

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

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1.0 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) will reveal much about internal pathways and changing patterns that will impact the carbon sinks on decadal time scales.

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.

Table 1. Sequence of Repeat Hydrography CO₂/tracer cruises in the oceans₂ for the decade starting in June of 2003.

| Schedule of US CO ₂ /CLIVAR Repeat Hydrography Lines (as of 10/06) | | | | | |
|--|-------------|------|---|------|--------------------------------------|
| Dates | Cruise | Days | Ports | Year | Contact/Chief Scientist |
| Overall Coordinator: Jim Swift, SIO | | | | | |
| 6/19/03-7/10/03 | A16N, leg 1 | 22 | Reykjavik-Madeira | 1 | Bullister, NOAA/PMEL |
| 7/15/03-8/11/03 | A16N, leg 2 | 28 | Madeira - Natal, Brazil | 1 | Bullister, NOAA/PMEL |
| 9/15/03-10/13/03 | A20 | 29 | WHOI - Port Of Spain | 1 | Toole, WHOI |
| 10/16/03-11/07/03 | A22 | 21 | Port Of Spain - WHOI | 1 | Joyce, WHOI |
| 6/13/04-7/23/04 | P2, leg 1 | 41 | Yokohama-Honolulu | 2 | Robbins, SIO |
| 7/26/04-8/26/04 | P2, leg 2 | 32 | Honolulu - San Diego | 2 | Swift, SIO |
| 1/11/05-2/24-05 | A16S | 45 | Punta Arenas-Fortaleza | 3 | Wanninkhof/Doney; NOAA/ACOML/WHOI |
| 1/8/05-2/18/05 | P16S | 40 | Tahiti-Wellington | 3 | Sloyan/Swift, WHOI/SIO |
| 2/13/06-3/30-06 | P16N | 57 | Tahiti-Alaska | 4 | Feely/Sabine, NOAA/PMEL |
| 2007 | I8S | 38 | Perth-Perth | 5 | Jim Swift, SIO |
| 2007 | I9N | 34 | Perth-Colombo | 5 | Janet Sprintall, SIO |
| 2008 | P18 | 32 | San Diego-Easter Island | 6 | John Bullister, PMEL |
| 2008 | P18 | 35 | Easter Island- Punta Arenas | 6 | Greg Johnson, PMEL |
| 2008 | I6S | 42 | Cape Town | 6 | |
| 2009 | I7N | 47 | Port Louis/Muscat | 7 | future planning |
| 2009 | S4P/P16S | 42 | Wellington-Perth | 7 | future planning |
| 2009 | S4P | 26 | Wellington-Perth | 7 | future planning |
| 2010 | I5 | 43 | Perth - Durban | 8 | future planning |
| 2010 | A13.5 | 62 | Abidjan-Cape Town | 8 | future planning |
| 2011 | A5 | 30 | Tenerife-Miami | 9 | future planning |
| 2011 | A21/S04A | 42 | Punta Arenas-Cape Town | 9 | future planning |
| 2012 | A10 | 29 | Rio de Janeiro-Cape Town | 10 | future planning |
| 2012 | A20/A22 | 29 | Woods Hole-Port of Spain- Woods Hole | 10 | future planning |

Years 1-6 are funded.

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 Objective 7 (Ocean Carbon Monitoring Network) of the Program Plan for Building a Sustained Observing Network for Climate. The sequence and timing for the sections (Figure 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 (Figure 2); 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. In addition, the proposed sections are selected so that there is roughly a decade between them and the WOCE/JGOFS occupations.

