in the head space of the equilibrator remains at atmospheric value.

During underway sampling operations ambient air is drawn through 100 m of 0.37 cm OD Dekoron™ tubing from the bow mast of the ship at a rate of 6 to 8 L/min. During 22 minutes of each hour, ambient air mixing ratios are measured in the IR analyzer by teeing off the air line at a flow rate of 75 mL/min.

Underway fCO_2 Calculations

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial fit through the response of the detector versus mixing ratio of the standards. Due to the need for sufficient time to flush the sample cell and lines leading to the IR from the previous gas, the first three minutes of each analysis run are not used in the calculations. The subsequent one-minute readings for each analysis are averaged, yielding one 19-minute average ambient air mixing ratio and one 20-minute average equilibrated headspace mixing ratio per hour. Typical standard deviations for air values are ±0.1 ppm and ±0.3 ppm for equilibrated headspace.

Mixing ratios of dried equilibrated headspace and air must be converted to fugacity of CO_2 in water and water saturated air in order to determine the driving force for the air-sea CO_2 flux. For ambient air, assuming 100% water vapor content, the conversion is:

$$fCO_{2a} = XCO_{2a}\ (P - pH_2O)\ \exp(B_{11} + 2\delta_{12})\ P/RT_{SW} \quad (11)$$

where pH_2O is the water vapor pressure at the sea surface temperature (T_{sw}), P is the atmospheric pressure, R is the ideal gas constant and T_{sw} is the sea surface temp (in K) as measured at the bow intake with a thermosalinograph. The exponential term is the fugacity correction where B_{11} is the second virial coefficient of pure CO_2 ($B_{11} = -1636.75 + 12.0408\ T - 0.0327957\ T^2 + 3.16528 \times 10^{-5}\ T^3$) and δ_{12} ($= 57.7 - 0.118\ T$) is the correction for an air-CO_2 mixture (Weiss, 1974).

The calculation for the fugacity in water includes an empirical temperature correction term for the increase of fCO_2 due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.2 °C warmer than intake temperature. First the fugacity of the air in equilibrium in the headspace (fCO_{2eq}) is calculated according to:

$$fCO_{2eq} = XCO_{2eq}\ (P - pH_2O_{eq})\ \exp(B_{11} + 2\sigma_{12})\ P/RT_{eq} \qquad (12)$$

where pH_2O_{eq} is the water vapor pressure at the temperature of the water in the equilibrator and T_{eq} is the temperature of the water in the equilibrator (in °K). The fCO_{2eq} is converted to the fugacity in surface seawater fCO_{2w} by applying an empirical correction suggested by Weiss et al., (1982):

$$\Delta\ln(fCO_2)/\Delta t_{SW} = 0.03107 - 2.785\ 10^{-4} t - 1.839\ 10^{-3} \ln(fCO_2) \quad (13)$$

where t is the SST in °C.

Comments on data

The cruise track is shown in Figure 1 and the data are presented in graphical format for each segment in Figures 21 to 25. The data are plotted either versus latitude or longitude depending if the track trended north-south or east-west. Figures 21 though 24 have a top panel with fCO_{2w} (filled circles with dashed line) and fCO_{2a} (empty circles) and a bottom panel with a double Y graph depicting SST (empty circles), and salinity (filled circles dashed line) as determined from the thermosalinograph at the bow intake. The figures show the large scale features along the track. Between Miami and Fortaleza the waters are on average supersaturated by approximately 20 μatm, except in the region with very low salinity (caused by Amazon

River outflow) near 10°N and 55°W which is undersaturated (Figure 21). The irregularities between 50°W and 40°W are caused by the ship steaming in a grid pattern in a region with significant gradients. Figure 22 is the transect from 5°S to Iceland. The ocean is supersaturated up to 40°N at which point the N. Atlantic turns into a strong sink. The low salinity region at 8°N, caused by excess precipitation and perhaps river outflow, is a CO_2 sink as well. The transect from Iceland to Miami shows undersaturation from Iceland to 50°E, the region from 50°E to 40°E is close to saturation while the region further to the southwest is a source for CO_2.

During the cruise segment from Fortaleza to 3°N, 25°W the air analyses drifted significantly during the 20-minute sampling period and were above the expected seasonal values for the region. This behavior was also observed for several other cruises with this system. Replacement and/or cleaning of nearly all the components in the air line (tubing to the bow, mass flow meters, and solenoids) eliminated the problem. We hypothesize that sea salt aerosols coated the air intake lines and that CO_2 was gradually released from the carbonate and bicarbonate salts due to heating of the lines and acidic air. The air mixing ratios for the region were extrapolated based on values before and after the problem arose. Stations of the NOAA/CMDL flask network (Ascension Island, and Key Biscayne, FL) were too far removed to improve the extrapolation.

The thermistors in the equilibrator were calibrated before the cruise and compared to 6-hourly readings of a mercury thermometer in the equilibrator throughout the cruise. Based on the pre-cruise calibrations the resistances of the thermistor were converted to temperatures using a second order polynomial fit. The agreement with the shipboard thermometer readings was reasonable (Figure 25) except for SST < 12 °C because the laboratory calibration was only performed down to 12 °C. A secondary correction was applied to the thermistor based on the comparison between the T_{eq} and the 6-hour thermometer readings. A fifth-order least squares best fit polynomial was applied to the difference in T_{eq} and $T_{thermometer}$ versus T_{eq} (Figure 25). This correction was subsequently applied to the T_{eq} values used to calculate the fCO_{2eq}.

The air XCO_2 values were compared at 6 locations with duplicate flask samples obtained from the bow of the ship during the cruise and analyzed at CMDL. Table 4 shows that the results agree to better than 1 ppm, suggesting good accuracy of the calibrated infrared analyzer used during the cruise.

Table 8: Dependence of headspace mixing ratio on water flow rate through equilibrator (from Chen, et al. 1995).

Flow	Mixing Ratio[A]	Equil.	Corr. X[B]	%Equil.[C]
20	389.57 ±0.06	24.05	389.57	96.7
15	390.72 ±0.25	24.05	390.72	99.6
10	391.54 ±0.35	24.09	390.87	
15	389.75 ±0.12	24.04	389.91	97.6
20	388.28	24.00	389.10	95.6

Comments:
a: The air mixing ratio during the test was 351.0 ± 0.2 ppm.
b: Corr. X is the ratio normalized to 24.05°C using $\delta X_{CO_2}/\delta T = 0.0423$.
c: percent equilibration is defined as:
$(X_{CO2}$water-air) @x L/min / $(X_{CO2}$water-air) @10 L/min * 100

Table 9: Comparison of in situ air values vs. flask samples analyzed at CMDL

J.D.	Lat	Long	AIR CO2	s.d.	CMDL 1	2	diff.
190.83	-1.29	-25.02	356.99	0.12	357.2	356.98	-0.1
198.08	13.4	-28.89	355.93	0.19	355.94	356.85	-0.47
202.83	22.8	-22.5	353.78	0.07	354.1	354.05	-0.3
217.63	26.64	-25.41	355.39	0.09	355.76		0.37
221.92	15.91	-29	353.61	0.1	353.88	353.83	-0.25
225.83	28.57	-24.36	353.54	0.07	353.8	354.06	-0.39
240.54	61.84	-19.75	348.39	0.09	347.57	347.46	0.88
						Average	-0.14
						St. Dev.	0.46

Comments:
J.D. = fractional Julian day (GMT)
Lat = Latitude (fractional degrees)
Long = Longitude (fractional degrees)
Air CO_2 = air mixing ratio obtained ship board
s.d. = standard deviation of 19 consecutive 1-minute averages
CMDL 1 = results of analysis of flask # 1 performed at NOAA/CMDL
2 = results of analysis of flask # 2 performed at NOAA/CMDL
diff. = difference between air CO_2 value and average of the two CMDL analyses

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The dedication and assistance of the officers and crew of the NOAA ship MALCOLM BALDRIGE is gratefully appreciated and hereby acknowledged. In particular, we would like to thank the Survey Department under the direction of Chief Survey Tech Dennis Sweeney for their capable assistance with the CTD and underway systems.

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APPENDIX A: Contour Plots

This appendix contains contour plots of all hydrographic and chemical parameters, plots of underway measurements (see Section 2.3 for explanation), and plots comparing AOML and U. W. nutrient values. Figures 2 through 20 were generated using Surfer™ for Windows™ version 6.04. Only values with a qc flag value of 2 (good) were used in gridding the data. Gridding was accomplished using the built-in Kriging algorithm with an anisotropy of four and no smoothing. The 0-6000 db plots were created from 140 column by 81 row grids and the 0-1000 db plots were created from 140 column by 34 row grids. Hachures in enclosed contours mark relative minima in the plot. Each contour plot includes a scale bar showing the contour levels used.

Nutrient plots (Figures 9 through 14) were done in two ways for each individual nutrient. Plots labelled "U.W. & AOML" use University of Washington nutrient values for Leg 1 (to about 15° N) and AOML values for all other stations. The plots labelled "AOML" use AOML nutrients for all stations. Figures 26 through 28 show a comparison of AOML and U.W. nutrients with the difference (U.W. value - AOML value) on the Y-axis and the U.W. value on the X-axis.

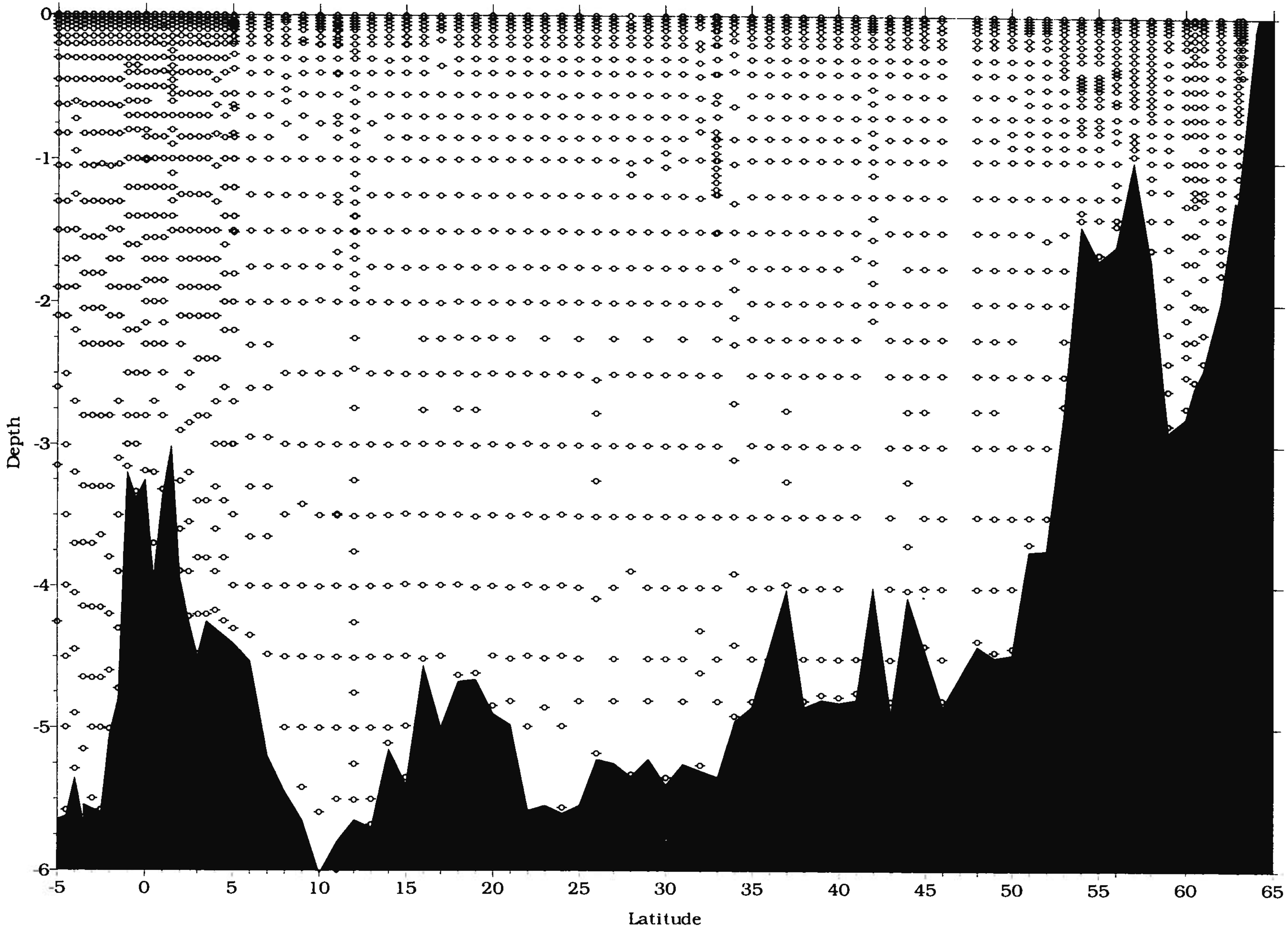


Figure 2: North Atlantic 1993 CTD Bottle Trip Depths

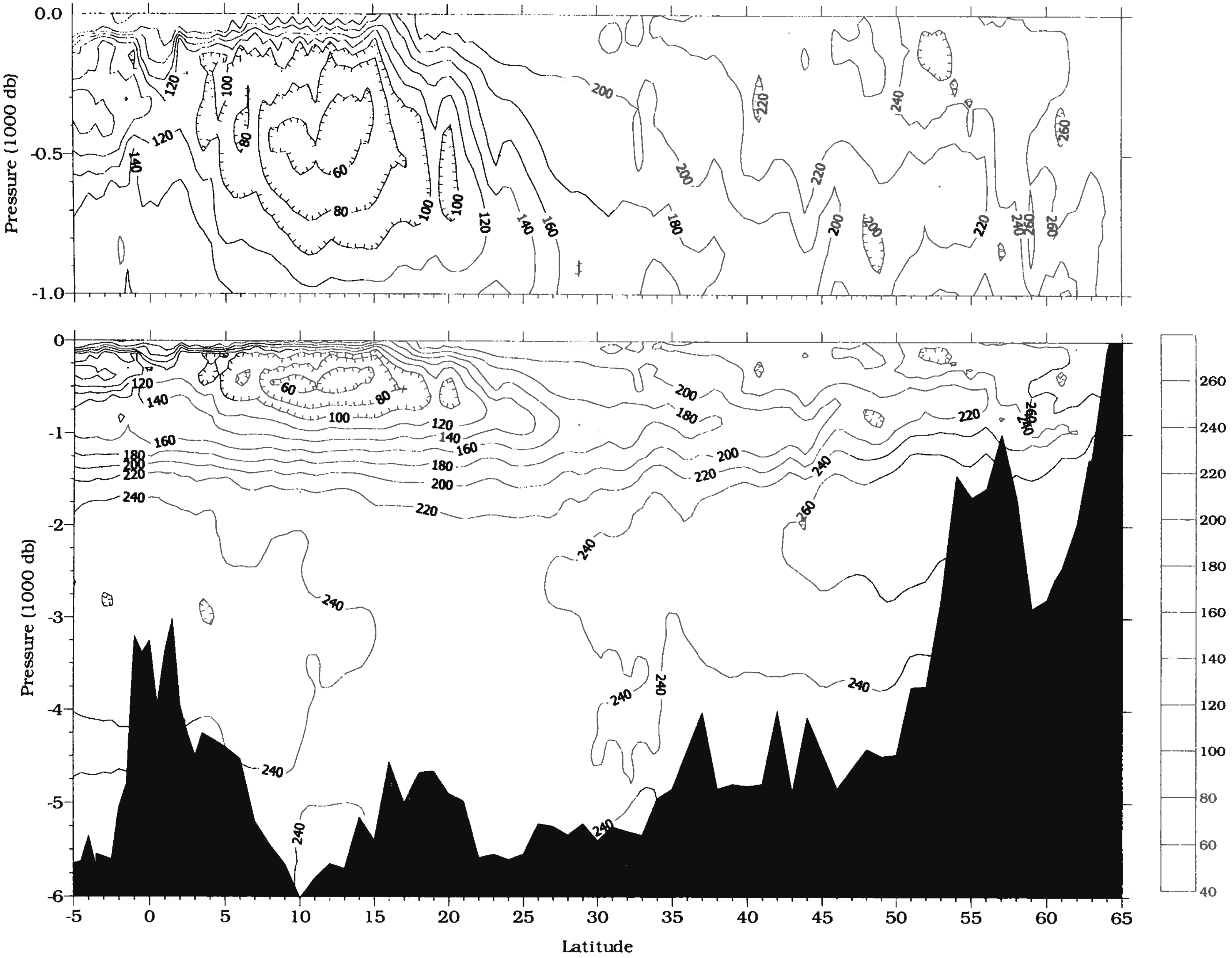


Figure 3: Oxygen (μmol/kg) vs. pressure from NATL 93, based on discrete bottle data.
Note: We recommend adding 7.5 μmol/kg to all O_2 values in this report (see Page 7).

