

Global Repeat Hydrographic/CO₂/Tracer Surveys in Support of CLIVAR and Global Carbon Cycle Objectives: Carbon Inventories and Fluxes

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1.PROJECT SUMMARY

The Repeat Hydrography CO₂/tracer Program is a systematic and global re-occupation of select hydrographic sections to quantify changes in storage and transport of heat, fresh water, carbon dioxide (CO₂), chlorofluorocarbon tracers and related parameters. It builds upon earlier programs (e.g., World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Survey (JGOFS) during the 1990s) that have provided full depth data sets against which to measure future changes, and have shown where atmospheric constituents are getting into the oceans. The Repeat Hydrography CO₂/tracer Program (Figure 1; Table 1) reveals much about internal pathways and changing patterns that will impact the carbon sinks on decadal time scales.

The program is designed to assess changes in the ocean's biogeochemical cycle in response to natural and/or man-induced activity. Global warming-induced changes in the ocean's transport of heat and freshwater, which could affect the circulation by decreasing or shutting down the thermohaline overturning, can also be followed through long-term measurements. Below the 2000-m depth of Argo, Repeat Hydrography provides the only global measurements for observing long-term trends in the ocean. The program also provides data for the Argo sensor calibration (e.g., www.argo.ucsd.edu), and support for continuing model development that will lead to improved forecasting skill for oceans and global climate. By integrating the scientific needs of the carbon and hydrography/tracer communities, major synergies and cost savings have been achieved. The philosophy is that in addition to efficiency, a coordinated approach will produce scientific advances that exceed those of having individual carbon and hydrographic/tracer programs. These advances will contribute to the following overlapping scientific objectives: 1) data for model calibration and validation; 2) carbon inventory and transport estimates; 3) heat and freshwater storage and flux studies; 4) deep and shallow water mass and ventilation studies; and 5) calibration of autonomous sensors.

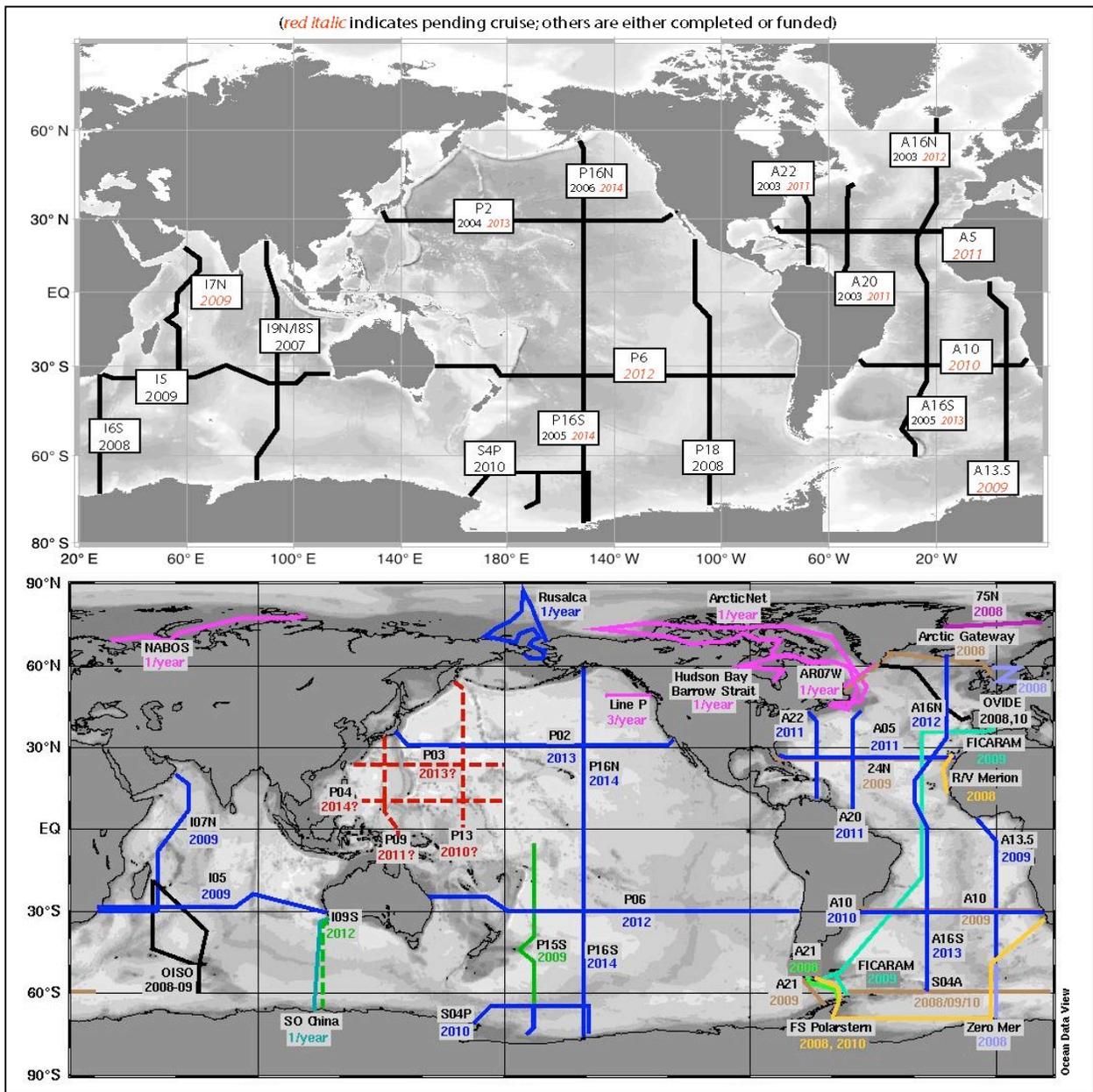


Figure 1. Global map of U.S. (Top) and international (Bottom) Repeat Hydrography CO₂/tracer Program hydrographic sections with carbon system measurements. In the bottom plan solid lines indicate funded lines. Dashed lines indicate planned lines that are not fully funded at this time. The U.S. cruises are designated with blue lines.

Table 1. Sequence of Repeat Hydrography CO₂/tracer completed and planned cruises in the oceans - from 2003 to 2014.

Schedule of US CO ₂ /CLIVAR Hydrography Lines (as of 8/31/07)						
Dates	Cruise	Days	Ports	Year	Contact/Chief Scientist	Ship
overall coordinator: Jim Swift, SIO						
06/19/03- 7/10/2003	A16N, leg 1 Planning Cruise results	22	Reykjavik-Madeira	1	Bullister, PMEL	Ron Brown
07/15/03- 8/11/2003	A16N, leg 2 Planning Cruise results	28	Madeira - Natal, Brazil	1	Bullister, PMEL	Ron Brown
09/15/03- 10/13/2003	A20 Cruise results	29	WHOI - Port Of Spain	1	Toole, WHOI	Knorr
10/16/03- 11/7/2003	A22 Cruise results	21	Port Of Spain - WHOI	1	Joyce, WHOI	Knorr
06/15/04- 7/25/2004	P2, leg 1 Cruise results	41	Yokohama-Honolulu	2	Robbins, SIO	Melville
07/28/04- 8/27/2004	P2, leg 2 Cruise results	32	Honolulu - San Diego	2	Swift, SIO	Melville
01/09/05- 2/22/2005	P16S Cruise results	45	Wellington-Tahiti	3	Sloyan/Swift, WHOI/SIO	Revelle
01/11/05- 2/26/2005	A16S Planning Cruise results	48	Punta Arenas - Fortaleza	3	Wanninkhof,Doney; NOAA/AOML,WHOI	Ron Brown
02/13/06- 3/3/2006	P16N, leg 1 Planning	18	Tahiti-Honolulu	4	Sabine; NOAA/PMEL	Thompson Schedule
03/10/06- 3/30/2006	P16N, leg 2 Planning	21	Honolulu-Kodiak	4	Feely; NOAA/PMEL	Thompson Schedule
02/04/07- 3/17/2007	I8S	38	Dunedin, NZ-Perth	5	Swift, SIO	Revelle
03/22/07- 5/2/2007	I9N	38	Perth-Colombo, Sri Lanka	5	Sprintall, SIO	Revelle
02/04/08- 3/17/2008	I6S	43	Cape Town	6	Speer, FSU	Revelle
12/06/07- 1/16/2008	P18, Leg 1	32	San Diego-Easter Island	6	Bullister PMEL	Ron Brown
01/19/08- 2/23/2008	P18, Leg 2	35	Easter Island- Punta Arenas	6	Johnson PMEL	Ron Brown
2009	I5	57	Capetown - Perth	7	scheduled	UNOLS
2009	I7N	51	Mutrah – Port Louis	7	scheduled	UNOLS
2010	A13.5	62	Abidjan-Cape Town	8	future planning	NOAA
2010	S4P	60	Lytelton – Punta Arenas	8	future planning	NSF
2011	A10/A5	30	Tenerife - Miami Woods Hole-Port of Spain-Woods Hole	9	future planning	NOAA
2012	A20/A22	59		10	future planning	UNOLS
2012	A16N	29		10	future planning	NOAA
2013	P06	95		11	future planning	UNOLS

2013	A16S		11	future planning	NOAA
2014	P16N		12	future planning	NOAA
2014	P16S or P2	42	12	future planning	UNOLS

The Repeat Hydrography CO₂/tracer Program is being implemented to maintain decadal time-scale sampling of ocean transports and inventories of climatically significant parameters in support of the Ocean Carbon Monitoring Network (Objective 7) of the Program Plan for Building a Sustained Observing Network for Climate. The sequence and timing for the sections (Figure 1; Table 1) takes into consideration the program objectives, providing global coverage, and anticipated resources. Also considered is the timing of national and international programs, including the focus of CLIVAR in the Pacific in the 2005-2008 timeframe; the Ocean Carbon and Climate Change Program (OCCC) that emphasizes constraining the carbon uptake in the Northern Hemisphere oceans, in part, in support of the North American Carbon Program (NACP); and the international Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) program. Emphasis in 2008-2010 is on the Southern Hemisphere. In addition, the proposed sections are selected so that there is roughly a decade between them and the WOCE/JGOFS occupations.