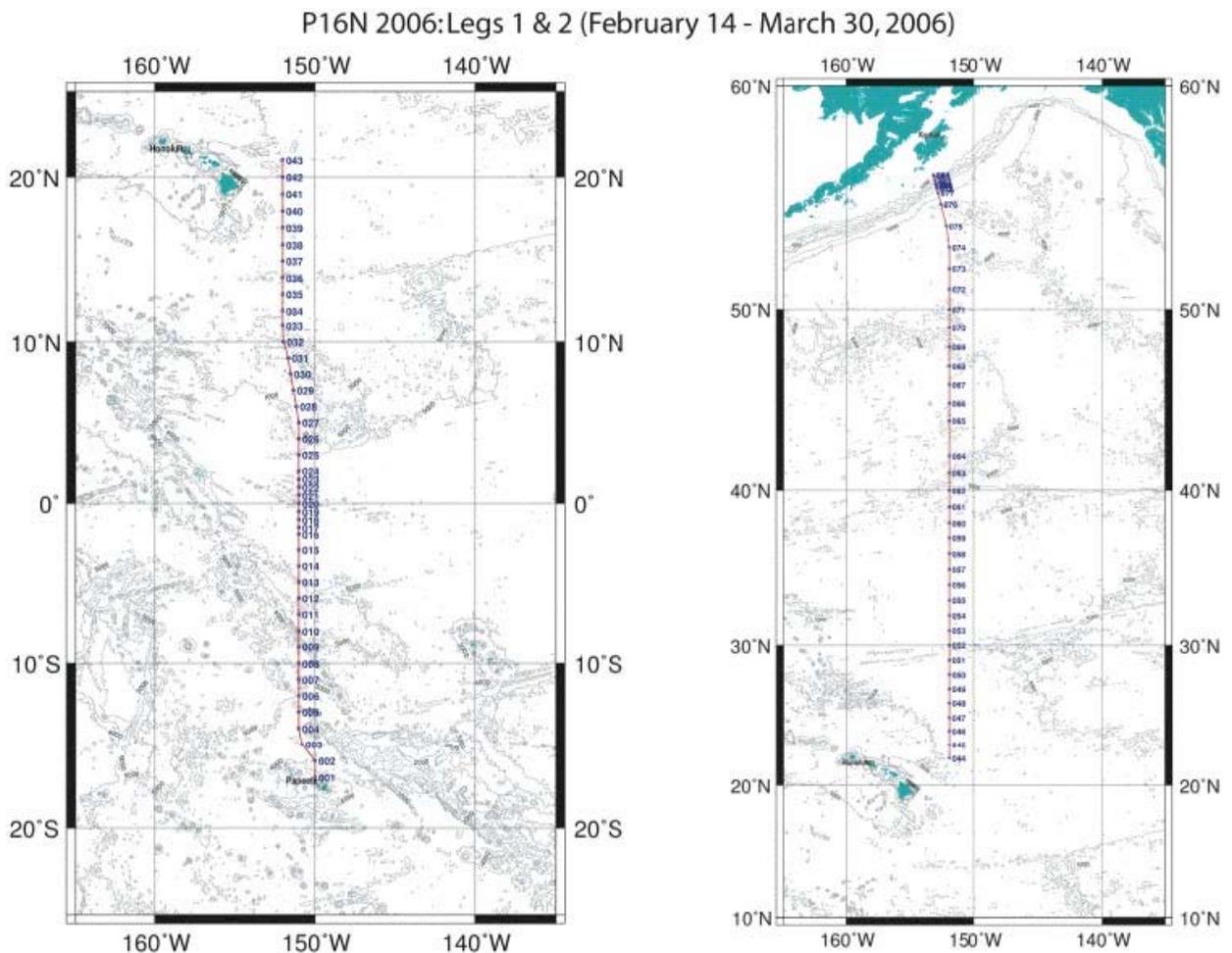


Figure 2. Cruise Track of Repeat Hydrography P16N along 152°W during Feb – Mar 2006 in the South and North Pacific.

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 OCCO 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; Figure. 1). 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 will develop 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. The goal of this plan is to build and sustain the ocean component of a global climate observing system that will respond to the long-term observational requirements of the operational forecast centers, international research programs, and major scientific assessments.

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 IOC-SCOR Ocean CO₂ Panel (<http://www.ioc.unesco.org/iocweb/co2panel/>) and the Global Carbon Project (GCP; <http://www.globalcarbonproject.org/>) have 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.