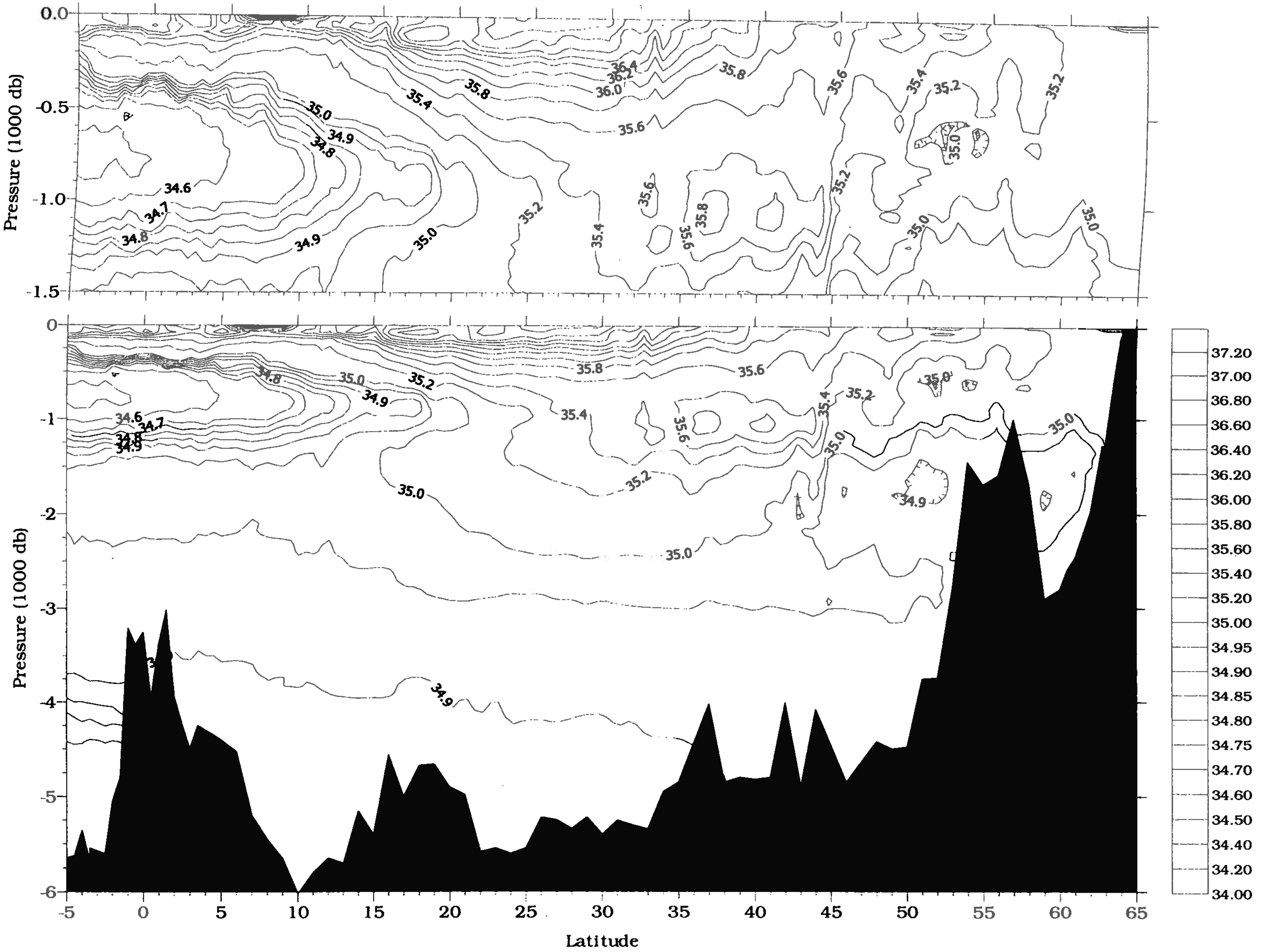


Figure 4: CTD bottle salinity vs. pressure for NATL 93 section.

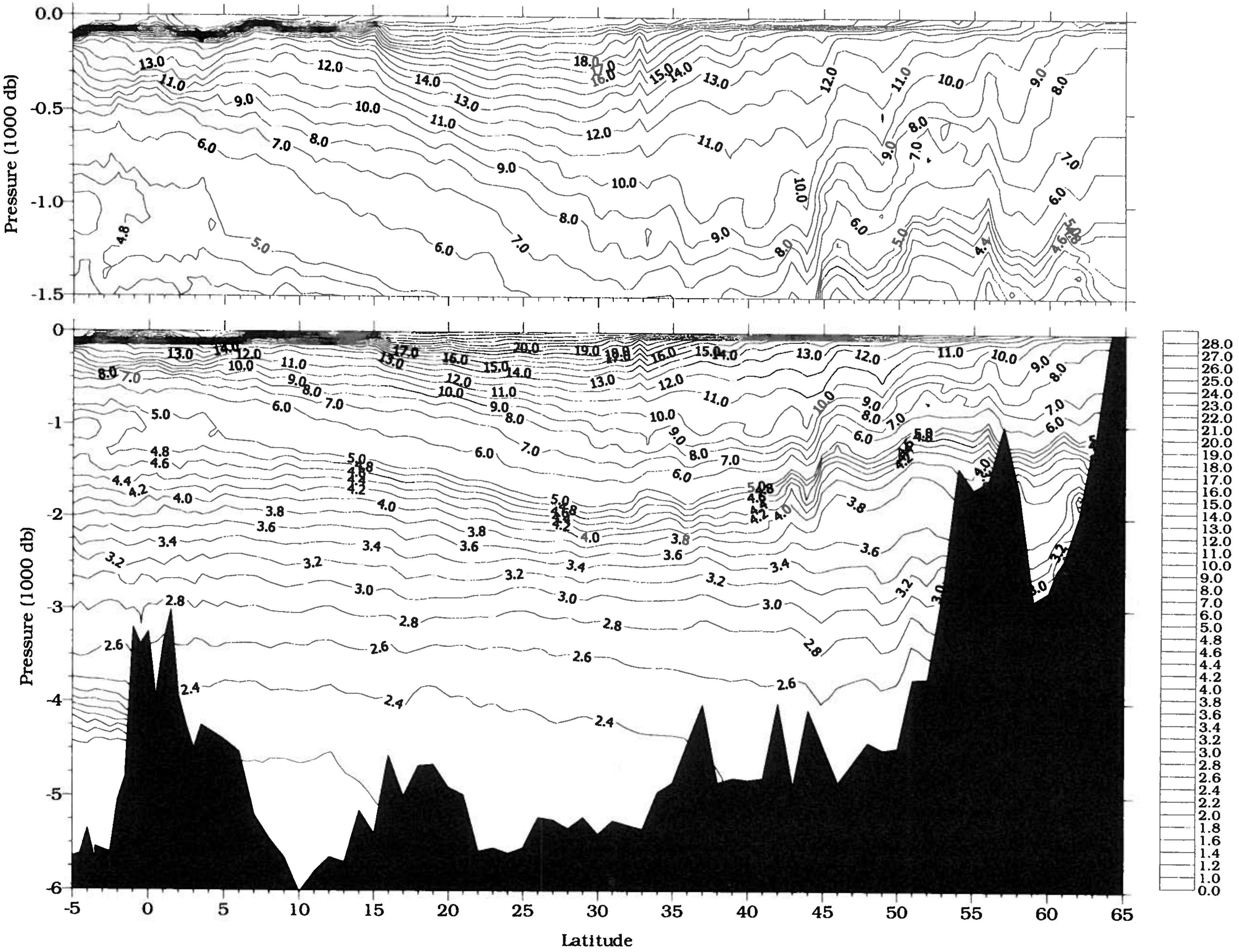


Figure 5: Potential temperature (ºC) vs. pressure from NATL 93 section.

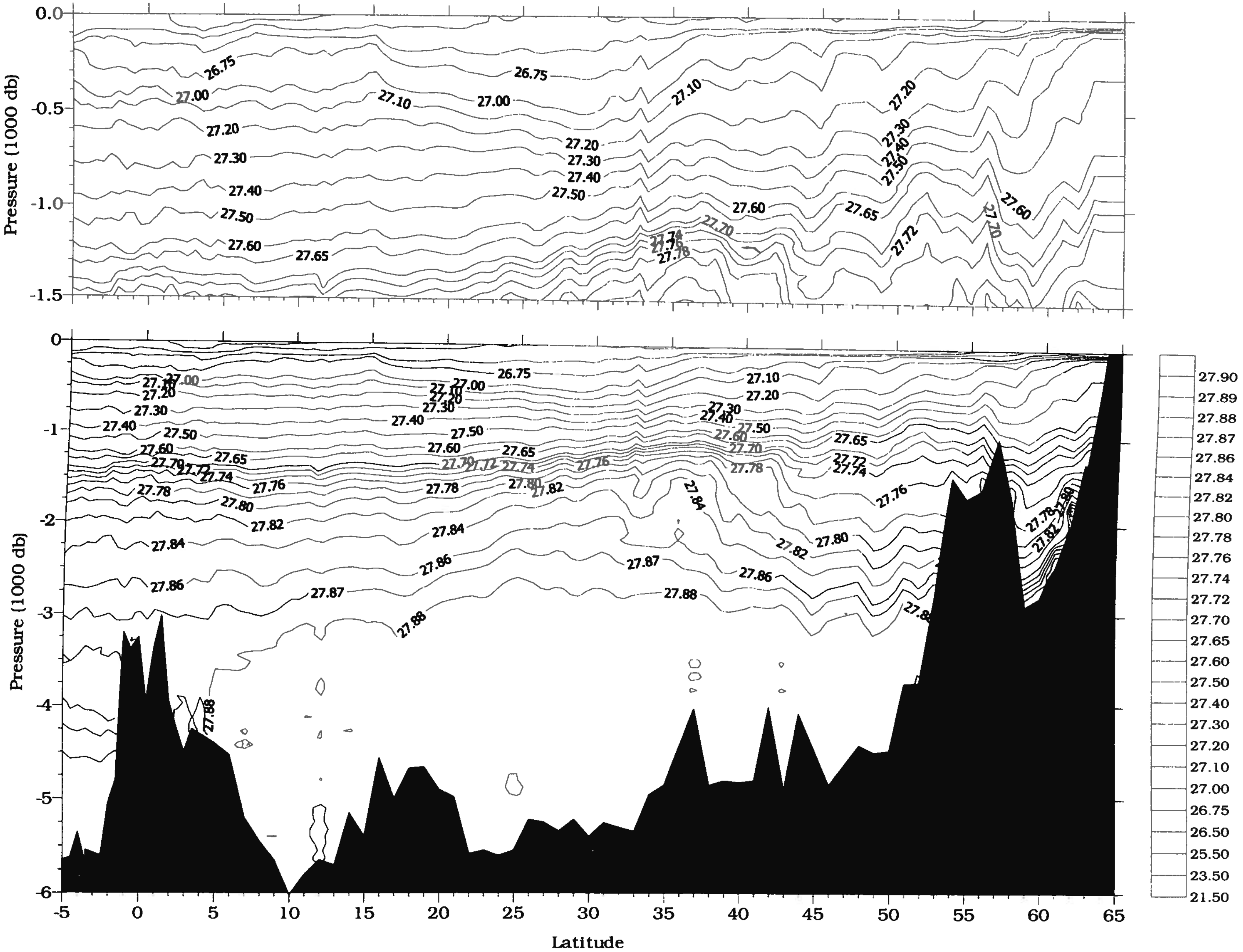


Figure 6: Sigma-theta (kg/m³) vs. pressure for NATL 93 section.

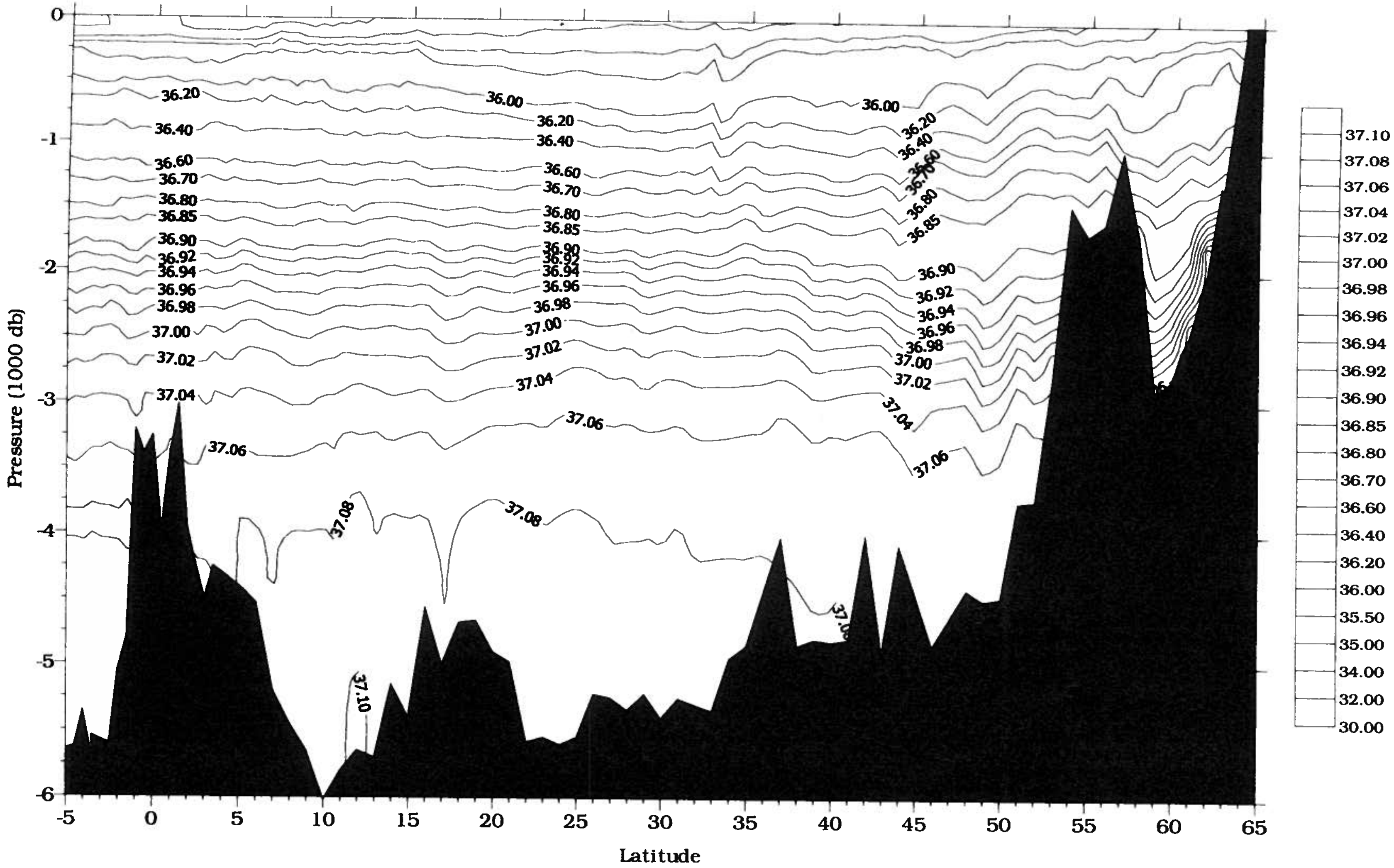


Figure 7: Potential density (sigma-2 in kg/m³) vs. pressure for NATL 93 section.