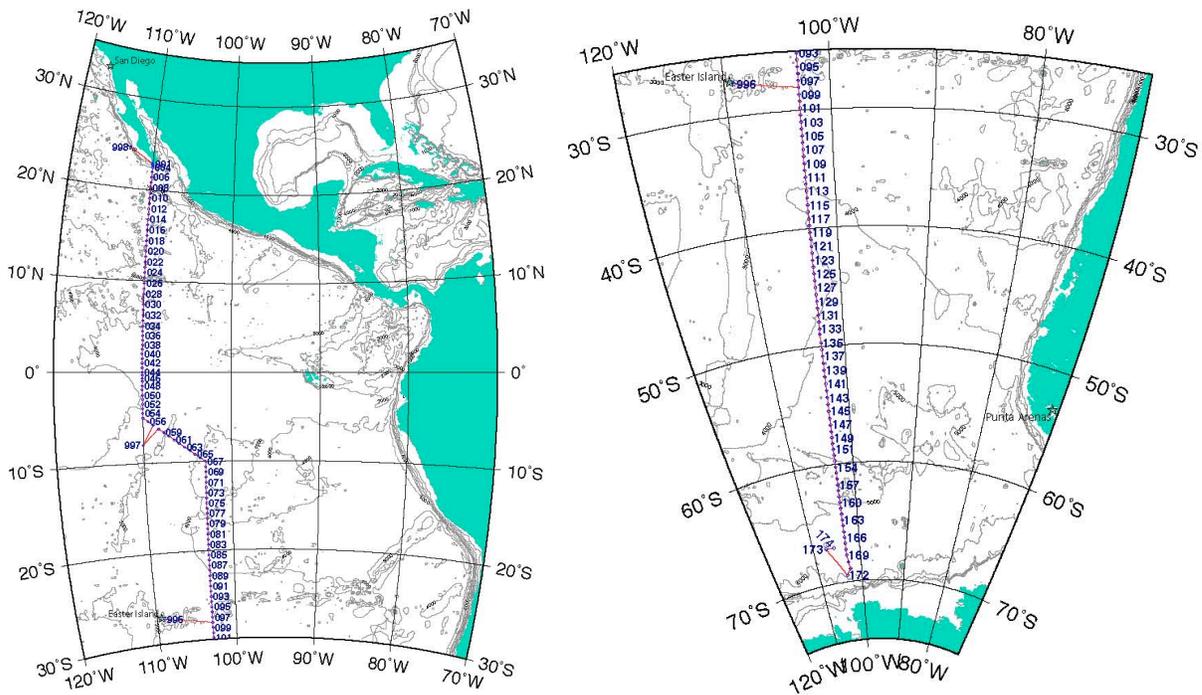


Figure 2. Cruise Tracks of Repeat Hydrography PI8 Legs 1 & 2 during Dec 2007 – Feb 2008 in the Pacific Ocean.

The scientific objectives are important both for the CLIVAR and the OCCC programs, and for operational activities such as Global Ocean Observing System (GOOS) and Global Climate Observing System (GCOS). In mid-2001 the US scientific steering committees of CLIVAR (www.clivar.org) and the Carbon Cycle Science Program, (CCSP; www.carboncyclescience.gov) proposed the creation of a joint working group to make recommendations on a national program of observations to be integrated with international plans. Several community outreach efforts have been implemented to provide information about the program, such as a web site with interactive forum (<http://ushydro.ucsd.edu/index.html>), articles in EOS (Sabine and Hood, 2003) and the JGOFS newsletter, as well as AGU and Ocean Science

meeting forums. The Repeat Hydrography CO₂/tracer Program addresses the need, as discussed by the First International Conference on Global Observations for Climate (St. Raphael, France; October 1999), that one component of a global observing system for the physical climate/CO₂ system should include periodic observations of hydrographic variables, CO₂ system parameters and other tracers throughout the water column (Smith and Koblinsky, 2000); (Fine et al., 2001). The large-scale observation component of the OCCC has also defined a need for systematic observations of the invasion of anthropogenic carbon in the ocean superimposed on a variable natural background (Doney et al., 2004). The CCSP has identified the critical need for the federal government to begin delivering regular reports documenting the present state of the climate system components. Through this plan NOAA has developed the infrastructure necessary to build, with national and international partners, the ocean component of a global climate observing system and to deliver regular reports on the ocean's contribution to the state of the climate and on the state of the observing system.

Recognizing the need to develop an international framework for carbon research, various working groups of programs like the International Geosphere-Biosphere Programme (IGBP), the World Climate Research Programme (WCRP), the International Human Dimensions Programme (IHDP), the Intergovernmental Oceanographic Commission (IOC), and the Scientific Committee on Oceanic Research (SCOR) have worked together to develop research strategies for global carbon cycle studies. Based on the recommendations coming from these programs, NOAA and NSF have co-sponsored the Repeat Hydrography CO₂/tracers Program, with program direction coming from the Repeat Hydrography Oversight Committee (Richard Feely and Lynne Talley, co-chairs; <http://ushydro.ucsd.edu/index.html>). Many other nations are also sponsoring similar carbon studies that are comparable in focus and have been designed to be complimentary to our program (http://www.clivar.org/carbon_hydro/index.htm). Consequently, there is an immediate need for global-scale coordination of these carbon observations and research efforts to achieve the goal of a global synthesis. There is also an urgent need to critically assess the overall network of planned observations to ensure that the results, when combined, will meet the requirements of the research community. Because of these issues, the Global Carbon Project (GCP; <http://www.globalcarbonproject.org/>) has initiated the International Ocean Carbon Coordination Project (IOCCP; <http://www.ioc.unesco.org/ioccp/>) to: (1) gather information about on-going and planned ocean carbon research and observation activities, (2) identify gaps and duplications in ocean carbon observations, (3) produce recommendations that optimize resources for international ocean carbon research and the potential scientific benefits of a coordinated observation strategy, and (4) promote the integration of ocean carbon research with appropriate atmospheric and terrestrial carbon activities. It is through the workings of the IOCCP and international CLIVAR that international coordination of data management, data synthesis and scientific interpretation of the global repeat sections results will be implemented. In addition, the Repeat Hydrography CO₂/tracer Program is being managed in accordance with the COSP Ten Climate Monitoring Principals.

2. PROGRESS REPORT AND ACCOMPLISHMENTS

2.1. PI8 Cruise Results

A hydrographic survey (CLIVAR/Carbon P18) was carried out on the NOAA Ship *Ronald H. Brown* from December 2007 through February 2008 in the eastern Pacific. John Bullister served as Chief Scientist on Leg 1 and Greg Johnson served as Chief Scientist on Leg 2. Most of the survey work was a repeat of a 1994 occupation of a meridional section nominally

along 110 – 103°W (WOCE P18). Two stations along a 1992 section along 67°S west of 103 deg. W (WOCE S4P) were also taken towards the end of the cruise. Operations included CTD/LADCP/Rosette casts and radiometer casts. Underway data collected included upper-ocean currents from the shipboard ADCP, surface oceanographic and meteorological parameters from the ship's underway systems, and bathymetry data. Ancillary operations included surface drifter deployments, Argo float deployments, and XBT drops. NDBC TAO buoy servicing was also performed during the first leg of the cruise.

After an 8-day delay, NOAA Ship Ronald H. Brown departed San Diego, CA on 15 December 2007 at 0215 UTC. The ship anchored off Easter Island, Chile from 18-21 January 2008 for a personnel change and short break between leg 1 and leg 2. CLIVAR/Carbon P18 ended in Punta Arenas, Chile on 23 February 2008.

A total of 174 stations and 7 TAO Buoy sites were occupied during P18. 179 CTD/LADCP/Rosette casts (including 2 Test casts, 2 TAO calibration casts and 2 casts at station 8: the first to end leg 1 and the second to start leg 2) plus 54 radiometer casts were made. Twenty-four ARGO floats were deployed, 17 SVP drifters were deployed, and approximately 82 XBTs were dropped. CTD data, LADCP data and water samples (up to 36) were collected on most Rosette casts, in most cases to within 10-20 meters of the bottom.

Salinity, dissolved oxygen and nutrient samples were analyzed for up to 36 water samples from each cast of the principal CTD/LADCP/Rosette program. Water samples were also measured for CFCs, pCO₂, Total CO₂ (DIC), Total Alkalinity, pH, CDOM and Chlorophyll a. Additional samples were collected for ³He, Tritium, ¹³C/¹⁴C, ³²Si, oxygen/Argon (ONAR), DOC, DON, POC, and CDOM2C/CDOM3C.

2.2. CTD/O₂ and Bottle Salinity (Baringer and Johnson)

The central goals of the project are to collect high-quality continuous profiles of Temperature, Salinity, and Dissolved Oxygen (CTD/O₂) as well to make high-quality discrete measurements of salinity on CLIVAR/CO₂ repeat hydrography sections, to calibrate and process these data, and make them available to the research community.

The oceans are the flywheel of the earth's climate system, storing large amounts of heat and water, transporting these quantities around the planet, and exchanging them with the atmosphere. Research goals for this project include:

1. Improve the estimates of variations in heat and freshwater storage and transport of the ocean, especially for the deep ocean below the reach of the Argo array.
2. Provide the physical oceanographic measurements required to support carbon system studies, as well as to perform deep and shallow water mass and ventilation studies.
3. Provide data for model calibration and validation.
4. Provide high quality in situ data to aid in the calibration of autonomous sensors such as the CTDs on Argo floats.