2.0 FY 2006 PROGRESS REPORT AND ACCOMPLISHMENTS

2.1 P16N Cruise Results

A hydrographic/carbon/tracer survey in the South and North Pacific Ocean was carried out from *R/V Thomas G. Thompson*. The cruise departed from Papeete, Tahiti 13 February 2006. A meridional transect from 17°S to 57°N along 152° West was completed (Figure 2). NOAA scientists were responsible for all cruise planning and logistics and Drs. Sabine and Feely served as chief scientist for legs 1 and 2 of the cruise, respectively. Water samples were collected at 34 depths at each full water-column CTD/O₂ station and analyzed for salinity, nutrients, dissolved oxygen, four inorganic carbon parameters, radiocarbon, dissolved organic matter, colored dissolved organic carbon, chlorofluorocarbons, helium/tritium, carbon isotopes, chlorophyll, and a suite of bacterial measurements. Trace metal casts to 1000m were conducted at approximately every other station. Optical profiles were collected once each day. Near surface seawater and atmospheric measurements were also made along the cruise track. The cruise ended in Kodiak, Alaska on 30 March 2006.

2.2 CTD/O₂ and Bottle Salinity (Baringer, Johnson, and Langdon)

The PMEL and AOML hydrography groups worked together on this cruise. In preparation for this cruise PMEL readied and assembled the bulk of the rosette frames, Niskin bottles, CTD/O₂ units, altimeters, load cells, 12 kHz pingers, LADCPs, cabling, terminations, and other underwater equipment. We also acquired the necessary standard seawater, cruise supplies, and shipped the bulk of the CTD/O₂ and LADCP gear to Tahiti. While at sea, we acquired CTD/O₂ data, monitored sensor performance, and performed preliminary calibrations of the CTD/O₂ temperature, salinity, and oxygen sensors. The AOML group provided a salinity analyst who ran bottle salts for every bottle from which water was available to take a sample, and an electrical engineer who stood watch and assisted with CTD and LADCP operations. Since the cruise we have shipped the PMEL gear back to Seattle, had post-cruise calibrations run on the CTD/O₂ sensors, completed

final calibrations of CTD/O₂ temperature, salinity, pressure, and oxygen data (which are believed to be accurate to within 0.002°C, 0.003 PSS-78, 3 dbar, and 1.0 μmol kg⁻¹ or better, respectively), revised the bottle salinity data quality flags, sent a list of suggested bottle oxygen flags to the bottle oxygen PI, submitted the final CTD/O₂ and salinity data and quality flags to the data center, and contributed to a cruise report documenting the final CTD/O₂ data calibration and processing.

In FY 2006 we wrapped up an analysis of data from the 2003 reoccupation of A16N and the three previous occupations on SubPolar Mode Water variability including analysis of regional substantial changes in oxygen and potential vorticity and their likely causes (ocean circulation). That paper (Johnson and Gruber, 2006) has now been accepted for publication. We also performed and published an analysis of abyssal changes in the South Atlantic using data from the 2005 reoccupation of A16S and the previous WOCE occupation to reveal a large and statistically significant warming of the bottom waters in the Argentine and Brazil Basins (Johnson and Doney, 2006).

In addition, we have begun an examination of deep temperature differences (Figure 3) for P16 that shows an abyssal warming over the 15-year time for almost the entire latitude range (all of the Pacific) occupied. Johnson is working with colleagues to analyze abyssal temperature changes in these and other repeat hydrographic sections. Analysis of data from these sections is the primary direct means to estimate the contributions of abyssal temperature variations to the global ocean heat budget. The global ocean heat budget is vital to climate change modeling and prediction. Early results suggest that abyssal temperature variations may contribute significantly, although probably not dominantly, to the global ocean heat budget.