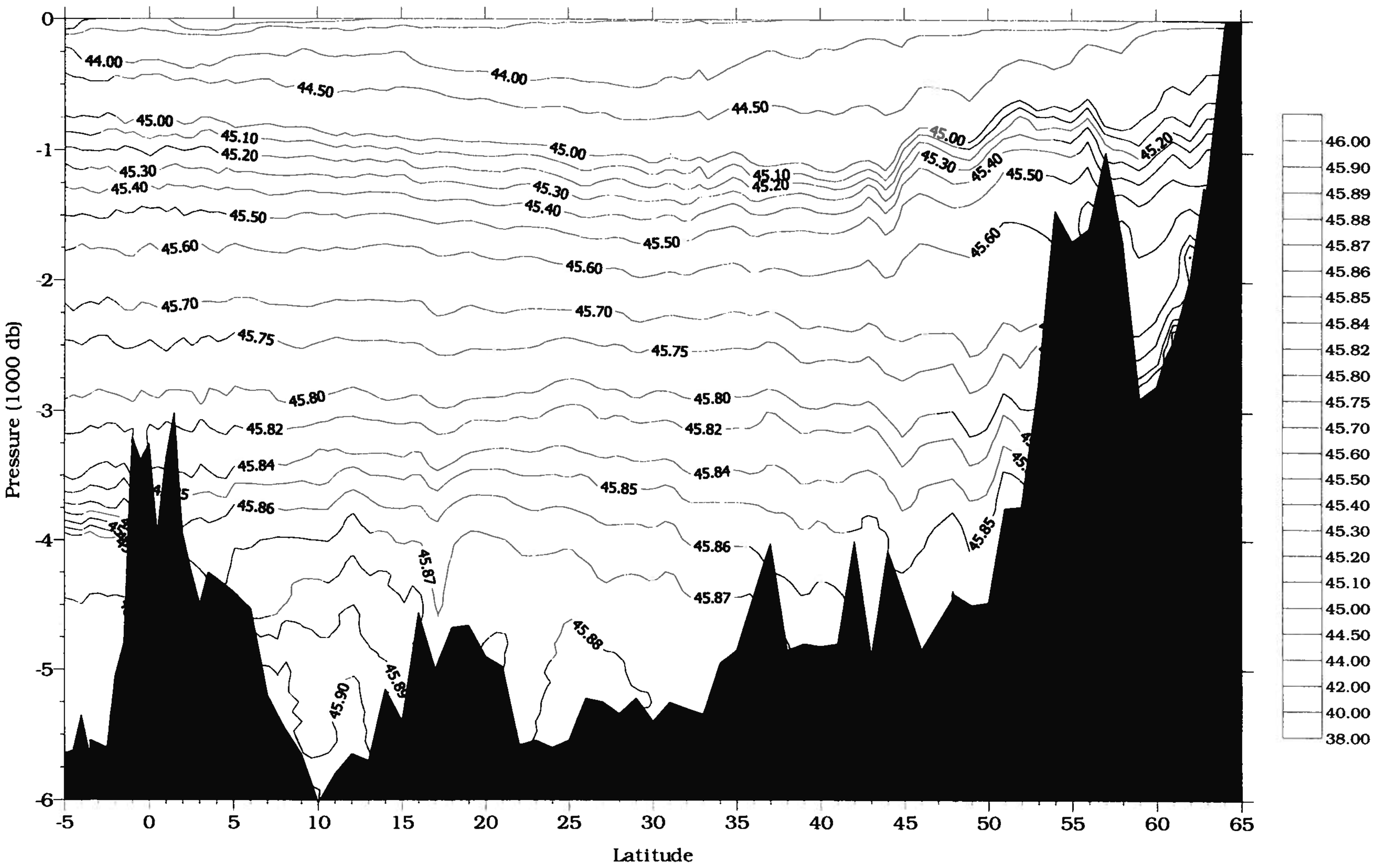


Figure 8: Potential density (sigma-4 in kg/m³) vs. pressure for NATL 93 section.

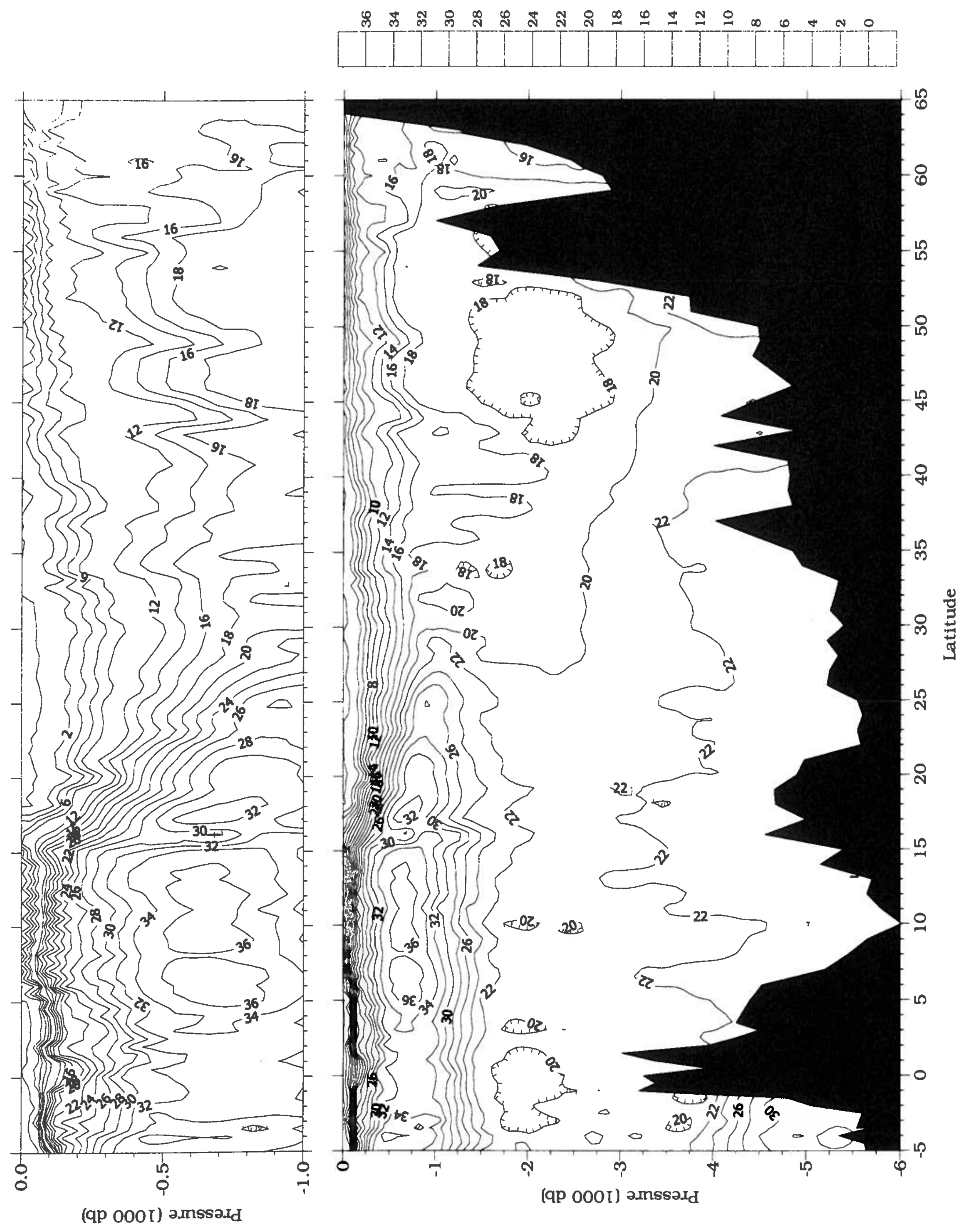


Figure 9: AOML NO$_3$ (μmol/kg) vs. pressure for NATL 93 section.

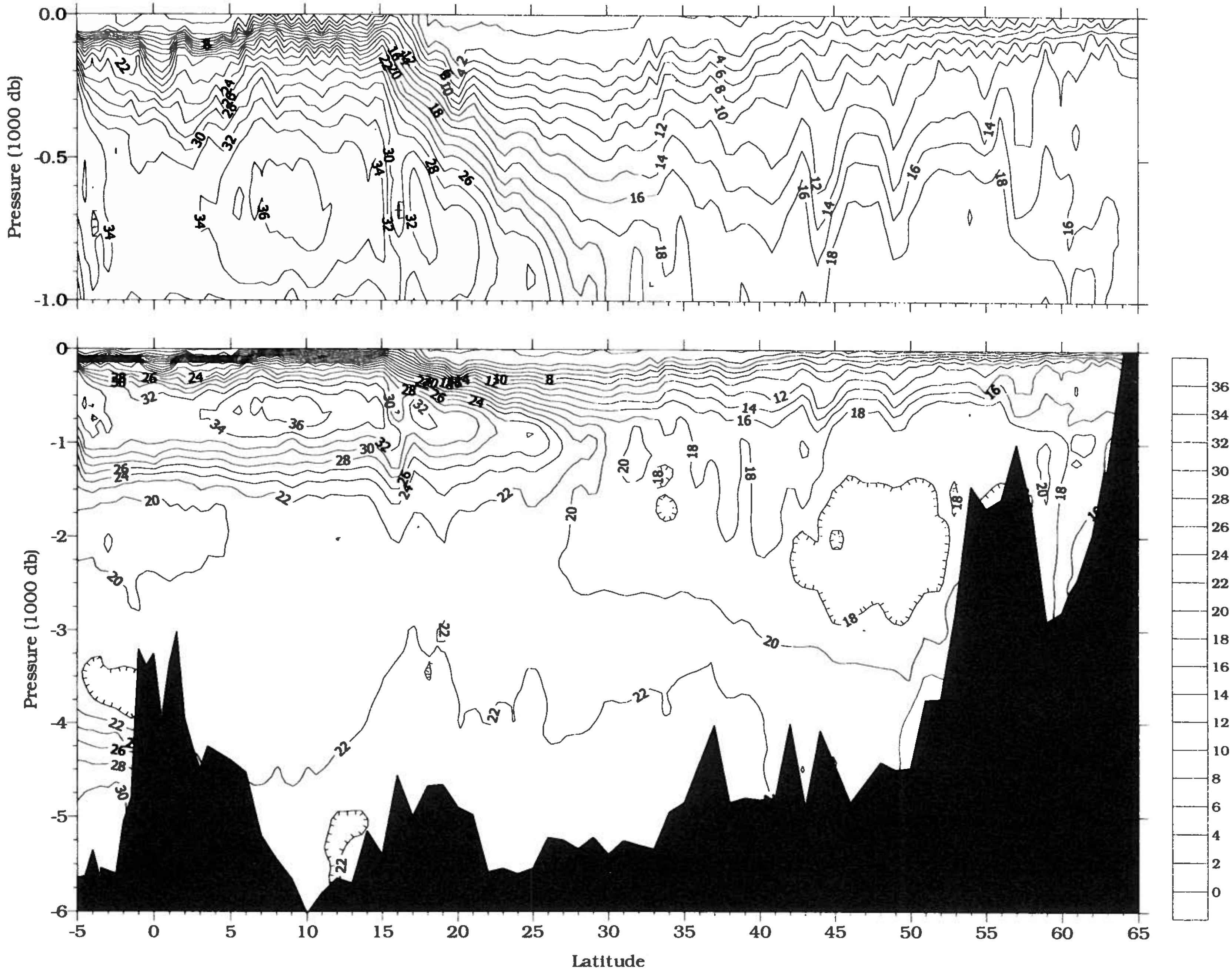


Figure 10: UW & AOML NO_3 (µmol/kg) vs. pressure for NATL 93 section.