While analyses of repeat hydrographic data are not funded through this proposal, they are vital to the success of the program, so our efforts in this regard in FY2008 are summarized here. This year we worked on analyses of repeat hydrographic section data demonstrating significant Antarctic Bottom Water (AABW) warming in the main deep basins of the Pacific Ocean (Johnson, 2007), warming in the Scotia Sea (Meredith et al., 2008), warming and freshening the southeast Indian Ocean (Johnson et al., 2008a), and even warming and reductions in northward transport the western North Atlantic (Johnson et al., 2008b). Analysis of bottom water variability

in the eastern Pacific Ocean by comparing the 2007-2008 repeat of P18 to the 1994 data along the same track is in progress. While there is little warming north of the Chile Rise crossed at about 36°S by this section, there is a statistically significant warming of roughly 0.03°C below about 3500 m, again in the Antarctic Bottom Water (AABW; Figure 3) and also evidence of freshening there (not shown). Together, the results in the S. Indian, Pacific, S. Atlantic, and even the N. Atlantic Oceans suggest the possibility of a global pattern of AABW warming (and freshening near the source) in the past decade, which could constitute an important mode of climate variability, and a significant contribution to the global heat and sea level budgets. Given the potential importance of global AABW variations mentioned above, we have worked to quantify the dominance of AABW in ventilating the deep global oceans (Johnson et al., 2008b). We have also used repeat hydrographic data in a study of continued warming in the deep Caribbean Sea (Johnson and Purkey, 2008), as well as in a study of increasing low-oxygen zones in the tropical oceans (Stramma et al., 2008) that garnered a lot of media attention.

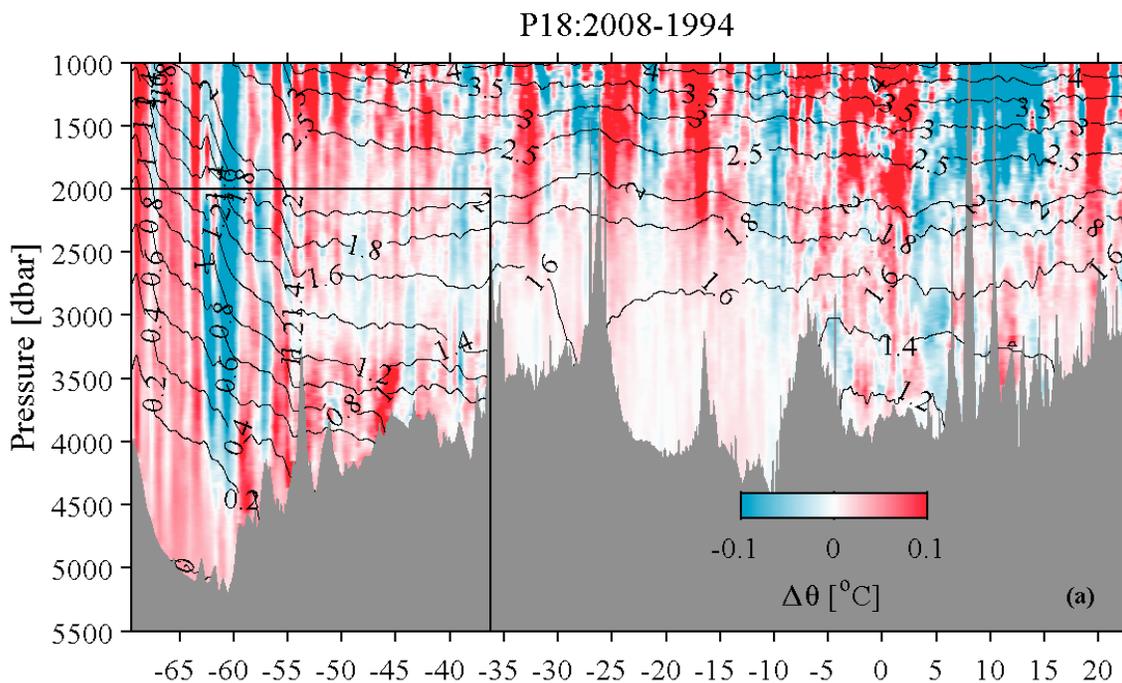


Figure 3. Difference of deep potential temperature, $\Delta\theta$ [°C], along WOCE Section P18 in the eastern Pacific resulting from subtracting the 1994 from the 2007/2008 data. Red areas indicate warming and blue areas cooling with color saturation at ± 0.1 °C. Mean potential temperatures from all the data are contoured (black lines).

In FY 2008 the PMEL CTD group supported the 2007/2008 reoccupation of WOCE Section P18 from San Diego, CA to Punta Arenas, Chile via Easter Island, Chile. We built, modified, or purchased necessary CTD/O₂ equipment, assembled the necessary gear, and arranged for pre- and post-cruise calibrations of all CTD/O₂ sensors. We shipped cruise gear to the ship for the cruise and back to Seattle after the cruise. Our lead CTD/O₂ data processor K. McTaggart participated on both legs of the cruise. Dr. G. Johnson served as chief scientist for the second leg, and JISAO employee S. Purkey stood a CTD watch. We have completed the final calibration of the cruise CTD/O₂ data, which are available at http://cchdo.ucsd.edu/data_access?ExpoCode=33RO20071215.

In FY 2008 the AOML CTD group was in charge of bottle salinity analyses, provided hardware support for the CTD/O₂ program, and assisted with the collection of Lowered ADCP

data. The group provided two people per cruise leg, for a total of 4 people over the duration of the cruise.

Bottle salinity analyses were performed in the ship's temperature-controlled salinity laboratory using a Guildline Model 8400B inductive autosalinometer, and a dedicated PC. Software allowed the user to standardize the autosalinometer. IAPSO Standard Seawater Batch P147 was used as the standard. The autosal was standardized a few times each day, as needed given stability of the instrument and laboratory temperature. 5708 salinity measurements were taken and approximately 200 vials of standard seawater (SSW) were used. A duplicate sample was drawn for each cast in order to confirm sampling accuracy. Comparisons of salinity measurements to historical data along the cruise suggest that the measurements were within the WOCE accuracy specifications of 0.002 PSS-78.

In addition to performing salinity measurements, the AOML group personnel on the cruise assisted with CTD/O₂ package hardware repair and maintenance, and the operation of the Lowered ADCP during the cruise.

2.3. Total Dissolved Inorganic Carbon (DIC) (Feely, Sabine and Wanninkhof)

The central goals of this project are to make high-quality measurements of dissolved inorganic carbon (DIC) on CLIVAR repeat hydrography sections, to calibrate these data and to make the data available to the research community.

Carbon dioxide concentrations in the atmosphere have increased rapidly over the past several decades, and these increases have been reflected in changing surface water concentrations. Our specific goals include:

- 1.) Improve estimates of uptake and storage of anthropogenic CO₂ in the ocean.
- 2.) Estimate the rates of key biogeochemical processes in the ocean.
- 3.) Provide data to initialize ocean carbon model simulations, evaluate strengths and weaknesses in the models, and suggest ways to improve the models.

a) P18

Samples for DIC measurements were drawn according to procedures outlined in the Guide to Best Practices for Ocean CO₂ Measurements (DOE, 1994) from 10.4-L Niskin bottles (except Niskin 34; 9.6L) into cleaned 300-mL glass bottles. Over 2500 samples were analyzed for discrete DIC; full profiles were completed on odd numbered stations, with replicate samples taken from the surface, oxygen minimum, salinity maximum, and bottom Niskin-type bottles. On the even numbered stations, samples were drawn throughout the water column with focus on the upper 1000 m. The replicate samples were interspersed throughout the station analysis for quality assurance of the integrity of the coulometer cell solutions. The coulometers were calibrated by injecting aliquots of pure CO₂ (99.995%) by means of an 8-port valve outfitted with two sample loops with known gas volumes bracketing the amount of CO₂ extracted from the water samples for the two PMEL systems. The stability of each coulometer cell solution was confirmed three different ways: the Certified Reference Material (CRM), Batch 78, supplied by Dr. A. Dickson of SIO, was measured at the beginning, gas loops in the beginning and at the end, and the duplicate samples at the beginning, middle, and end of each cell solution. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9-12 hours of continuous use.

Calculation of the amount of CO₂ injected was according to the Guide to Best Practices for Ocean CO₂ Measurements (DOE, 1994). The concentration of CO₂ ([CO₂]) in the samples was determined according to:

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

Where Cal. Factor is the calibration factor, 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 solution, Run Time is the length of coulometric titration (in minutes), and K is the conversion factor from counts to μmol.

The instrument has a salinity sensor, but all DIC values were recalculated to a molar weight (μmol/kg) using density obtained from the CTD's salinity sensor. The results underwent initial quality control on the ship using property plots: DIC-depth, DIC-potential temperature, DIC-salinity and DIC-LAT-depth contour plots were used to analyze the quality of the data (Figure 4). The difference plot indicates DIC anomalies ranging from 5-55 μmol/kg in the upper 1000 m of the water column. These anomalies are due to uptake of anthropogenic CO₂, changes in mixing and ventilation of the water masses, and changes in biogeochemical processes. Our synthesis project will determine the relative contributions of each process to the total change in DIC over the 12-year interval.