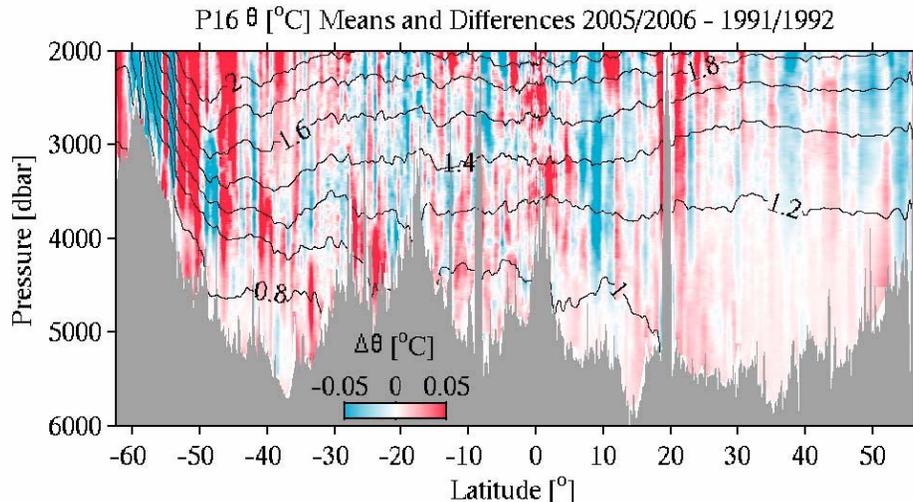


Figure 3. Potential Temperature (θ) means (solid black lines at 0.2 °C intervals) and differences (red warming and blue cooling) along WOCE Section P16 based on data from the 1991/1992 original occupations and 2005/2006 reoccupations.

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

The DIC analytical equipment was set up in a seagoing container modified for use as a shipboard laboratory. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) operated simultaneously on the cruise by Alex Kozyr (CDIAC) and Robert Castle (AOML) on leg 1 and Dana Greeley and David Wisegarver of PMEL on leg 2. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson (Johnson, 1992; Johnson et al., 1985; Johnson et al., 1987; Johnson et al., 1993) of Brookhaven National Laboratory (BNL). Samples were drawn from the Niskin-type bottles into cleaned, precombusted 300-mL Pyrex bottles using silicone tubing. DIC values were reported for 2622 samples or approximately 92% of the tripped bottles on this cruise. Full profiles were completed at stations on whole degrees, with replicate samples taken from the surface, oxygen minimum, and bottom depths. Duplicate samples were drawn from 192 bottles and interspersed throughout the station analysis for quality assurance of the coulometer cell solution integrity. The average of the absolute value of the difference between duplicates was $0.85 \mu\text{mol kg}^{-1}$ for both systems. No systematic differences between the replicates were observed. The coulometers were each calibrated by injecting aliquots of pure CO_2 (99.99%) by means of an 8-port valve outfitted with two sample loops (Wilke et al., 1993). The instruments were calibrated at the beginning of each station with a set of the gas loop injections. Secondary standards were run throughout the cruise on each analytical system; these standards are Certified Reference Materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), and their accuracy is determined shoreside manometrically. On this cruise, the overall accuracy for the CRMs on both instruments combined was $0.8 \mu\text{mol/kg}$ ($n=66$).

The DIC data have been completed and submitted to CDIAC and CCHDO for distribution to the oceanic community. They have been integrated with the P16S cruise data (see Figure 4 above) and are of very high quality. A complete P16 section of the DIC data shows strong vertical and horizontal gradients in the concentrations consistent with anticipated circulation features (Figure 4). The black dots in the figure indicate the location of the carbon measurements. The previous occupation of this line was during the WOCE global survey in 1991. Figure 4 also shows the change in DIC between these cruises (approximately 15 years). Preliminary results indicate significant increases in DIC in the upper 1000 m in 2006 compared with 1991.