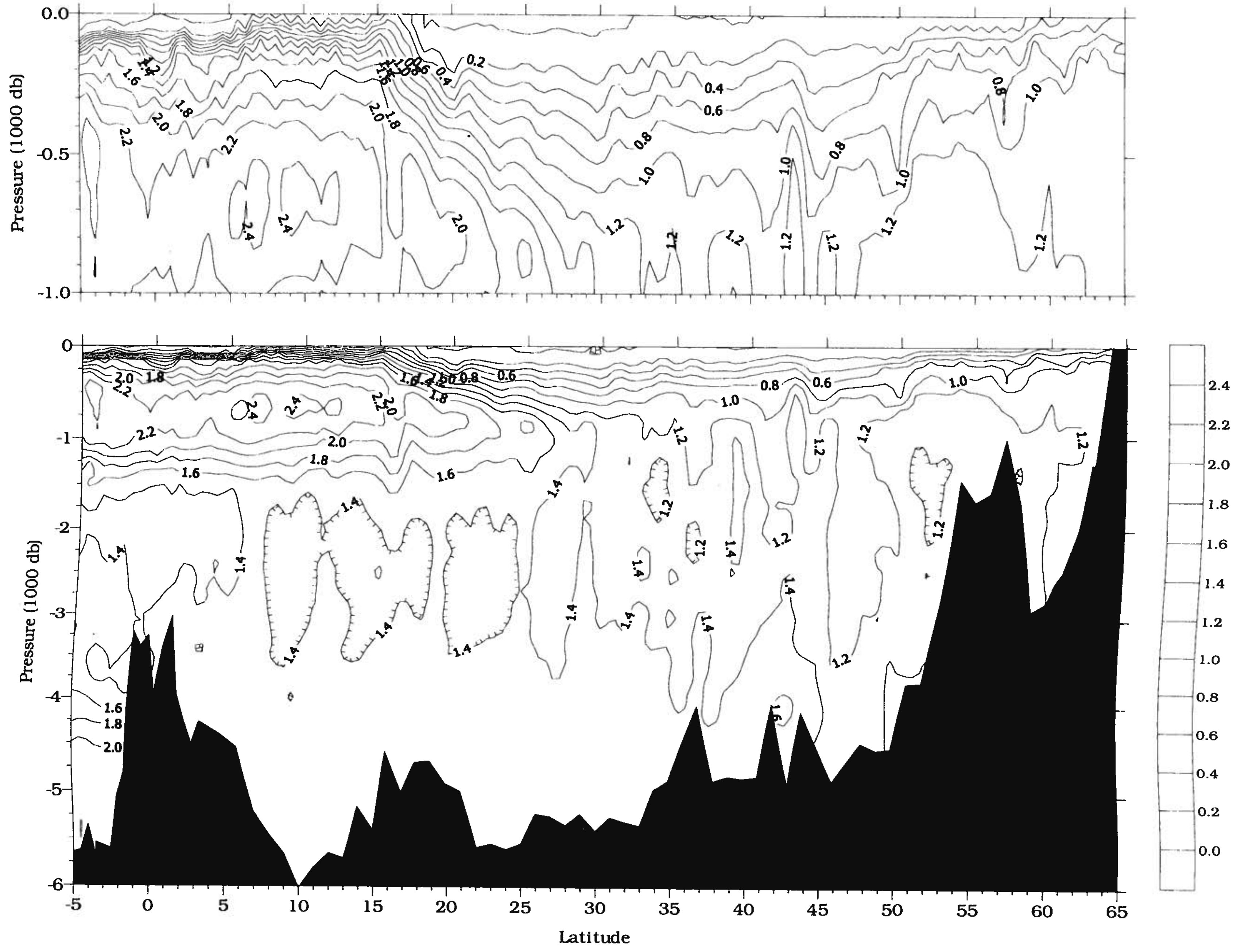


Figure 11: AOML PO_4 (µmol/kg) vs. pressure for NATL 93 section.

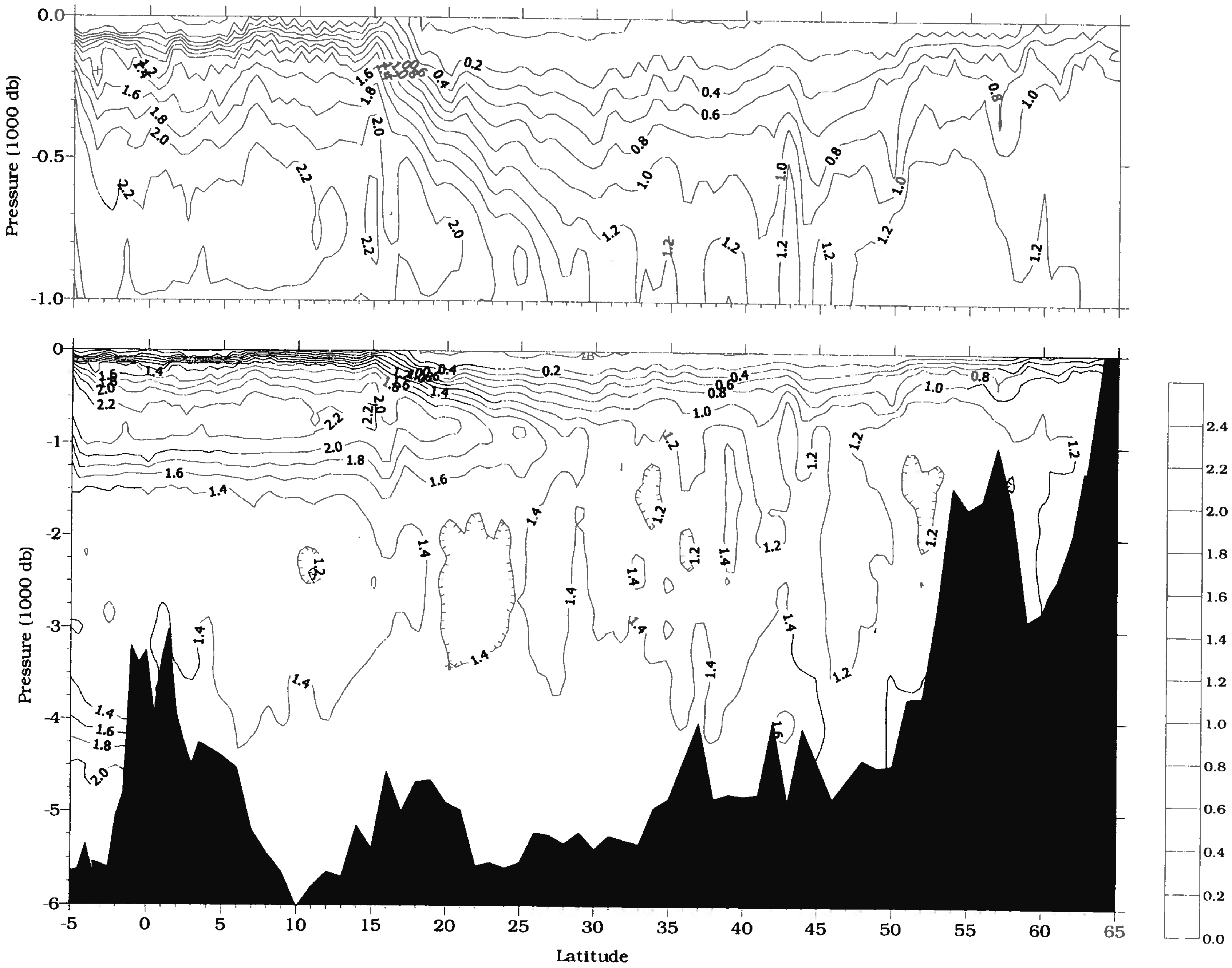


Figure 12: UW & AOML PO_4 (µmol/kg) vs. pressure for NATL 93 section.

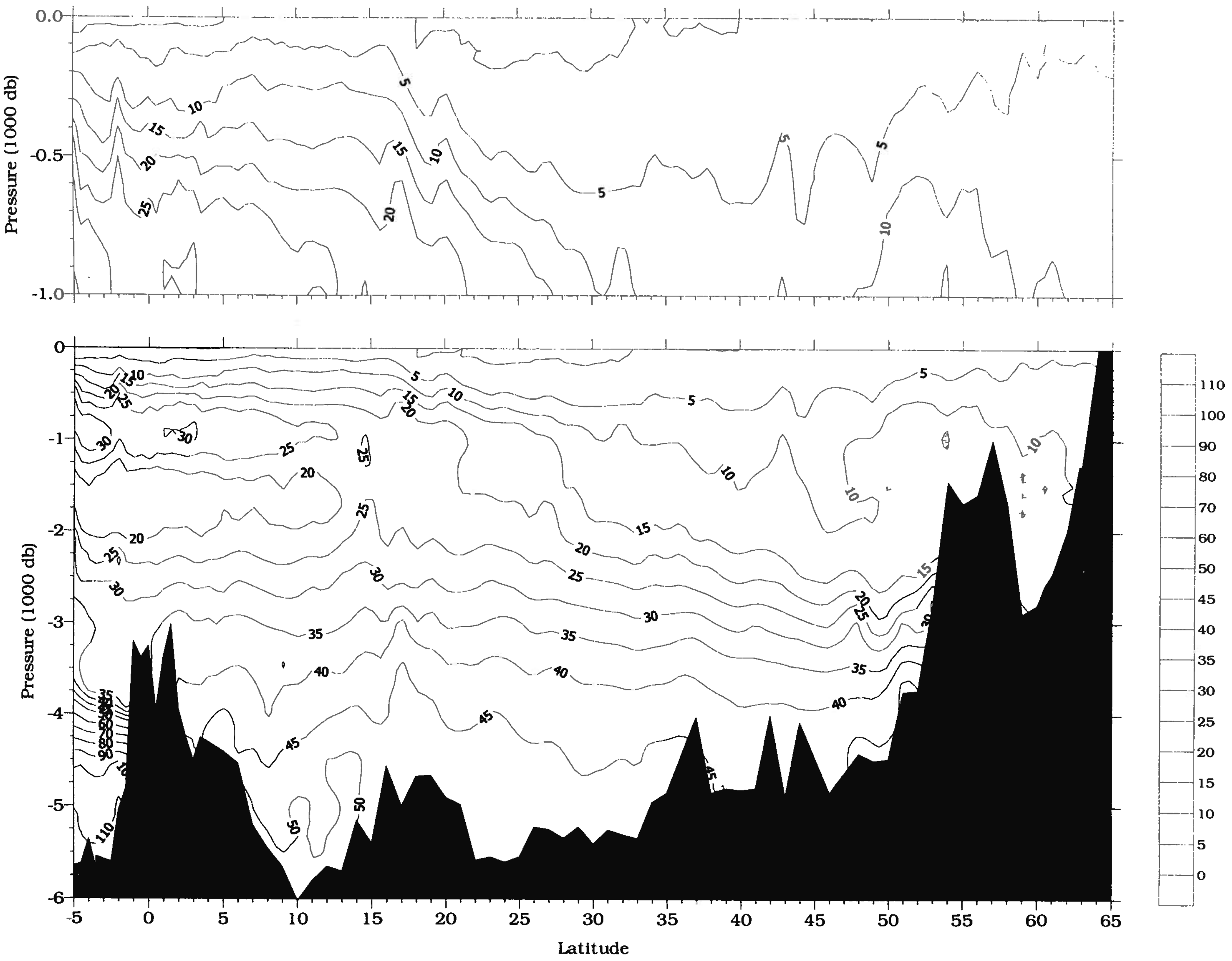


Figure 13: AOML SiO_4 (µmol/kg) vs. pressure for NATL 93 section.

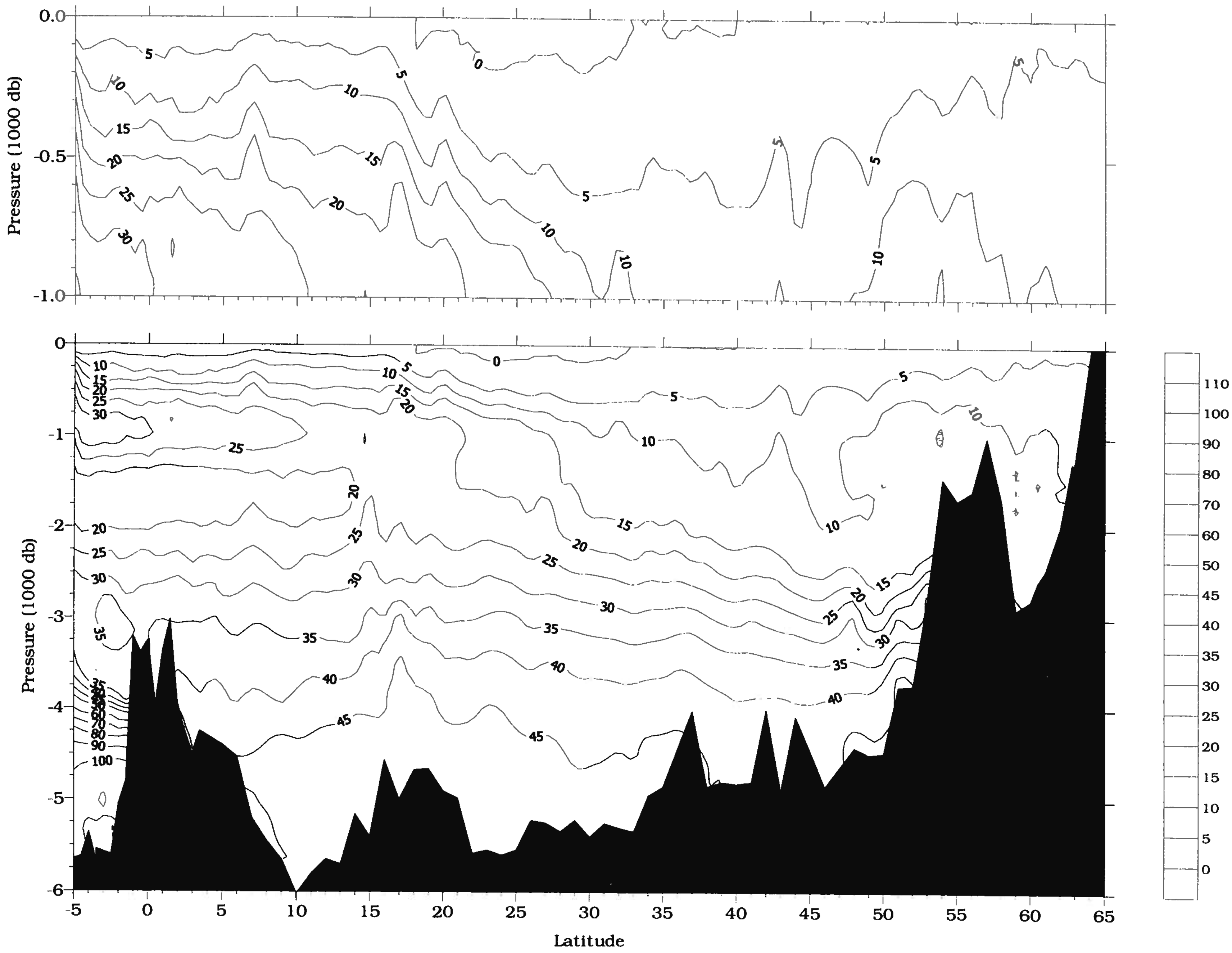


Figure 14: UW & AOML SiO_4 (µmol/kg) vs. pressure for NATL 93 section.