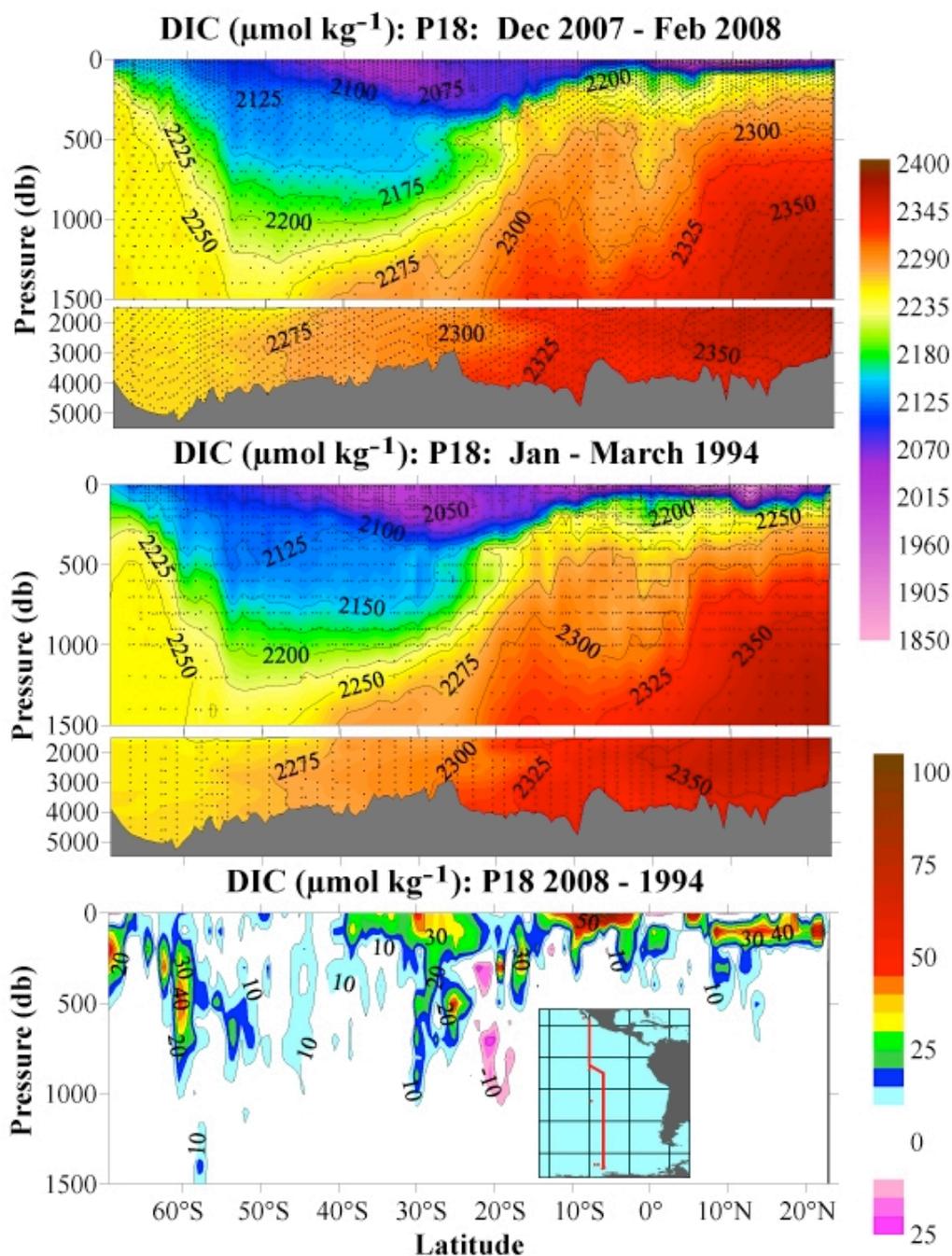


Figure 4. DIC in $\mu\text{mol kg}^{-1}$ along the P18 section in the Pacific Ocean along 110-103 °W. The gridded difference plot is shown on the bottom panel for the fourteen year time difference between the cruises. The increases in DIC are the result of a combination of processes including anthropogenic CO₂ invasion and changes in circulation and biogeochemistry.

b) I6S

In addition to the inorganic carbon measurements on the P18 cruise, DIC and underway PCO₂ measurements were performed on the I6S cruise that was run under the auspices of NSF. Cruise I6 S on UNOLS vessel *Roger Revelle* departed Durban, South Africa on February 4, 2008 entered the southward-flowing Agulhas Current and traveled due south along a transect coinciding with Longitude 30 °E into the Antarctic Circumpolar Current down to the ice edge at 70 °S, and returned to Cape Town, South Africa on March 16, 2008.

Analyses were performed with newly fabricated instruments patterned after the SOMMA but with improved interfaces and software. The DICE (Dissolved Inorganic Carbon Extractors) performed well during the study. A total of 2089 samples were analyzed. There were 177 duplicate samples and 89 underway samples. The average difference of the duplicate samples was 1.4 $\mu\text{mol/kg}$. The CRM batch was #85 with an assigned DIC value of 2000.44 $\mu\text{mol/kg}$ (as certified by Prof. A. Dickson at SIO) and a salinity of 33.326. The average measured CRM value for the DICE was 1998.2 $\mu\text{mol/kg}$. All data was corrected to the first CRM run on each coulometer cell on a per cell basis.

A cross section of the DIC data from the cruise is shown in Figure 5. Very high DIC values are observed in the Southern Ocean with a shallow thermocline south of 55 $^{\circ}\text{S}$. The penetration of North Atlantic Deep Water from the North at a depth of 2000-3500 m is manifested by lower DIC values. This is attributed to better ventilation of this water mass compared to the older waters of Antarctic origin.

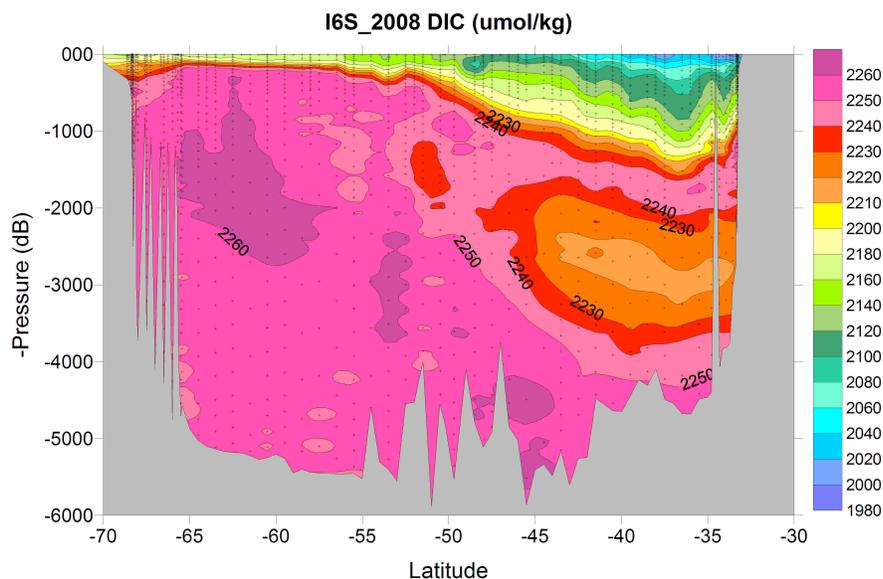


Figure 5. Cross-section of DIC values for the I6S cruise. Note the higher resolution scale for values greater than 2200 $\mu\text{mol/kg}$ to accentuate small changes in deep water values.

2.4 Discrete and Underway $f\text{CO}_2$ on I6S and P18

a) I6S

The cruise went from South Africa to the ice edge and back (Figure 6). A total of 7240 $f\text{CO}_2$ water measurements were made and 2715 air XCO_2 measurements. Several hours of data were lost due to insufficient water and air flows due to blockages and other minor issues were encountered as described in the metadata file accompanying the data. The data is served from the AOML $f\text{CO}_2$ website: <http://www.aoml.noaa.gov/ocd/gcc/clivari6s/>. A color-coded map indicating surface water CO_2 levels ($f\text{CO}_{2w}$) is shown in Figure 6. A cross section for the southbound leg is given in Figure 7. A distinguishing feature in this cruise is the very sharp gradients in $f\text{CO}_2$, SST and surface salinity corresponding with the Argulhas Current front and the south subtropical front near 43 $^{\circ}\text{S}$. Highly variable values are found near the ice edge due to the interplay of upwelling waters from depth with high CO_2 and patchy biological productivity drawing down the CO_2 .

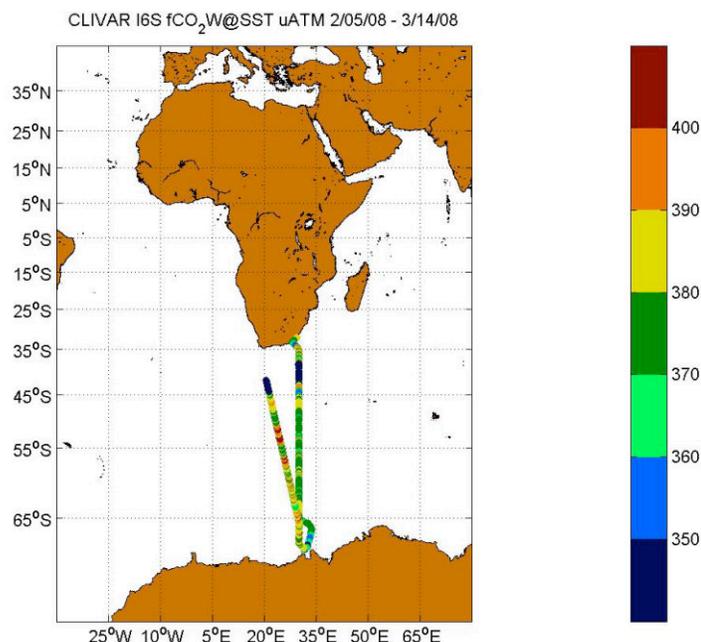


Figure 6. Map of the cruise track with colors indicating the $f\text{CO}_2\text{w}$ levels (see color bar in μatm).