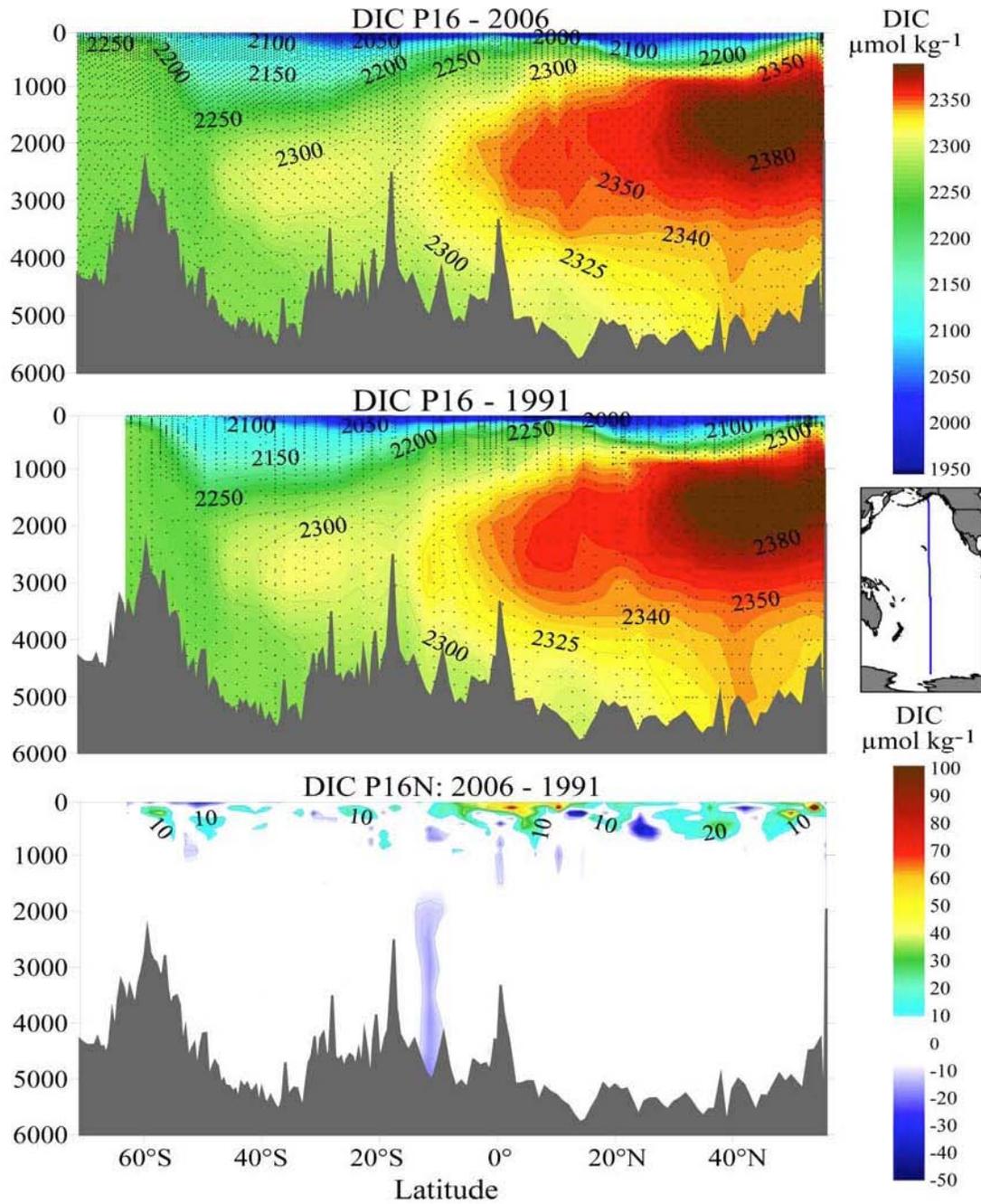


Figure 4. DIC in $\mu\text{mol kg}^{-1}$ along the P16 section (top: 2005-2006; middle: 1991) in the Pacific Ocean along 150-152°W. The gridded difference plot is shown on the bottom panel. The increases in DIC are the result of a combination of processes including: anthropogenic CO₂ invasion, and changes in circulation and biogeochemistry.

| Table 2. Summary of number of DIC samples taken and the estimated precision for the P16 cruise | |
|---|------------|
| | DIC |
| Number of samples | 2622 |
| Number of replicates | 192 |
| Average standard deviation ($\mu\text{mol kg}^{-1}$) | 0.85 |

2.4 Discrete $p\text{CO}_2$ (Wanninkhof)

Samples were drawn from the Niskin-type bottles into 500 ml volumetric flasks. About 5 ml of water was withdrawn to allow for expansion of the water as it warms. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at room temperature generally for no more than 5 hours.