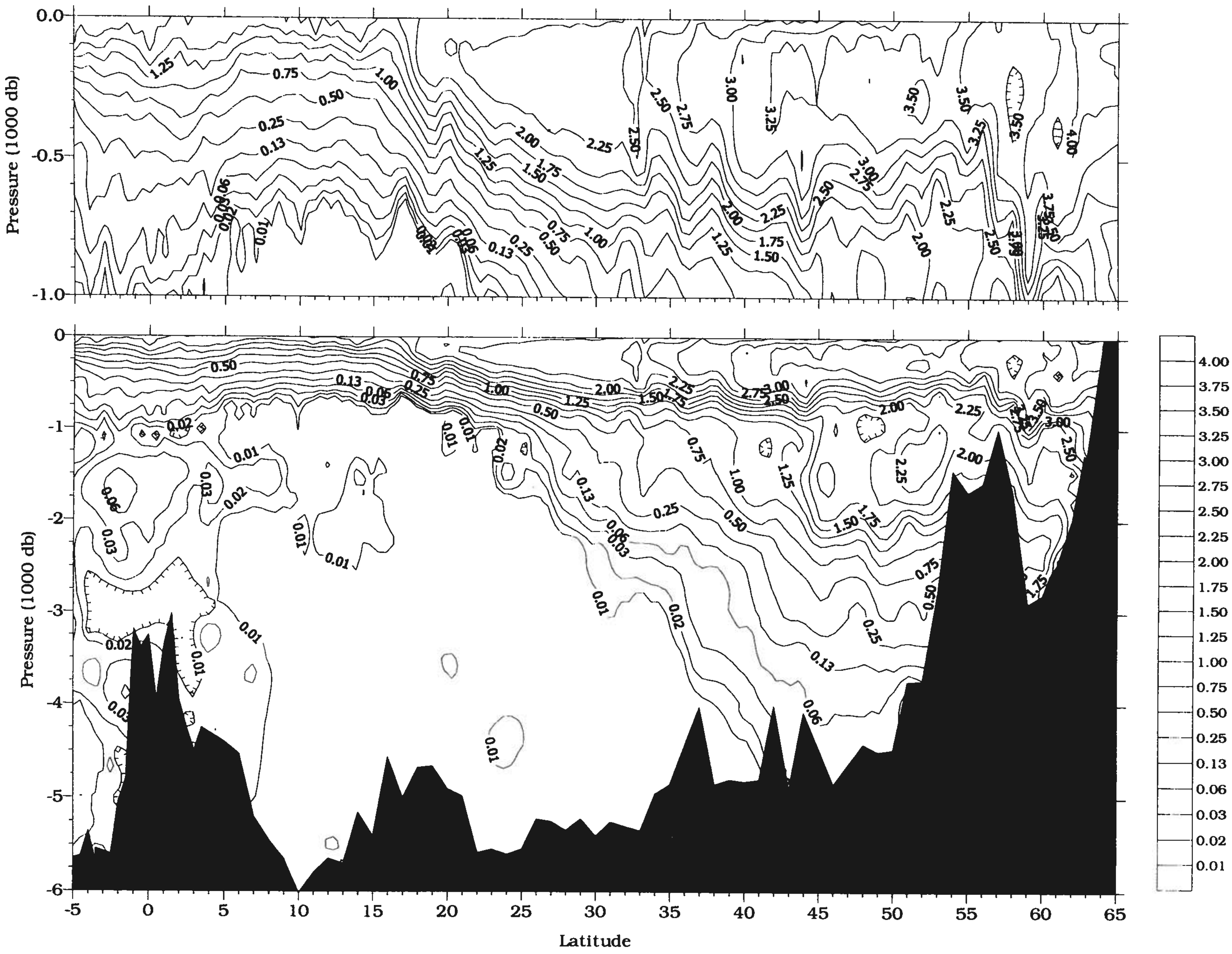


Figure 15: CFC-11 (pmol/kg) vs. pressure for the NATL 93 section.

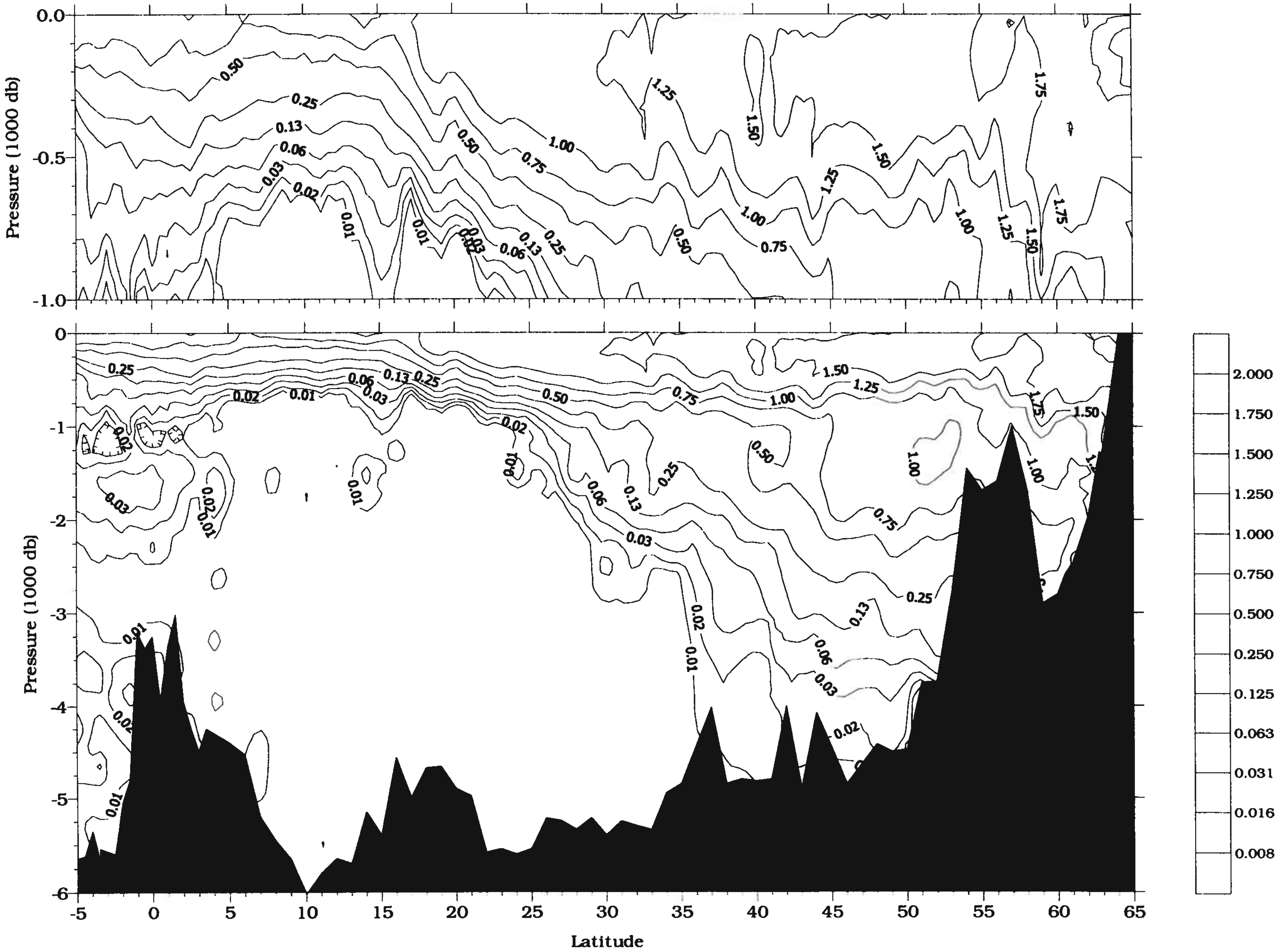


Figure 16: CFC-12 (pmol/kg) vs. pressure for the NATL 93 section.

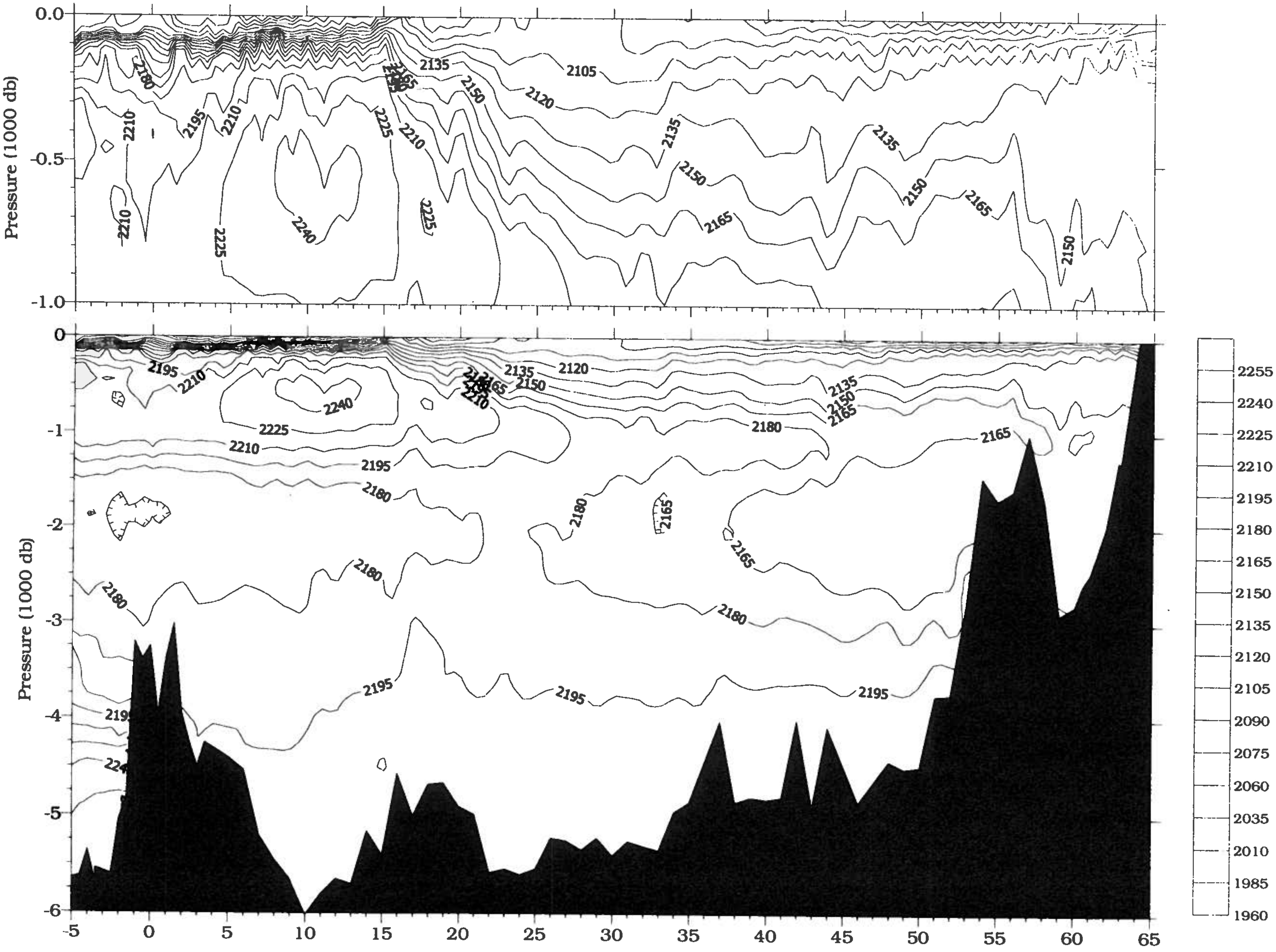


Figure 17: Total CO_2 (μmol/kg) vs. pressure for the NATL 93 section.

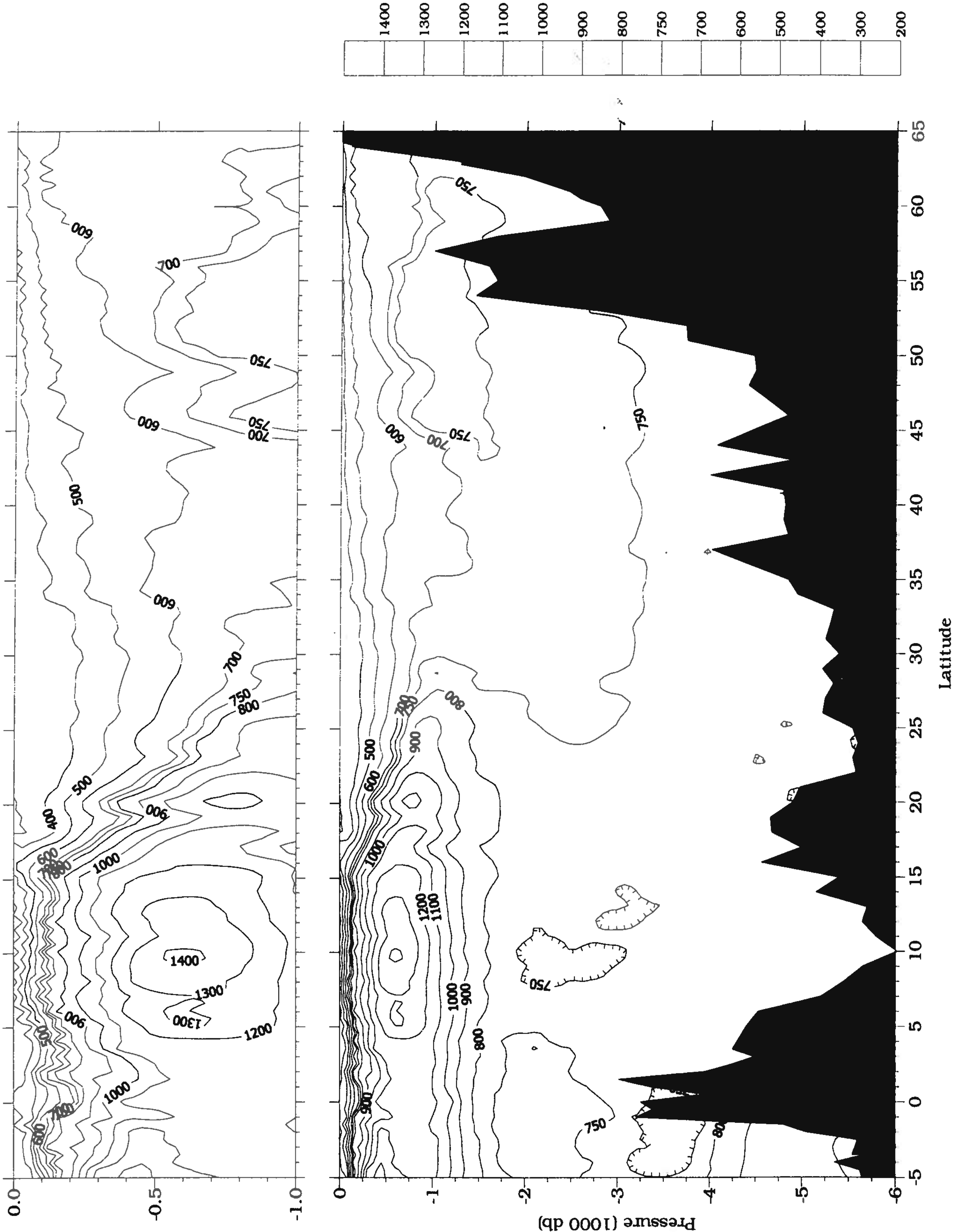


Figure 18: fCO_2 (µatm) vs. pressure for the NATL 93 section.