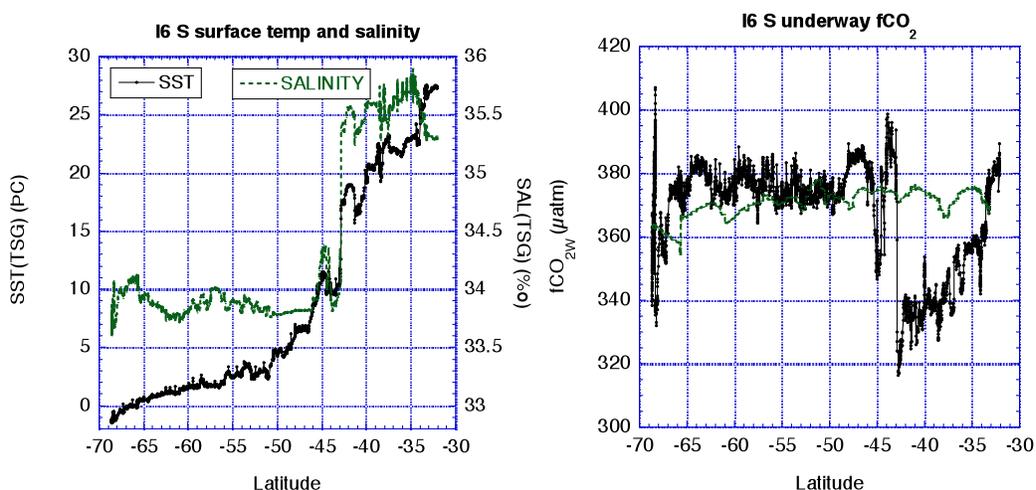


Figure 7. Left panel: Sea surface temperature (left axis) and salinity (right axis). Right panel: surface water $f\text{CO}_2$ (black) and air $f\text{CO}_2$ (green). The data are for the southbound leg of I6 from Durban to the ice edge.

b) Underway $f\text{CO}_2$ measurements for P18

Underway $f\text{CO}_2$ measurements were made on NOAA ship *Ronald H. Brown* along the entire two-legged cruise track from San Diego, Ca (32 °N, 117 °W) to Punta Arenas (53 °S, 71 °W). A total of 12534 surface water samples and 4700 air samples were taken. Sampling and data reduction followed standard protocol as outlined in Pierrot et al., (2007). The only major problem encountered was that the analog/digital converter on the thermistor in the equilibrator failed to register temperature readings below 6 °C. Utilizing the data from the thermosalinograph at the intake and an auxiliary thermosalinograph next to the underway system in the hydrolab, an empirical algorithm was developed to estimate equilibrator temperatures < 6 °C. The correction procedure is believed to yield results with an error less than 0.1 °C.

The results are shown in Figure 8. During the end of 2007 and beginning of 2008 there was a very strong outgassing of the Equatorial Pacific. The boundaries of the high $f\text{CO}_2$ associated with upwelling are sharp near the equator and at 12°S . The Southern hemisphere subtropics were a strong source as well associated with seasonal warming. A large sink was observed at high southern latitudes near the ice edge associated with sea-ice melt and a strong algae bloom as indicated by high chlorophyll values. Small CO_2 sinks are observed at the start of the cruise track and just north of the Equator. These are believed to be caused by seasonal cooling and year-round biological productivity at lower latitudes. Air $f\text{CO}_2$ values are relatively constant with most of the variability attributed to changes in barometric pressure. Of note are persistent high air $f\text{CO}_2$ values at the start of the cruise when the ship sailed near the coast of the Baja California. These are attributed to continental air masses and point towards possible biases in estimating air-sea CO_2 fluxes near land using marine air background values.

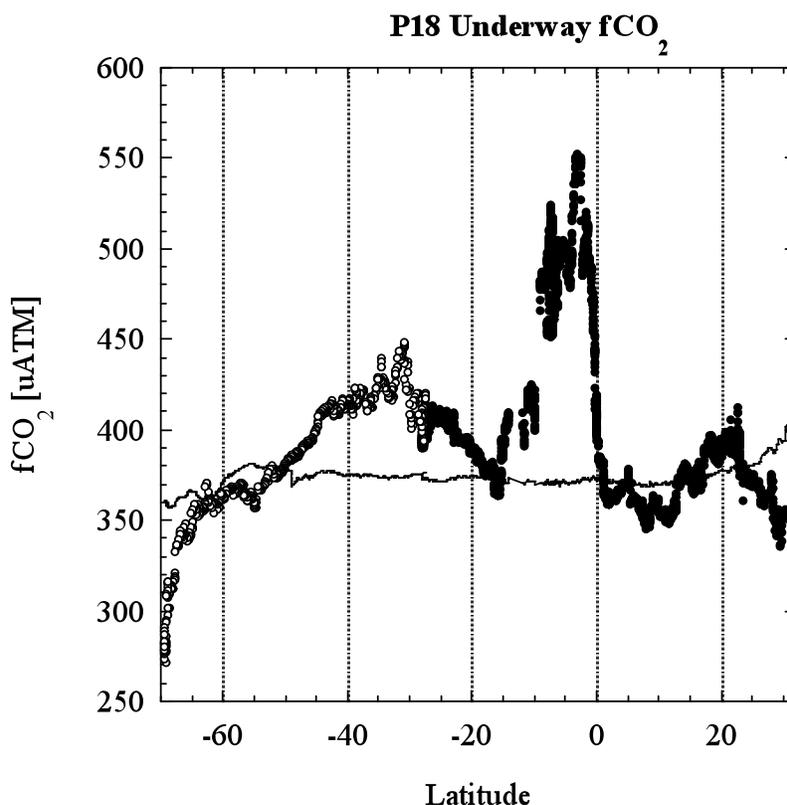


Figure 8. Surface water and air $f\text{CO}_2$ values along the transect of P18. The solid circles are the water values for leg 1 and the open circles those of leg 2. The thin line is the air $f\text{CO}_2$ values.

A comparison with underway $f\text{CO}_2$ data obtained in 1994 along the same transect shows a significant increase in surface water values that corresponds closely with the 26 ppm increase air XCO_2 values over the 14 year time period (Figure 9). Although the 1994 and 2008 cruises were run in different seasons and directions, a significant increase in surface water values along most of the transect is apparent clearly indicating the atmospheric imprint on the surface ocean. The offset in the equatorial $f\text{CO}_{2w}$ maximum is attributed to the spatial variation in the core of the upwelling water attributed to tropical instability waves. Data can be found at: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_introduction.php under years 2007 (leg 1) and 2008 (leg 2)

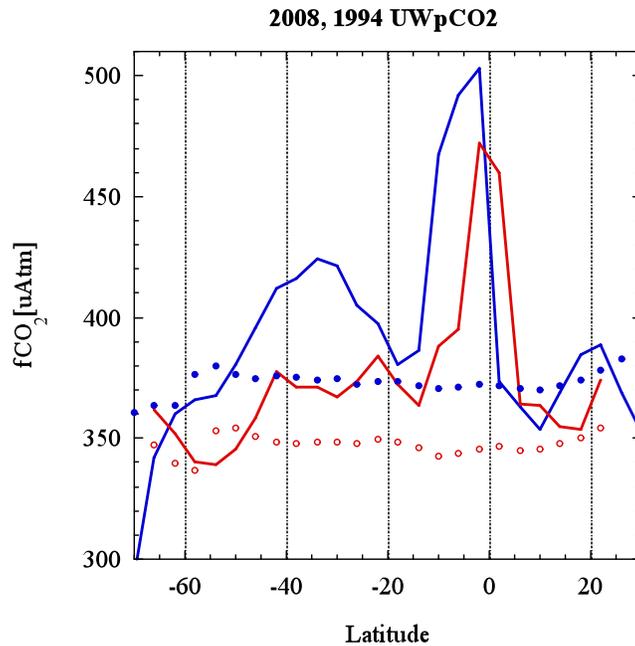


Figure 9. Surface water (solid line) and air (circles) $f\text{CO}_2$ values in 1994 (red) and 2008 (blue) along the P18 line. The increases in surface water $f\text{CO}_2$ values due to invasion of anthropogenic CO_2 are apparent. The data are 4-degree averages to smooth out smaller scale variability.

c) Discrete $p\text{CO}_2$ measurements for P18

Rationale

Discrete $p\text{CO}_2$ measurements were made on P18 to ascertain complete understanding of inorganic carbon system dynamics and to have a sensitive carbon system parameter to discern changes over time. Figure 10 shows the difference in $p\text{CO}_2$ measured at 20°C , $p\text{CO}_2(20)$ at 40°S , 110°W between this cruise and the initial occupation during WOCE in 1994. [Note, following common but incorrect nomenclature we refer to the measured quantity as $p\text{CO}_2$ while the data has been corrected for non-ideality and should accordingly be listed as $f\text{CO}_2$]. The data shows the increase of $p\text{CO}_2(20)$ in the thermocline indicative of the invasion of anthropogenic CO_2 . The $p\text{CO}_2$ calculated from DIC and Total Alkalinity (TA) had a poorer agreement and larger standard deviation and points to the strong need to include a third inorganic carbon system parameter if the data from the CLIVAR/ CO_2 cruises are to be used effectively to address the pressing concerns about biota in a high CO_2 /low pH ocean.

Sampling and analyses

Every other station was sampled with samples drawn from at least 15 Niskin-type bottles with one duplicate at each station. Near the equator an effort was made to increase the sampling density across stations. South of Easter Island we increased the number of samples per station due to the increase in ocean depth. We also reduced the station resolution from every other station to alternating every other station with every third station.