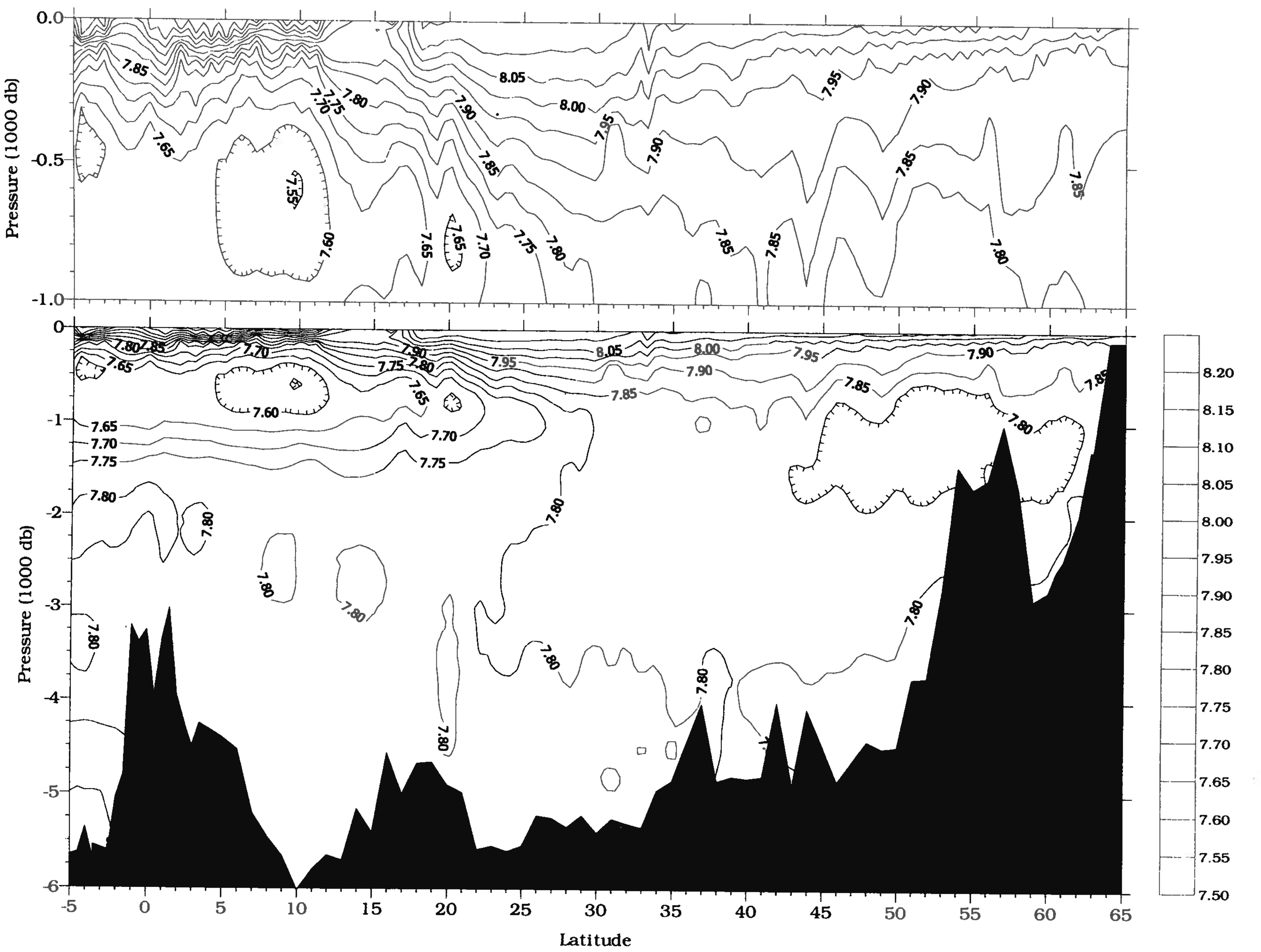


Figure 19: pH vs. pressure for the NATL 93 section.

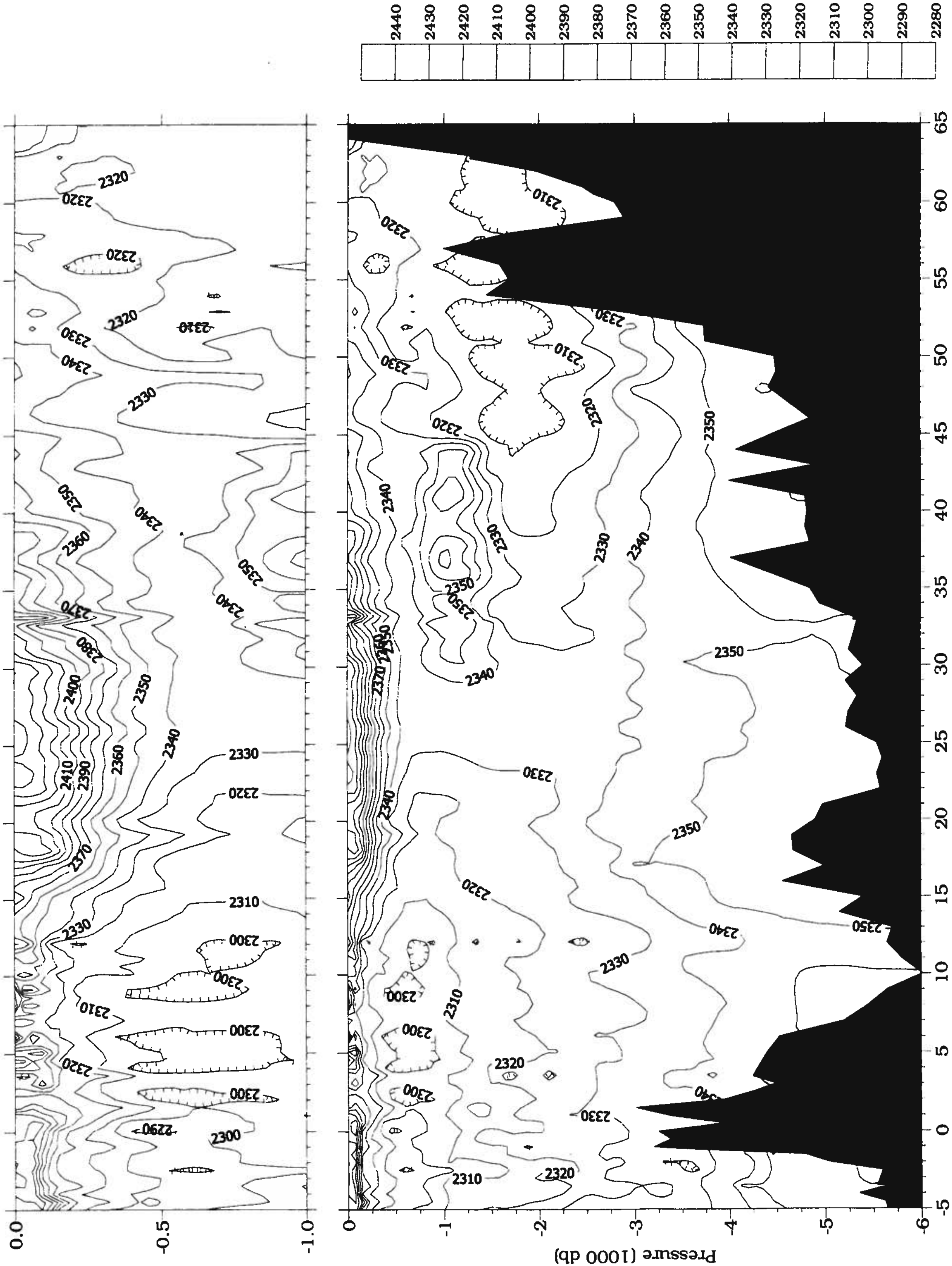
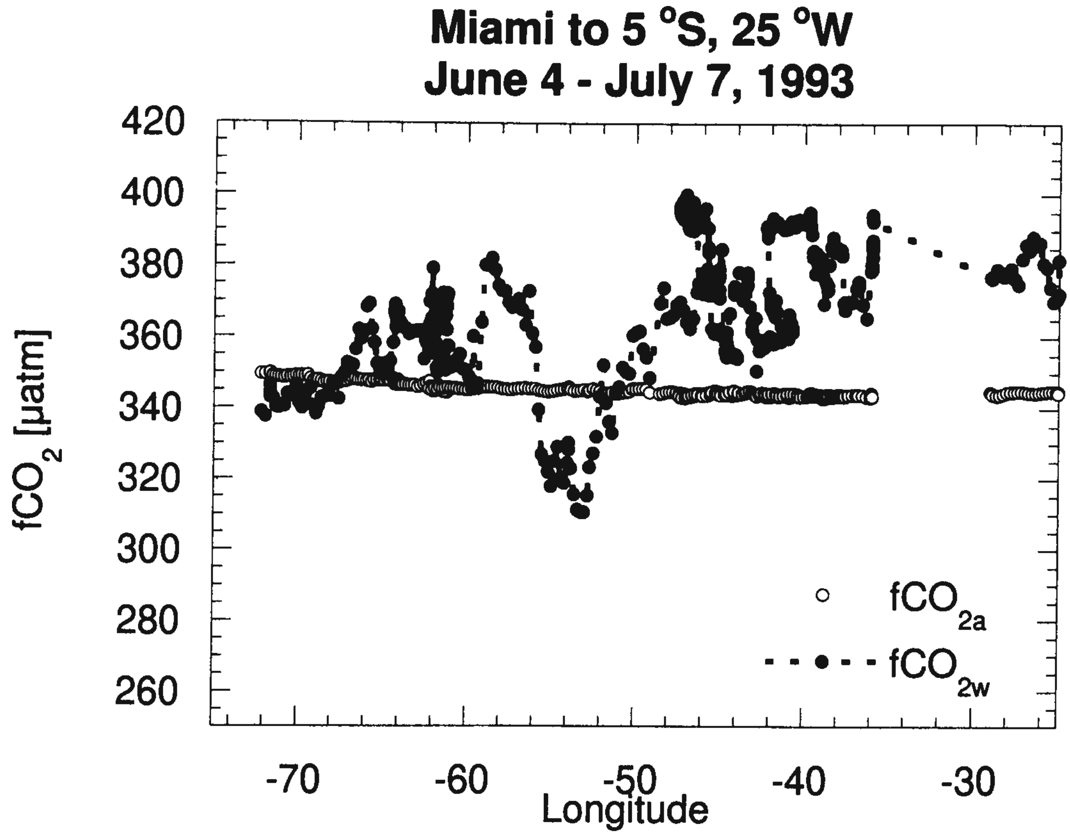


Figure 20: Total alkalinity (µEq/kg) vs. pressure for the NATL 93 section.