The sampling statistics are as follows:

	# bottles sampled	# pCO ₂ samples taken	#duplicates
Leg 1	736	782	46
Leg 2	542	589	47
Total	1278	1371	93

The precision of the duplicates was on average 0.5 % (4 μ atm).

Samples were drawn into 500 ml volumetric flasks using Tygon© tubing. About 5ml of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with a screwcap containing a polyethylene liner. The samples were stored in coolers at room temperature generally for no more than 5 hours. All analyses were done at 20°C. No flask was analyzed without spending at least two hours in a bath close to the analytical temperature.

The discrete pCO₂ system is patterned after the instrument described in Chipman et al., (1993) and is discussed in detail by Wanninkhof and Thoning (1993) and Chen et al., (1995). Once the samples reach the analytical temperature, a~50-ml headspace is created by displacing the water using a compressed standard gas with a CO₂ mixing ratio close to the anticipated pCO₂ of the water. The headspace is circulated in a closed loop through the infrared analyzer that measures CO₂ and water vapor levels in the sample cell. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differ by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 minutes. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at room pressure.

In order to maintain analytical accuracy, a set of six gas standards are run through the analyzer before and after every ten seawater samples. The standards are obtained from Scott-Marín and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale. Prior to station 60, many values at depths from 400 to 2000 meters were higher than the highest standard (1533.7 ppm). For this reason, these values have been flagged as "questionable" (3) for the time being, but after further quality control it is likely that many if not most of these values will be flagged as "good" (2). For most of the stations after 155, nearly all of the samples were within the range of only two standards: 792.51 ppm and 1036.95 ppm.

Table 2. Gas standards for the determination of discrete pCO₂.

Cylinder Serial Number	Value
CA5998	[205.07 ppm]
CA5989	[378.71 ppm]
CA5988	[593.64 ppm]
CA5980	[792.51 ppm]
CA5984	[1036.95 ppm]
CA5940	[1533.7 ppm]

The calculation of pCO₂ in water from the headspace measurement involves several steps. The CO₂ concentrations in the headspace are determined via a second-degree polynomial fit using the nearest three standard concentrations. Corrections for the water vapor concentration, the barometric pressure, and the changes induced in the carbonate equilibrium by the headspace-water mass transfer are made. The corrected results are reported at the analytical temperature and at a reference temperature of 20°C.

No instrumental problems occurred during the cruise. The relatively time-consuming analyses and the presence of only one analyst limited the spatial coverage. Sampling and analyses focused on precision and accuracy rather than high throughput.

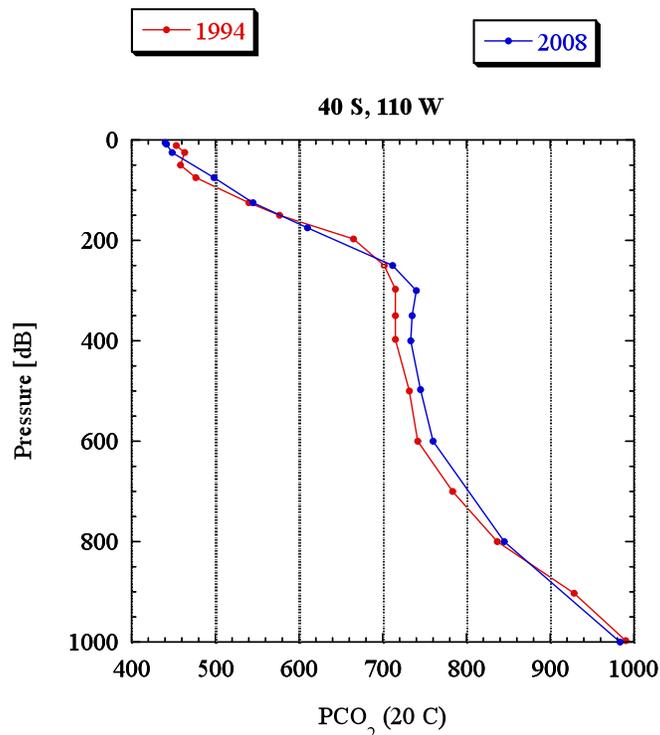


Figure 10. An example of the difference in pCO₂ (20) between the 2008 and 1994 occupation of a station near 40 °S and 103 °W. The increase of pCO₂ in the thermocline is indicative of the invasion of anthropogenic CO₂.

2.5. Nutrients (Mordy and Zhang)

The objectives of this project are to make high-quality measurements of inorganic nutrient (nitrate, nitrite, phosphate and silicate) concentrations in seawater on CLIVAR/repeat hydrography cruises and to perform data quality control and make it available to the climate and carbon research community.

Nutrient concentrations in seawater are traditionally considered a core hydrographic parameter in any oceanographic program. In combination with other hydrographic parameters (such as salinity, temperature and dissolved oxygen concentration), it has been used as a water mass tracer to identify the change in ocean circulation. Availability of nutrients in surface water controls the primary production of the ocean and thus the flux of carbon sequestration through the biological pump. Change in nutrient concentration over space and time has been used to separate anthropogenic CO₂ from changes in total carbon inventory in the ocean. The scientific goals of our project are:

1. Improve estimates of uptake and storage of anthropogenic CO₂ in the ocean.
2. Estimate the rates of key biogeochemical processes, such as remineralization, in the ocean.
3. Provide essential hydrographic data for testing and improving the numerical ocean model simulations.

The primary task of the nutrient group was to collect and process nutrient data from the P18 repeat hydrographic line in the eastern Pacific. Preparations included re-building much of the autoanalyzer (all new glass coils and tubing, new debubblers), creating new software for data reduction and quality control, and a 4 day visit of Erik Quiroz to PMEL to review the procedures and software required for the cruise. Erik Quiroz was the lead nutrient chemist on Leg 1, and Calvin Mordy was the lead nutrient chemist on Leg 2.

There were 5,596 samples collected for the analysis of phosphate, nitrate, nitrite, and orthosilicic acid. Nutrients were analyzed with a continuous flow analyzer (CFA) using the standard and analysis protocols for the WOCE hydrographic program as set forth in the manual by (Gordon et al., 1994). Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. Mixed standards were verified against standards purchased from Ocean Scientific.

There were several problems encountered on the cruise. Temperatures in the ship's bioanalytical laboratory fluctuated greatly with temperatures ranging from 17.2°C to 25.3°C with an average temperature of 20.9±1.9°C; however, temperatures were generally stable during an individual analytical run. On leg one, a 24-channel Ismatec pump failed and was replaced with an identical spare pump. On leg 2, an Alpkem sampler using 35 ml polyethylene sample bottles failed and was replaced with a Westco CS9000 sampler that used 20 ml plastic sample bottles.

A typical analytical run included replicates for the 3 deepest Niskin bottles from each cast, plus any samples with questionable peaks. The standard deviation of these replicates was used to estimate the overall precision for nitrate and silicic acid were <0.2% full scale, and within quality standards set forth by the WOCE and CLIVAR programs. The standard deviation of phosphate replicates was higher due to problems with extensive carryover. Preliminary data was available at the end of the cruise, and final data was submitted after quality control procedures.

Table 3. Nutrient Sample Replicates.

	<u>Phosphate</u>	<u>Silicic Acid</u>	<u>Nitrate</u>
Number of Replicates	494	503	511
Mean Standard Deviation	0.02 μM	0.2 μM	0.1 μM
Percent Deviation	0.8%	0.1%	0.2%

Sections of the major nutrients show familiar patterns of high concentrations in the North Pacific, an intense sub-surface nitrate and phosphate maximum in the Equatorial Pacific, and lower nutrients the central South Pacific Subtropical Gyre. The sub-surface nutrient maximum occurs in sub-oxic waters that support vigorous denitrification (the loss of nitrate as nitrogen gas). The loss of nitrate is evident as deviations from linearity in the nitrate-phosphate plot (Figure 12).

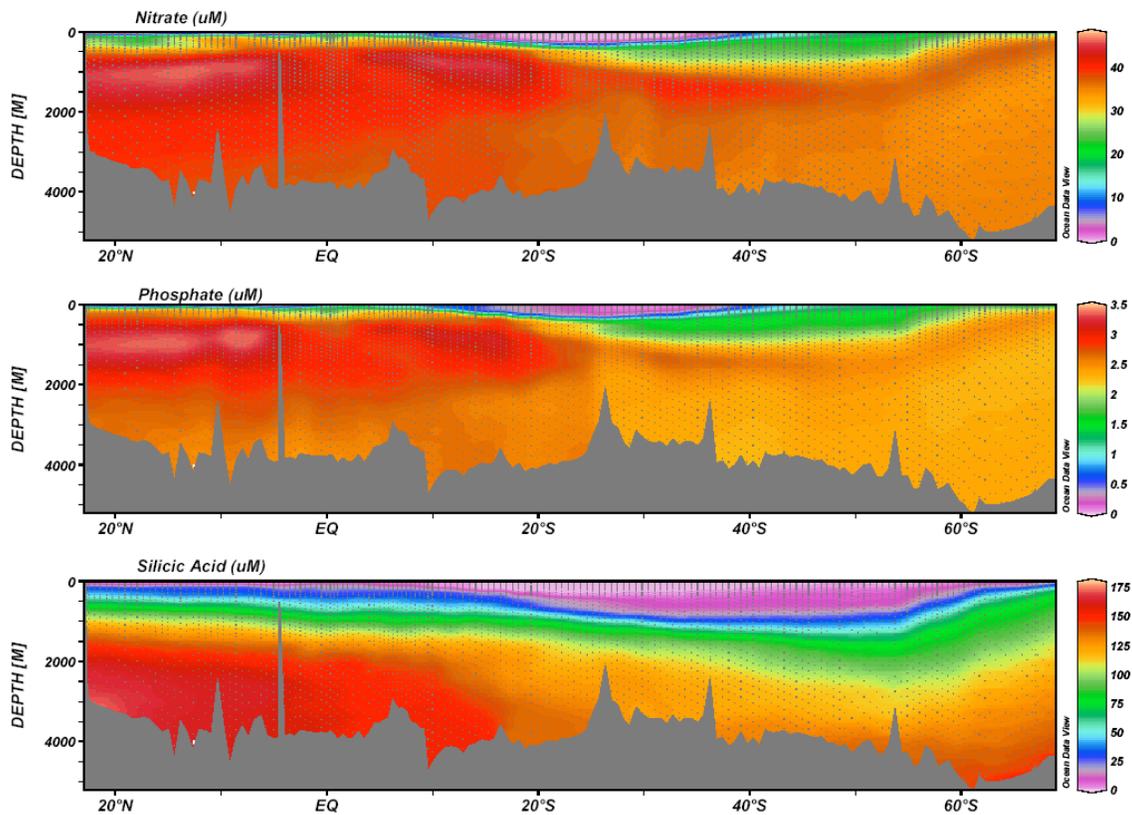


Figure 11. Sections of nitrate, phosphate and silicic acid along the P18 cruise track.