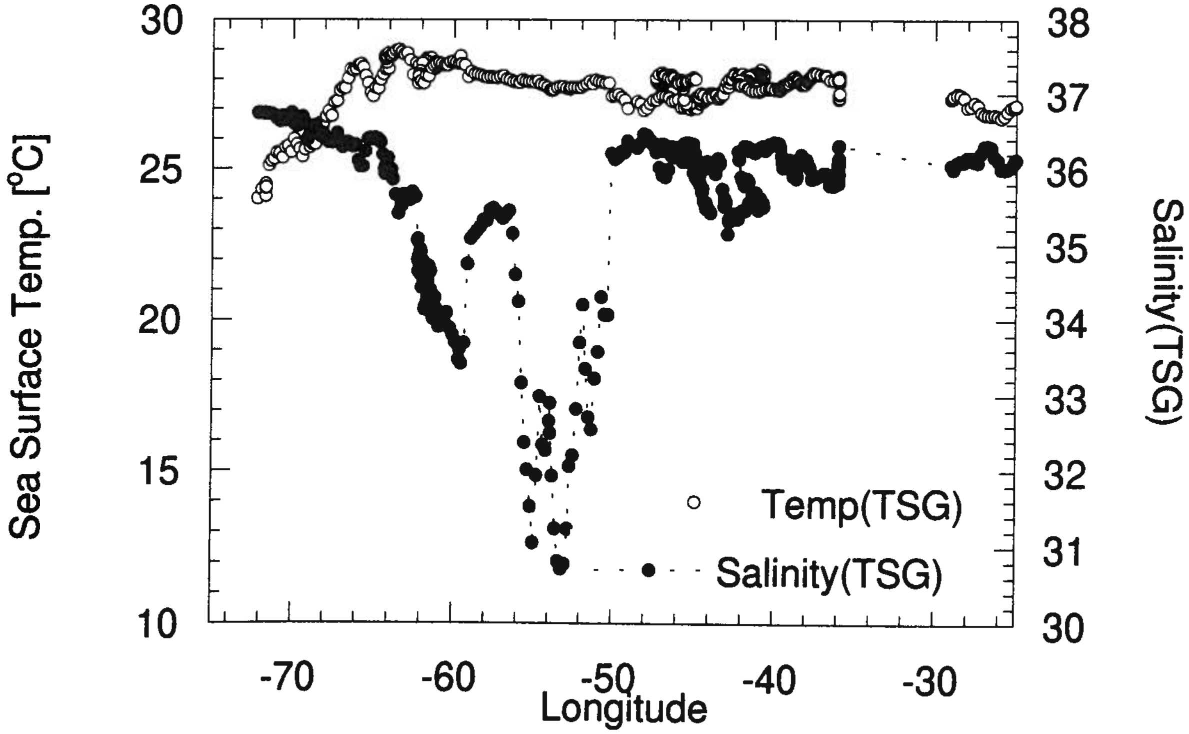


Figure 21: fCO_2 & Sea Surface Temperature for NATL93 Leg 0

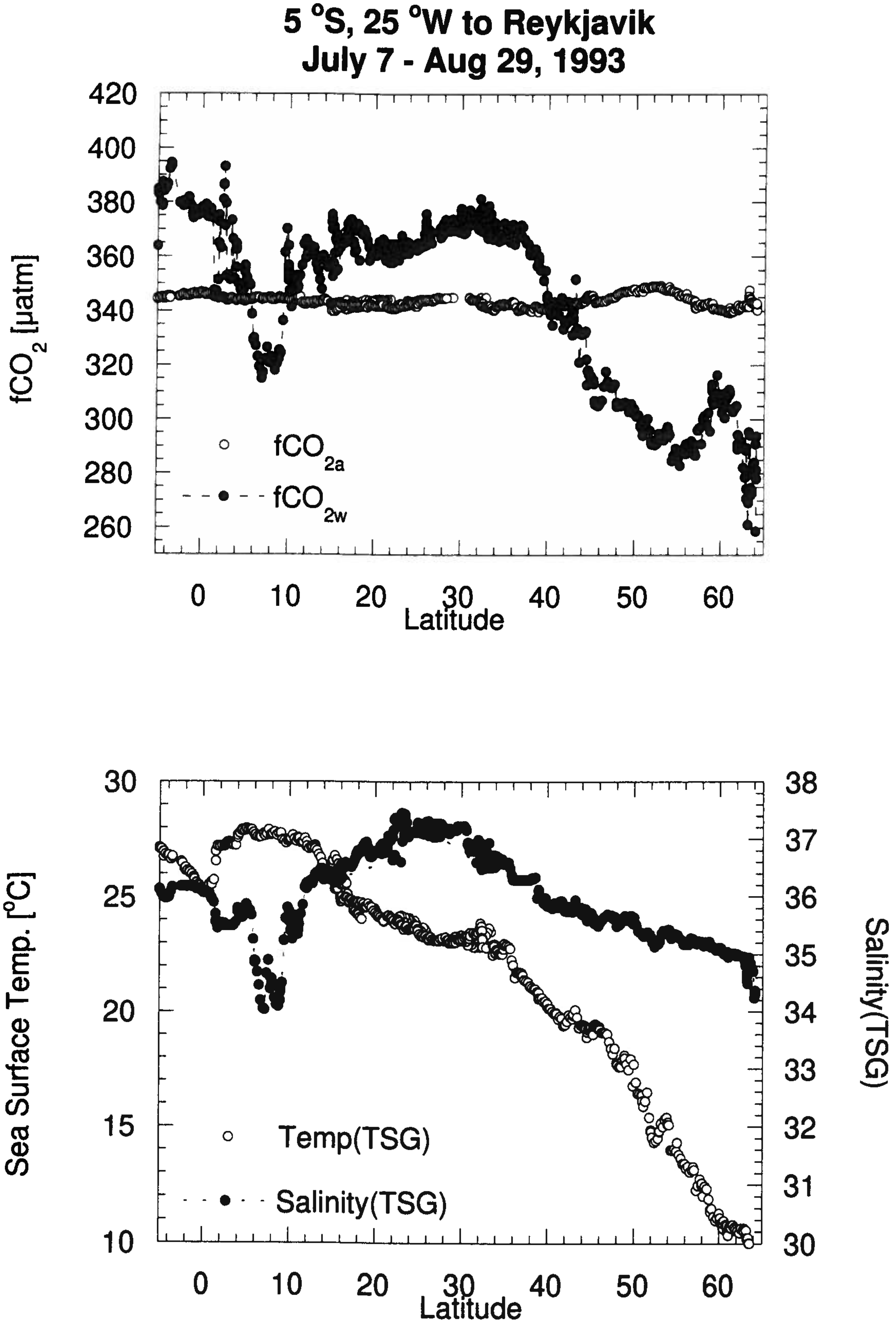


Figure 22: fCO_2 & Sea Surface Temperature for NATL93 Leg1

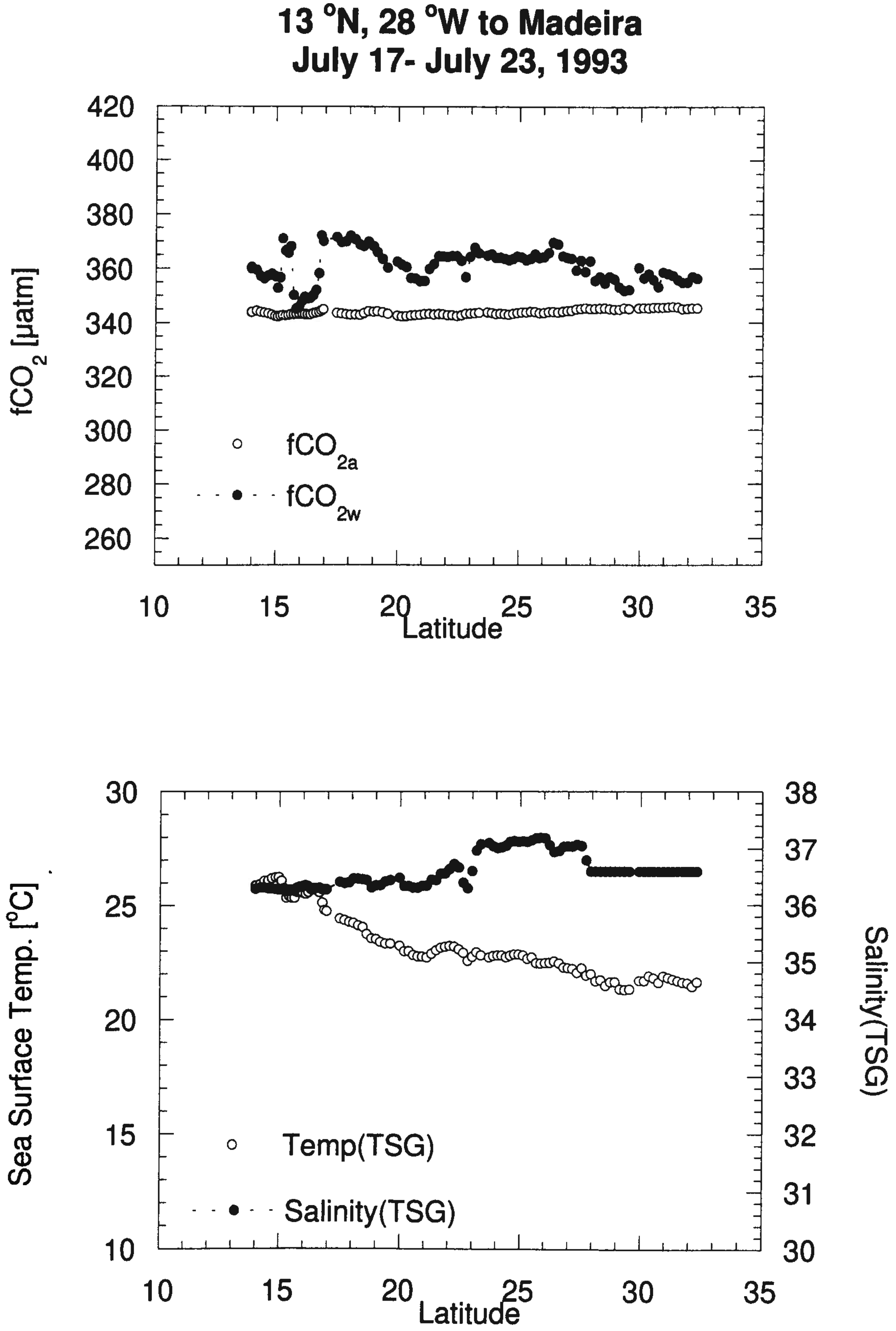
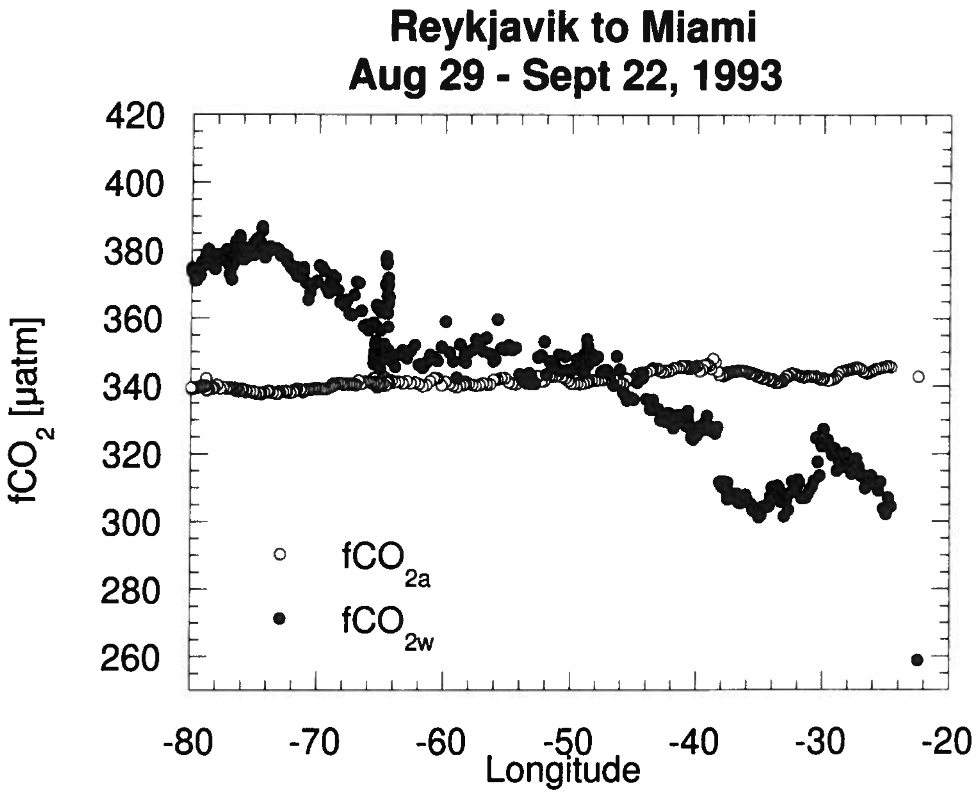


Figure 23: fCO$_2$ & Sea Surface Temperature for NATL93 Leg 2



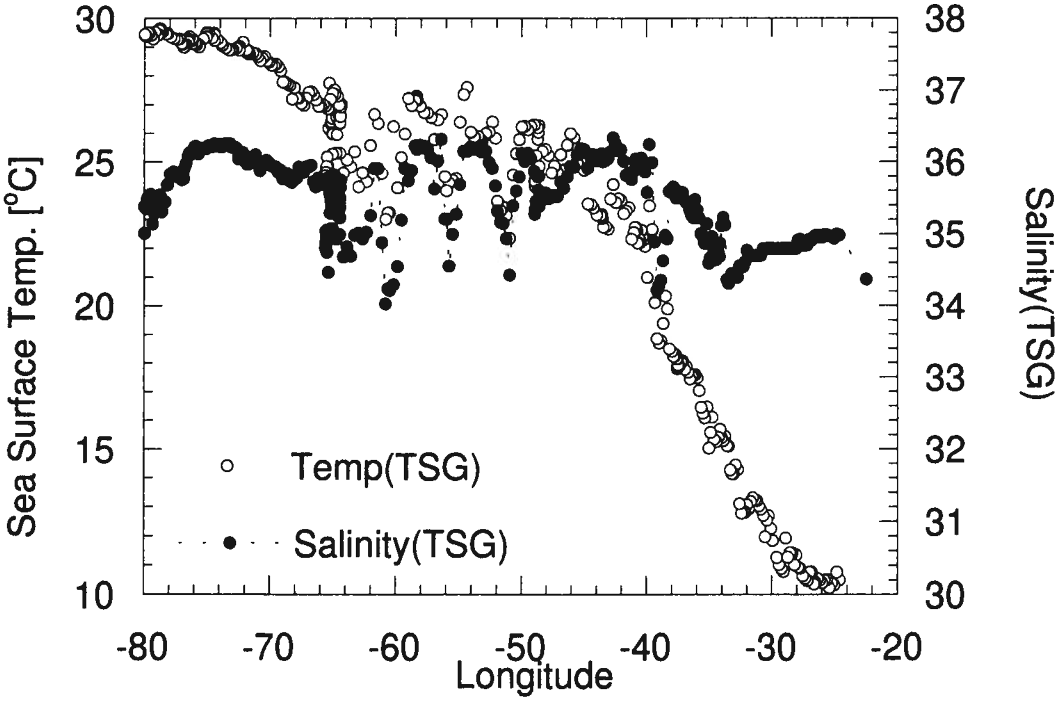
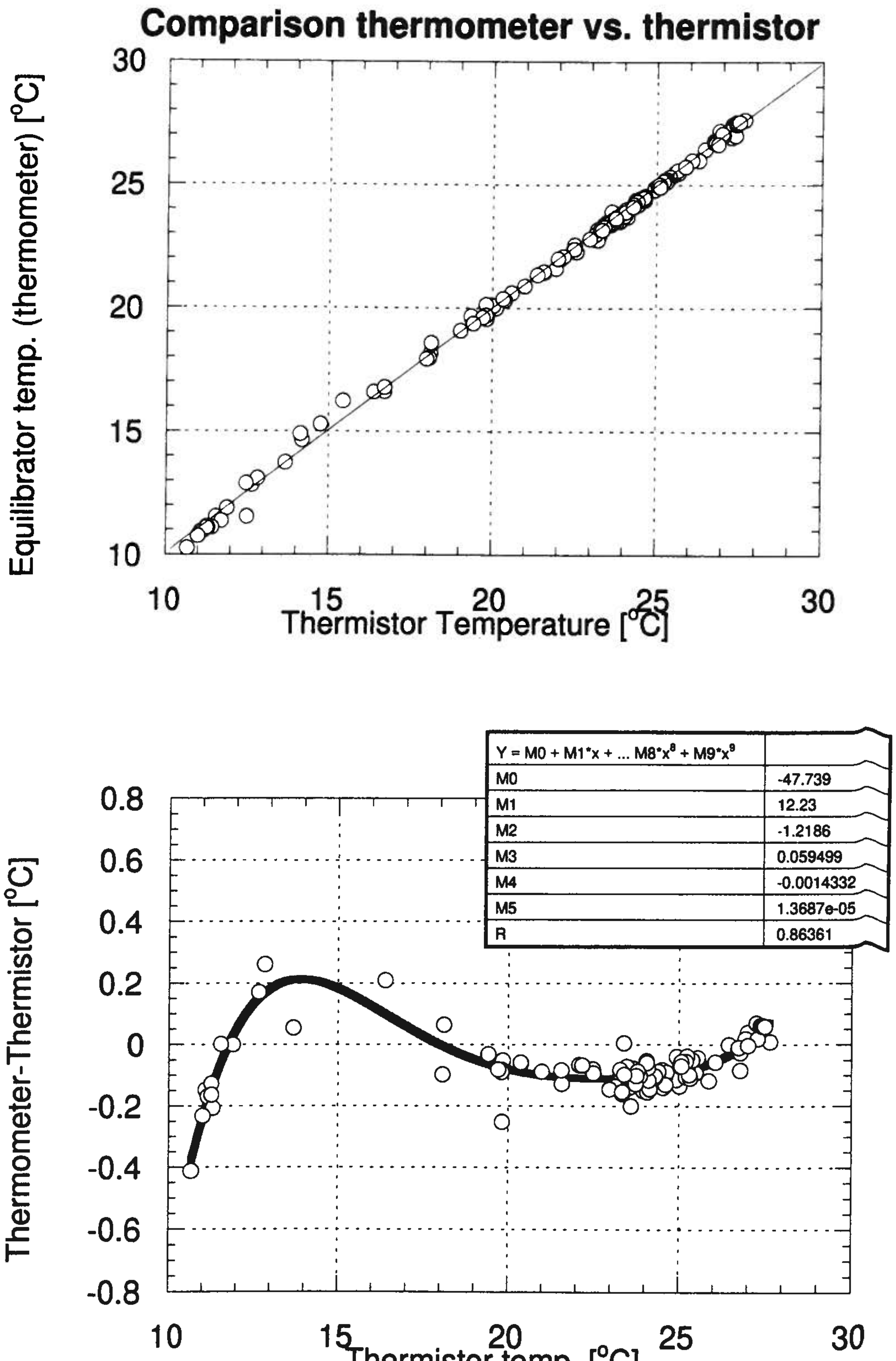


Figure 24: fCO_2 & Sea Surface Temperature for NATL93 Leg 3



$Y = M0 + M1{*}x + \ldots M8{*}x^8 + M9{*}x^9$	
M0	-47.739
M1	12.23
M2	-1.2186
M3	0.059499
M4	-0.0014332
M5	1.3687e-05
R	0.86361

Figure 25: Thermometer vs. Thermistor Comparison (UW fCO_2 system)