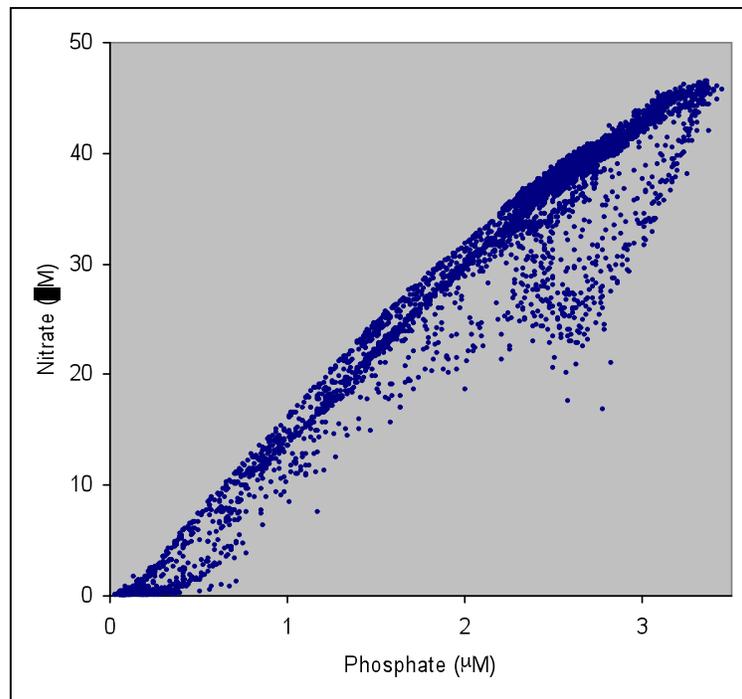


Figure 12. Property-property plot of nitrate and phosphate.

In addition to the P18 cruise, the AOML group participated in an international inter-comparison for nutrient in seawater organized by Dr. Aoyama of the Japanese Meteorological Research Institute who is also responsible for nutrient measurements in the repeat hydrography

program sponsored by the Japanese government. A total of 55 laboratories from 15 counties participated in this exercise, including our repeat hydrography program partner, the nutrient lab at Scripps Institution of Oceanography. Our measurements provided high quality data to the inter-comparison.

2.6. Discrete Oxygen (Baringer and Langdon)

Results from P18

Discrete oxygen samples were collected along 110 W from 20N to 69S. Dissolved oxygen samples were drawn from Niskin bottles into calibrated 125-140 ml iodine titration flasks using silicone tubing to avoid contamination of DOC and CDOM samples. Bottles were rinsed three times and filled from the bottom, overflowing three volumes while taking care not to entrain any bubbles. The draw temperature was taken using a digital thermometer with a flexible thermistor probe that was inserted into the flask while the sample was being drawn. These temperatures were used to calculate mmol kg^{-1} concentrations and as a diagnostic test of Niskin bottle integrity. 1-ml of MnCl_2 and 1-ml of NaOH/NaI were added immediately after drawing the sample using Repipetor, the flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. 24 or 36 samples plus two replicates were drawn from each station, depending on which rosette was used. The total number of samples collected was 5598. The flasks were stored in plastic totes at room temperature for 1.5 hours before analysis.

Oxygen analyses were performed with an automated titrator using an amperometric end-point detection (Culberson and Huang, 1987). The titration of the samples, data logging and graphical display were performed on a PC running a LabView program written by Ulises Rivero of AOML. The titrations were done in a climate-controlled lab at 18.5 - 22.5°C. Thiosulfate was dispensed by a 2-ml Gilmont syringe driven with a stepper motor controlled by the titrator. Tests were conducted pre-cruise to confirm that the precision and accuracy of the volume dispensed was comparable or superior to the Dosimat 665. The whole-bottle titration technique of (Carpenter, 1965), with modifications by (Culberson and Knapp, 1991) was used. Four replicate 10 ml iodate standards were run every 24 hours. The reagent blank was determined from the difference between V_1 and V_2 , the volumes of thiosulfate required to titrate successive 1-ml aliquots of the iodate standard in the same DIW sample. The reagent blank was determined at the beginning and end of the cruise and was found not to have changed significantly. This method was found in pre-cruise testing to produce a more reproducible blank value than the value determined as the intercept of a standard curve. The temperature-corrected molarity of the thiosulfate titrant was determined as given by (Dickson, 1994).

A total of 351 sets of duplicates were run during the cruise. The standard deviation of replicates averaged $0.89 \text{ mmol kg}^{-1}$ for stations 1-52. Correcting a problem with the NaOH/NaI dispenser improved reproducibility significantly. The standard deviation for stations 52-89 average $0.14 \text{ mmol kg}^{-1}$. The standard deviation of replicates for stations 99-174 averaged $0.15 \text{ mmol kg}^{-1}$.

The P18 oxygen data revealed a decline in oxygen and an increase in apparent oxygen utilization (AOU) in the main thermocline across the entire section (Figure 13). This is similar to change that was observed in the North Pacific along the P16N line. The current consensus is that these changes reflect physical changes in the circulation of the ocean. Less ventilation of the thermocline as outcrop waters become warmer and fresher is likely part of the story however changes in isopycnal depth, water mass variability and changes in the biological pump are other possible contributors.

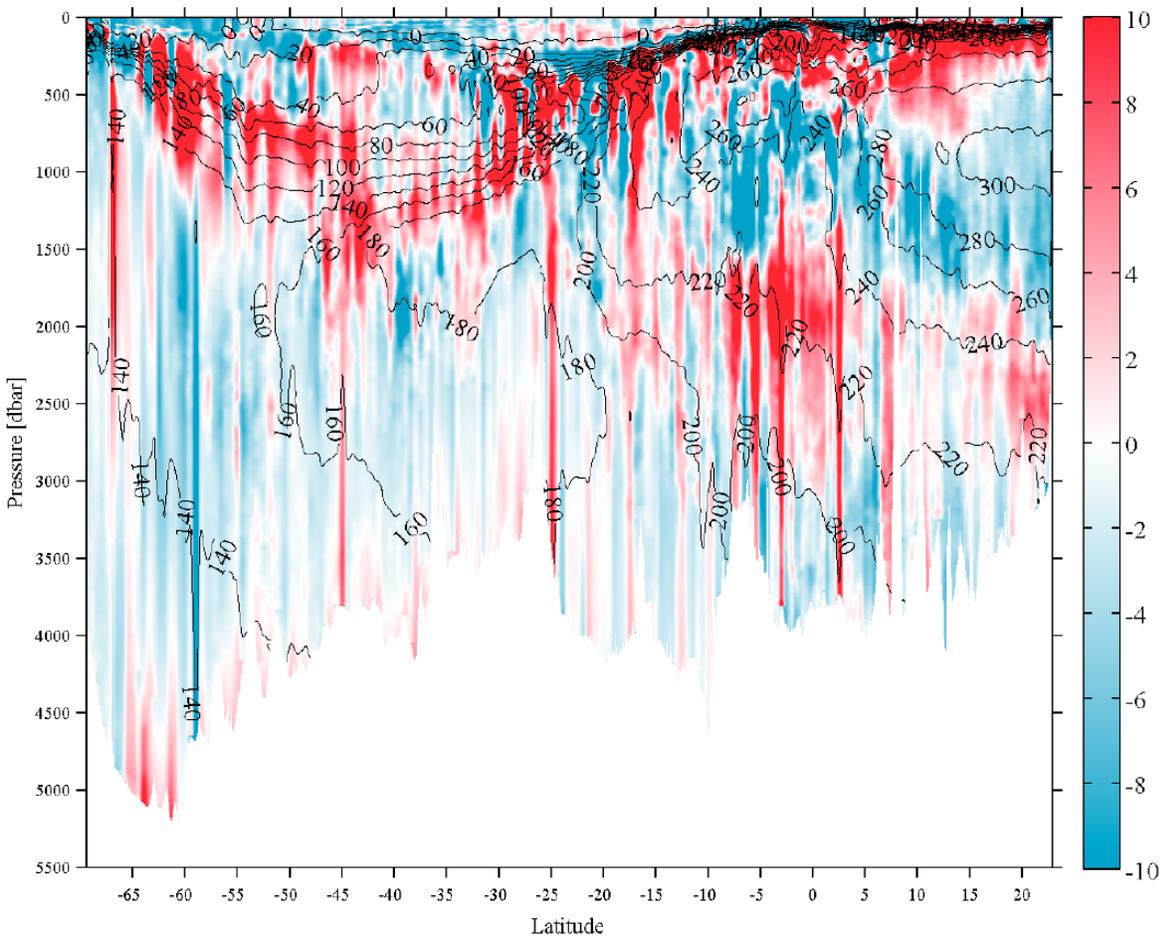


Figure 13. Section of the apparent oxygen utilization change along the P18 line between 1994 and 2008 (14 year difference).

2.7. PMEL CFC Tracer Group Project Summary

The central goals of this project are to make high-quality measurements of dissolved chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) on CLIVAR repeat hydrography sections, to calibrate these data and to make the data available to the research community.

The concentrations of these anthropogenic compounds in the atmosphere have increased rapidly in the past decades, and these increases can be reconstructed as functions of location and time. Atmospheric CFCs and SF_6 dissolve in surface seawater and the equilibrium concentrations can be calculated as a function of seawater temperature and salinity.

The entry of these compounds into the surface layer of the ocean and their subsequent transfer into the ocean interior makes them extremely useful as time-dependent (transient) tracers to:

- 1.) Determine the rates and pathways of ocean circulation and mixing processes.
- 2.) Estimate water mass formation rates and decadal changes in ventilation.
- 3.) Estimate the rates of key biogeochemical processes in the ocean.
- 4.) Improve estimates of uptake and storage of anthropogenic CO_2 in the ocean.
- 5.) Provide a unique way to test numerical ocean model simulations, evaluate strengths and weaknesses in the models, and suggest ways to improve the models.

We have developed extraordinarily sensitive analytical techniques for the rapid shipboard analysis of CFC11, CFC12 and SF₆ in seawater, with limits of detection currently: CFC11 and CFC12 ~1 x 10⁻¹⁵ mole kg⁻¹; SF₆ ~2 x 10⁻¹⁷ mole kg⁻¹.

We have successfully included measurements of SF₆ simultaneously with the CFCs on several of our recent CLIVAR expeditions and have demonstrated the enhanced value of routinely including SF₆ along with CFC11 and CFC12 measurements on future hydrographic sections. We are continuing to work to improve these techniques.

Coupled with the CFCs, this dual tracer pair approach provides improved CO₂ uptake estimates, and an opportunity to diagnose ventilation rate changes.

Recent work (Johnson et al., 2008a) has revealed significant warming during the past 15 years in the abyssal waters along the southern end of CLIVAR section I8SI9N. This warming is strongly correlated with the region of significant CFC and SF₆ invasion in the abyssal waters along the section. CFCs may prove to be a sensitive indicator of regions of the ocean where climate change signals (e.g. warming) propagate into the interior of the ocean on decadal time scales.

2.8. Preparations for the CLIVAR P18 section on NOAA Research Vessel Ronald H. Brown

We prepared, tested and calibrated a CFC/SF₆ analytical system and shipped this in our PMEL CFC laboratory van from Seattle to San Diego, CA and returned it from Punta Arenas, Chile to Seattle at the completion of the expedition. J. Bullister led in the preparation of the P18 Cruise Project Instructions, assisted with the planning and execution of the ~15 major science projects on this expedition, and coordinated the science programs with the ship personnel. J. Bullister participated as Chief Scientist on Leg 1 of this expedition. D. Wisegarver coordinated preparing the CFC/SF₆ equipment for the cruise, assisted by F. Menzia.

Perform CFC measurements on the P18 cruise:

The field measurement program was shared with Dr. M. Warner at the University of Washington. We sent 2 CFC analysts on Leg 1. We matched whenever possible the sampling of CFC/SF₆ with carbon-system measurements collected along this section.

David Wisegarver from PMEL was the lead analyst for the CFC measurements. Because of health issues, F. Menzia was unable to participate on the cruise and the second CFC analyst was hired for this work on a contract negotiated with the University of Miami.

D. Wisegarver processed the data sets, calibrated and maintained the equipment for the P18 Cruise in the Pacific.

Data collected on this cruise are available and archived at:

http://whpo.ucsd.edu/data/co2clivar/pacific/p18/p18_33RO20071215/p18_33RO20071215_hy1.csv

Samples for the analysis of dissolved CFC-11, CFC-12 and SF₆ were drawn from ~3168 of the water samples collected during the P18 expedition. Efforts were made to sample CFCs and SF₆ (CFCs/SF₆) from the same bottles sampled for carbon parameters (DIC, alkalinity, pCO₂ and pH) and other tracers. Special water sampling bottles designed at PMEL were used on the cruise to minimize CFC/SF₆ contamination. When taken, water samples for CFCs/SF₆ analysis were the first samples drawn from the sample bottles. Care was taken to coordinate the sampling of CFCs/SF₆ with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, CFCs/SF₆, helium-3, dissolved oxygen, DIC, alkalinity and pH samples were collected within several minutes of the initial opening of each bottle.

Concentrations of CFC-11, CFC-12 and SF₆ in air samples, seawater and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988) and Bullister and Wisegarver

(2008). The analytical system was calibrated frequently using a standard gas of known CFCs/SF₆ composition. Multiple injections of these loop volumes were made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFCs/SF₆-free gas) were injected and analyzed in a similar manner.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale and concentrations of SF₆ are reported relative to the NOAA-GMD calibration scale (Bullister et al., 2006). Concentrations in air and standard gas are reported in units of mole fraction CFC/SF₆ in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (1 pmol kg⁻¹ = 1 x 10⁻¹² mol kg⁻¹). Dissolved SF₆ concentrations are given in units of femtomoles per kilogram seawater (1 fmol kg⁻¹ = 1 x 10⁻¹⁵ mol kg⁻¹). CFC/SF₆ 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 working standard.

The estimated precisions for the CFC-11 and CFC-12 seawater analyses are shown in the following tables.

Table 4. Summary of number of CFC-11 samples taken and the estimated precision for the CLIVAR P18 cruise.

	CFC-11
Number of samples	3168
Number of replicates	505
Average standard deviation	0.003 pmol kg ⁻¹ (or 1.0%), whichever is greater

Table 5. Summary of number of CFC-12 samples taken and the estimated precision for the CLIVAR P18 cruise.

	CFC-12
Number of samples	3168
Number of replicates	505
Average standard deviation	0.003 pmol kg ⁻¹ (or 1%), whichever is greater

Table 6. Summary of number of SF₆ samples taken and the estimated precision for the CLIVAR P18 cruise.

	SF ₆
Number of samples	3168
Number of replicates	505
Average standard deviation	0.02 fmol kg ⁻¹ (or 2.0%), whichever is greater

A small number of water samples had anomalous CFC/SF₆ concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g. anomalous dissolved oxygen, salinity or temperature features). This suggests that these samples were probably contaminated with CFCs and/or SF₆ during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the data set, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). Approximately 68 samples out of 3168 (~1.7%) were assigned quality flags of 3 or 4.

A section of CFC-12 concentrations along P18 in 2007/2008 is shown in Figure 14.

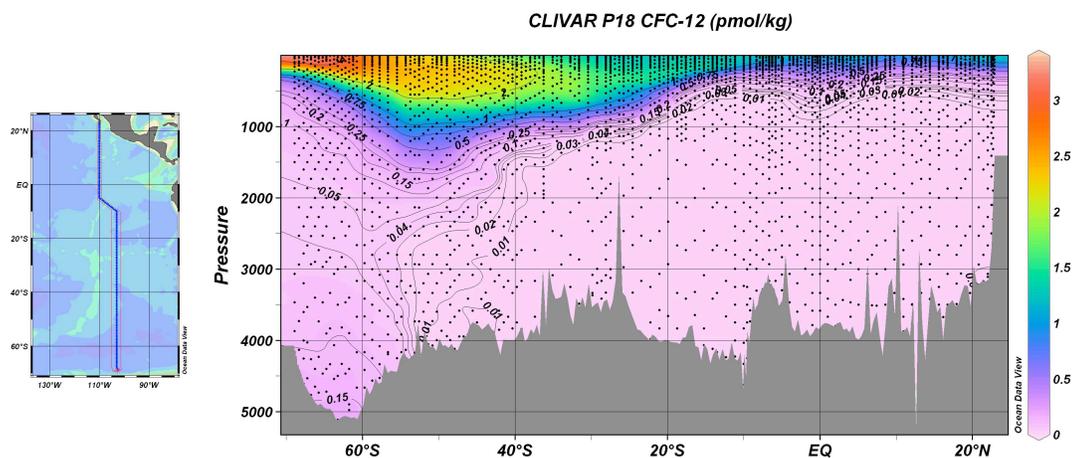


Figure 14. CFC-12 concentration (in picomoles kg^{-1}) along CLIVAR repeat section P18 in the Pacific Ocean in 2007/2008. Dots indicate locations where samples were collected.

The strong latitudinal gradient in surface concentrations primarily reflects the latitudinal gradient in surface temperature, since the solubility of CFCs is greater at cold temperatures. CFC concentrations are highest in surface waters, and in general decrease with depth, reflecting the relative isolation of deeper waters from recent exchange with the atmosphere. There is especially strong penetration of CFC-12 in abyssal, mode and intermediate waters in the southern hemisphere south of 40°S , reflecting vigorous ventilation of these waters on decadal timescales and indicating the potential of this region to rapidly take up atmospheric gases, including CO_2 .

There is a clear CFC signal in the abyssal waters to $\sim 40^{\circ}\text{S}$, reflecting ventilation via Antarctic Bottom Waters from the south. The extremely sensitive analytical techniques for measuring dissolved CFCs allows the ventilation pathways to be detected in regions where the corresponding anthropogenic CO_2 signal is difficult to detect.

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