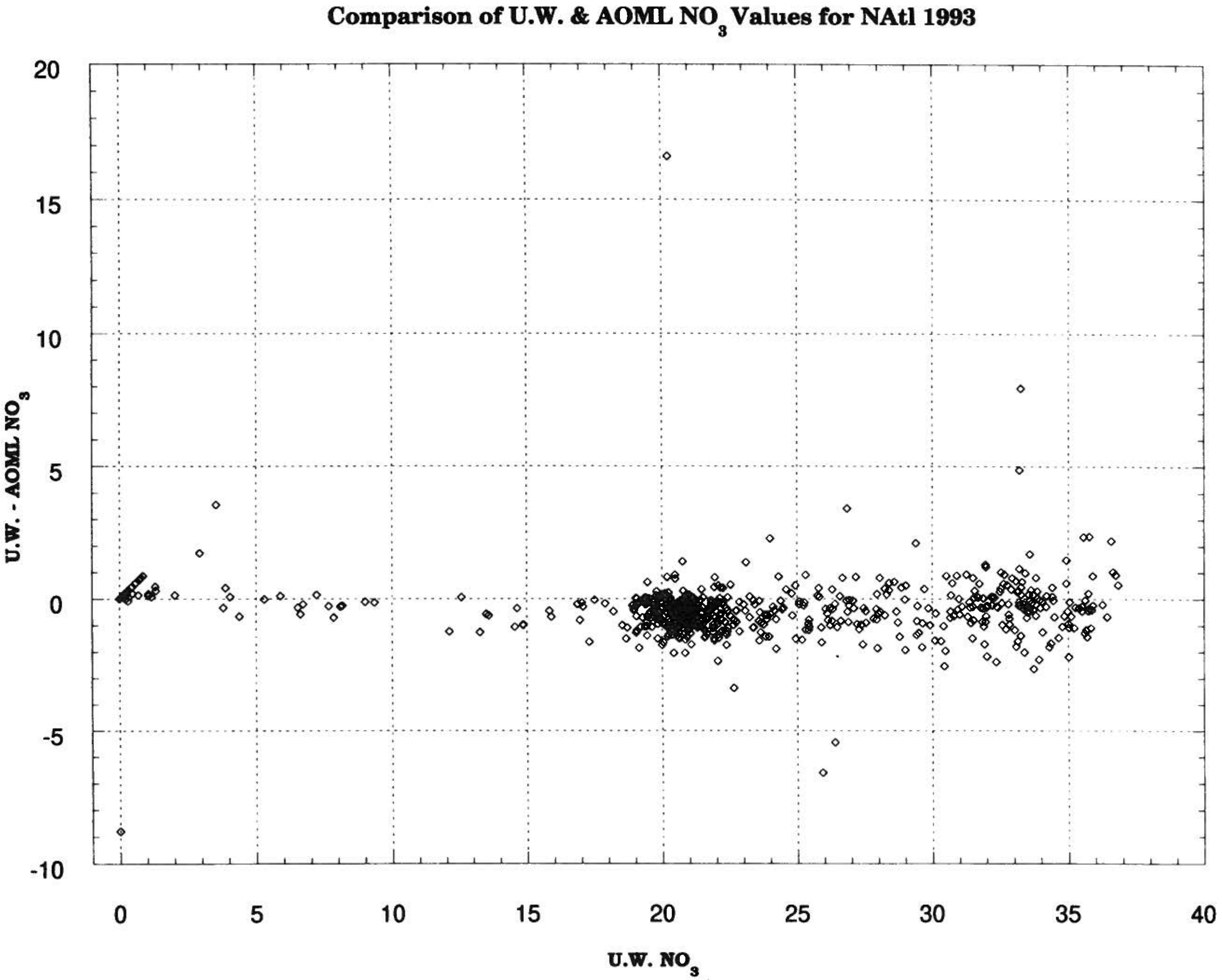


Figure 26: U.W. - AOML NO_3 vs. U.W. NO_3

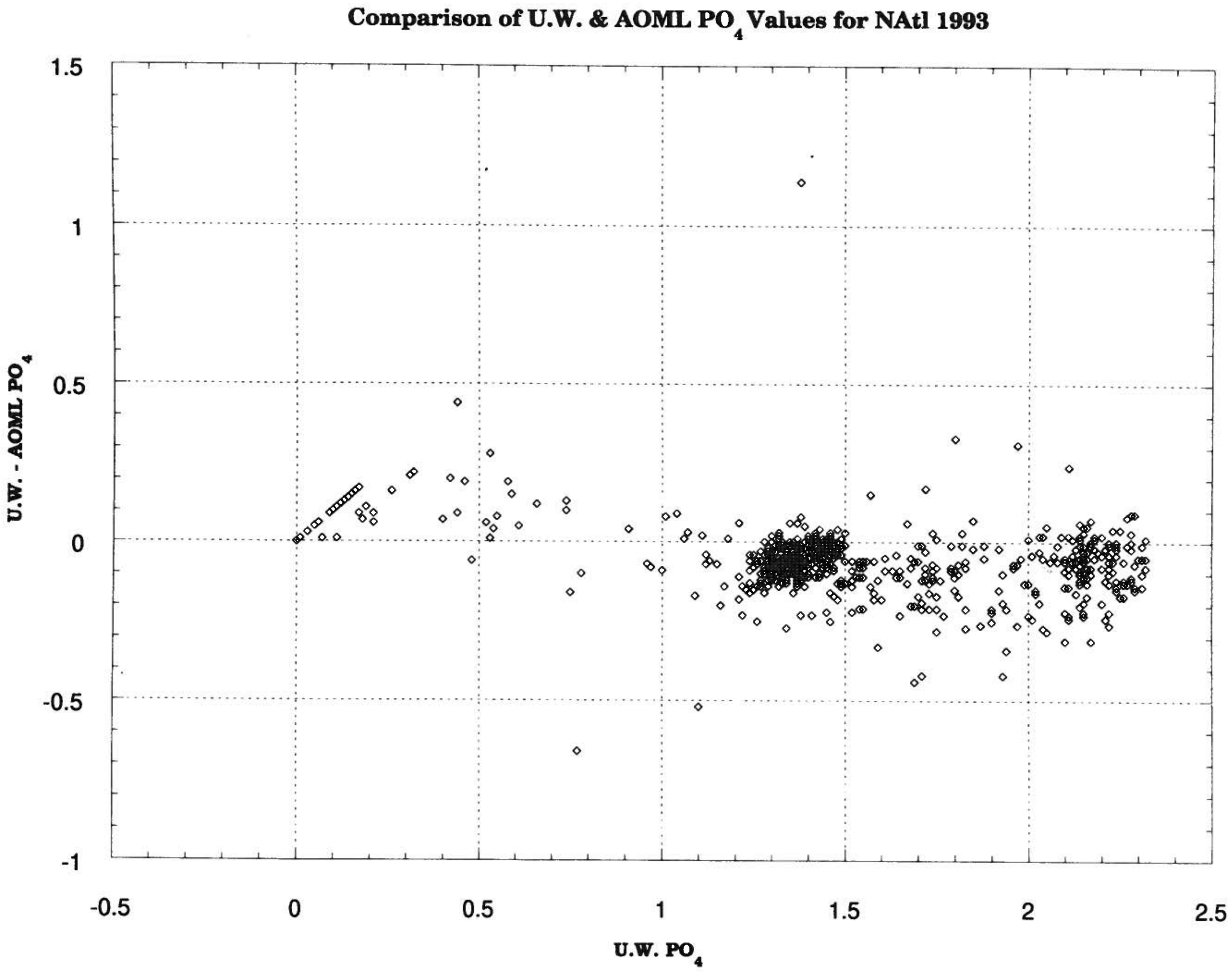


Figure 27: U.W. - AOML PO_4 vs. U.W. PO_4

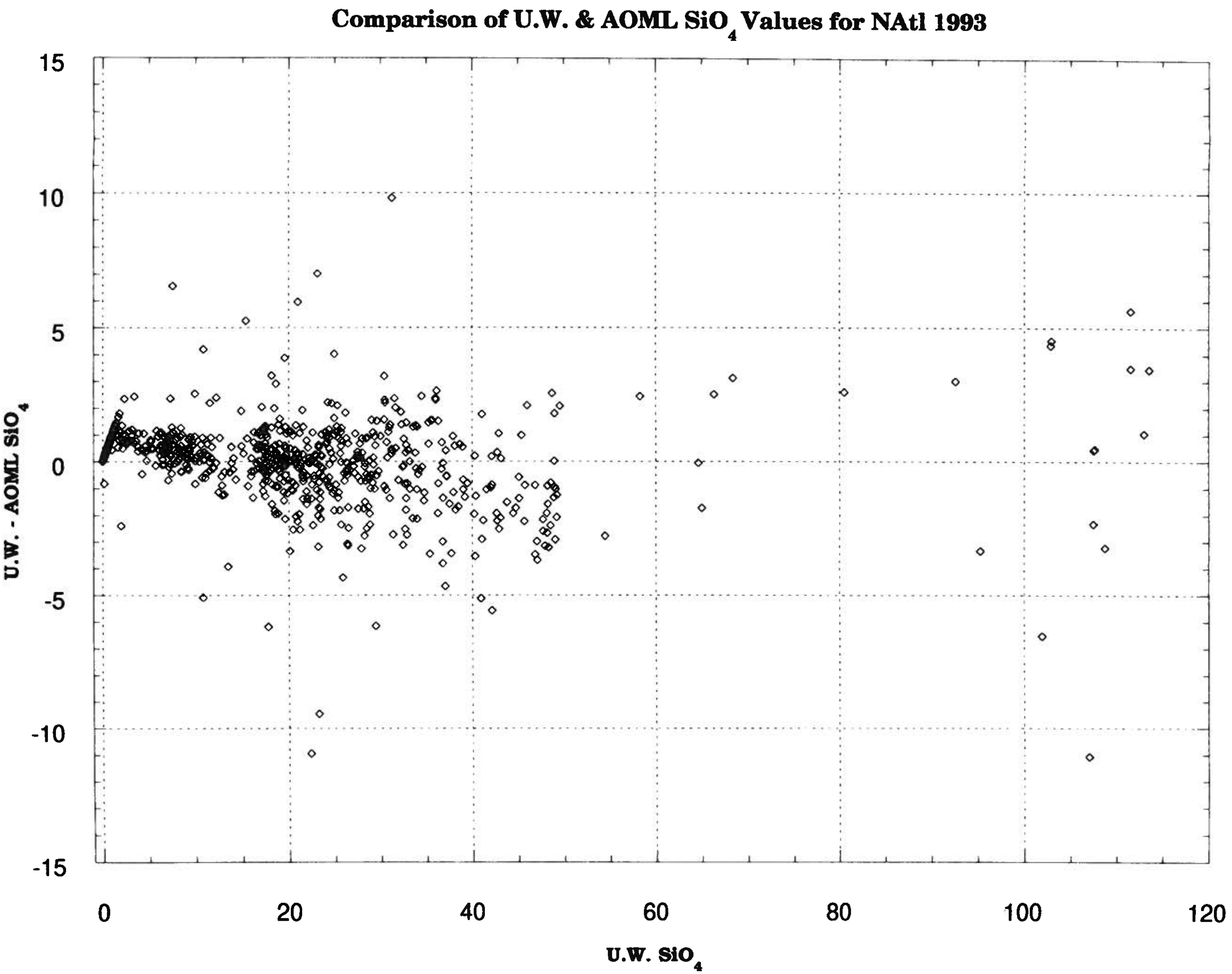


Figure 28: U.W. - AOML SiO_4 vs. U.W. SiO_4

APPENDIX B: Data File Format and Availability

Data files can be downloaded from AOML's web site or by anonymous ftp. The address of the web site is http://www.aoml.noaa.gov/ocd/oaces/data. The ftp site is at ftp.aoml.noaa.gov and the data files are in the directory pub/ocd/carbon/pc/natl93.

If any problems are experienced in downloading please contact either:

Betty Huss	**305-361-4395**	**huss@aoml.noaa.gov**
Bob Castle	**305-361-4418**	**castle@aoml.noaa.gov**

or fax to the attention of either of the above at:

305-361-4392

or send regular mail to either of the above at:

NOAA/AOML/OCD
4301 RICKENBACKER CAUSEWAY
MIAMI, FL 33149

The data is stored in two formats: .DBF (dBase™) and .CSV (comma-delimited text). Three auxilliary files that give information about the data are also stored at these sites. The following files are available:

NATL93D.DBF -	Version D of the NATL93 database.
NATL93D.CSV -	Comma-delimited ascii data file containing all the fields in the NATL93 database.
NATL93.DES -	Text file containing a chronological description of all updates/changes to the NATL93 database. This file also contains the file structure for the current version of the NATL93 database.
NATL93.UNI -	Text file which lists each field (in the order they appear in the NATL93 database) and the units associated with that field.
NATL93.QC -	Text file which lists the WOCE WHP QC (quality control) flags and describes the investigator specific qc flags for the pCO2 and nutrient data.

Table 10: Data Fields and Units

Field	Name	Type	Width	Dec	Index
1	OPS_NO	Numeric	9		N
2	STATION	Numeric	6		N
3	SAMP_NO	Numeric	5		N
4	BOTTLE_QC	Character	1		N
5	DEC_LAT	Numeric	8	4	N
6	DEC_LONG	Numeric	9	4	N
7	PRESSURE	Numeric	9	1	N
8	DEPTH	Numeric	5		N
9	TEMP	Numeric	6	3	N
10	THETA	Numeric	6	3	N
11	BOT_SAL	Numeric	7	3	N
12	BOTSAL_QC	Character	1		N
13	CTD_SAL	Numeric	7	3	N
14	CTDSAL_QC	Character	1		N
15	SIGMATHETA	Numeric	9	3	N
16	OXY_WINK	Numeric	8	2	N
17	OXY_QC	Character	1		N
18	AOU	Numeric	9	3	N
19	GBN_PO4	Numeric	6	2	N
20	PO4_QC	Character	1		N
21	GBN_NO3	Numeric	6	2	N
22	NO3_QC	Character	1		N
23	GBN_NO2	Numeric	6	2	N
24	NO2_QC	Character	1		N
25	GBN_SIO4	Numeric	6	2	N
26	SIO4_QC	Character	1		N
27	KK_PO4	Numeric	6	2	N
28	KK_NO3	Numeric	6	2	N
29	KK_NO2	Numeric	6	2	N
30	KK_SIO4	Numeric	6	2	N
31	NOAA_TCO2	Numeric	8	2	N
32	N_TCO2_QC	Character	1		N
33	FM_TALK	Numeric	6	1	N
34	FMTALK_QC	Character	1		N
35	PCO2_20	Numeric	6	1	N
36	PCO2_QC	Character	1		N
37	PH20CSPEC	Numeric	7	3	N
38	PCO2INSITU	Numeric	6	1	N
39	F11	Numeric	8	3	N
40	F11_QC	Character	1		N
41	F12	Numeric	8	3	N
42	F12_QC	Character	1		N
43	CHLORO_A	Numeric	7	3	N
44	PHAEO	Numeric	7	3	N
45	MONTH	Numeric	2		N
46	DAY	Numeric	2		N
47	YEAR	Numeric	4		N
48	CAST	Numeric	4		N
49	CTD_CAST	Numeric	4		N
50	LEG	Character	6		N

WOCE QC FLAGS

Cited from WOCE WHP Data Reporting Requirements (Rev. 1, July 1991)

Water Sample Quality Flag Definitions

FLAG DEFINITION
1 = Sample for this measurement was drawn from water bottle but analysis not received.
2 = Acceptable measurement.
3 = Questionable measurement.
4 = Bad measurement.
5 = Not reported.
6 = Mean of replicate measurements (No. of replicates should be specified in the -.DES file and replicate data tabulated).
7 = Manual chromatographic peak measurement.
8 = Irregular digital chromatographic peak integration.
9 = Sample not drawn for this measurement from this bottle.

NOTE: A,B,C,D,E,F = Investigator specific flags. Concise, accurate definitions must be included. Please check these flags before using in order to to avoid conflict with other investigators.

Bottle Quality Flag Definitions

FLAG DEFINITION
1 = Bottle information unavailable
2 = No problems noted
3 = Leaking
4 = Did not trip correctly
5 = Not reported
6 = Significant discrepancy in measured values between Gerard and Niskin bottles
7 = Unknown problem
8 = Pair did not trip correctly. Note that Niskin Bottles can trip at an unplanned depth while the Gerard trips correctly and vice versa.
9 = Samples not drawn from this bottle

Note: flags 6 and 8 refer to Gerard Barrel samples, which were not collected on NAtl93.

*U.S. GOVERNMENT PRINTING OFFICE 1998-0-673-018/40082