Samples were analyzed at a constant temperature of either 20°C or 12°C. The $p\text{CO}_2$ in intermediate waters of the North Pacific reach the highest values in the world's oceans and even with samples run at 12°C some analyses would exceed the working range of the detector of about 2000 ppm. The depth range of the very high $p\text{CO}_2$ concentrations gets progressively deeper going northward. Samples were not collected in the waters that would exceed the instrument range. For example, no $p\text{CO}_2$ samples were taken between 700 and 1200 db at station 53 and the range progressively increased from 175 to 1500 db at station 77.

When samples were taken on a particular cast, flasks were drawn on all the Niskin-type bottles including four duplicates. Two of the duplicates were analyzed at the two different temperatures. A total of 30 stations were sampled and the tally of samples is listed below.

| Table 3. Summary of number of $p\text{CO}_2$ samples taken and the estimated precision for the P16 cruise | |
|--|-----|
| Number of stations sampled | 30 |
| Total number of unique $p\text{CO}_2$ samples | 880 |
| Good values (QC=2 or QC =6) | 849 |
| Questionable values (QC=3) | 15 |
| Bad values (QC=4) | 16 |
| Duplicate values (QC=6) | 104 |

Table 4 shows the statistics for the three types of duplicates that were taken. The average difference: $[\text{ABS}(\text{sample 1}-\text{sample 2})/(\text{sample 1}+\text{sample 2})]$, std. dev. and number for the three types are listed below:

| Table 4. Standard deviations of duplicate samples. | | |
|---|------------------------|----------------------------|
| Duplicates run at 20°C: | av. dif. =0.3 ±0.23% | n = 33 (one value omitted) |
| Duplicates run at 12°C: | av. dif. = 0.3 ±0.18 % | n= 23 (one value omitted) |
| Duplicates run at 12°C & 20°C* | av. dif = 0.7 ±0.75 % | n= 59 (two values omitted) |
| *For comparison of the duplicates run at 12°C, the 12°C results were normalized to 20°C | | |

The discrete pCO₂ system is patterned after the instrument described in (Chipman et al., 1993) and is discussed in detail in (Wanninkhof and Thoning, 1993) and (Chen et al., 1995). Once the samples reach the analysis 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 is run through the analyzer before and after every ten seawater samples. The cylinder serial numbers and mole fractions of CO₂ with balance artificial air of the standards are:

| Table 5. Cylinder serial numbers and mole fractions of CO ₂ | |
|---|------------|
| CA5998 | 205.1 ppm |
| CA5989 | 378.7 ppm |
| CA5988 | 593.6 ppm |
| CA5980 | 792.5 ppm |
| CA5984 | 1037.0 ppm |
| CA5940 | 1533.7 ppm |

The standards were obtained from Scott-Marrin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale. 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.

Key reasons for the discrete $p\text{CO}_2$ measurements are to ascertain complete understanding of inorganic carbon system dynamics and to have a sensitive carbon system parameter to discern changes over time. The figure below shows the excellent agreement between the measured $p\text{CO}_2$ and calculated $p\text{CO}_2$ using total inorganic carbon (DIC) and pH. A weak trend is observed going northward (higher station numbers) that needs to be further investigated. Possibilities are that standardization of pH and/or $p\text{CO}_2$ are not entirely consistent or that other poorly constrained parameters such as the dissociation constants of Si and borate are biasing the use of pH in these internal consistency calculations. The much poorer agreement and larger standard deviation of the $p\text{CO}_2$ calculated from DIC and Total Alkalinity (TA) points to the strong need to include a third carbon system parameter if the data are to be used effectively to address the pressing concerns about biota in a high CO_2 /low pH ocean.

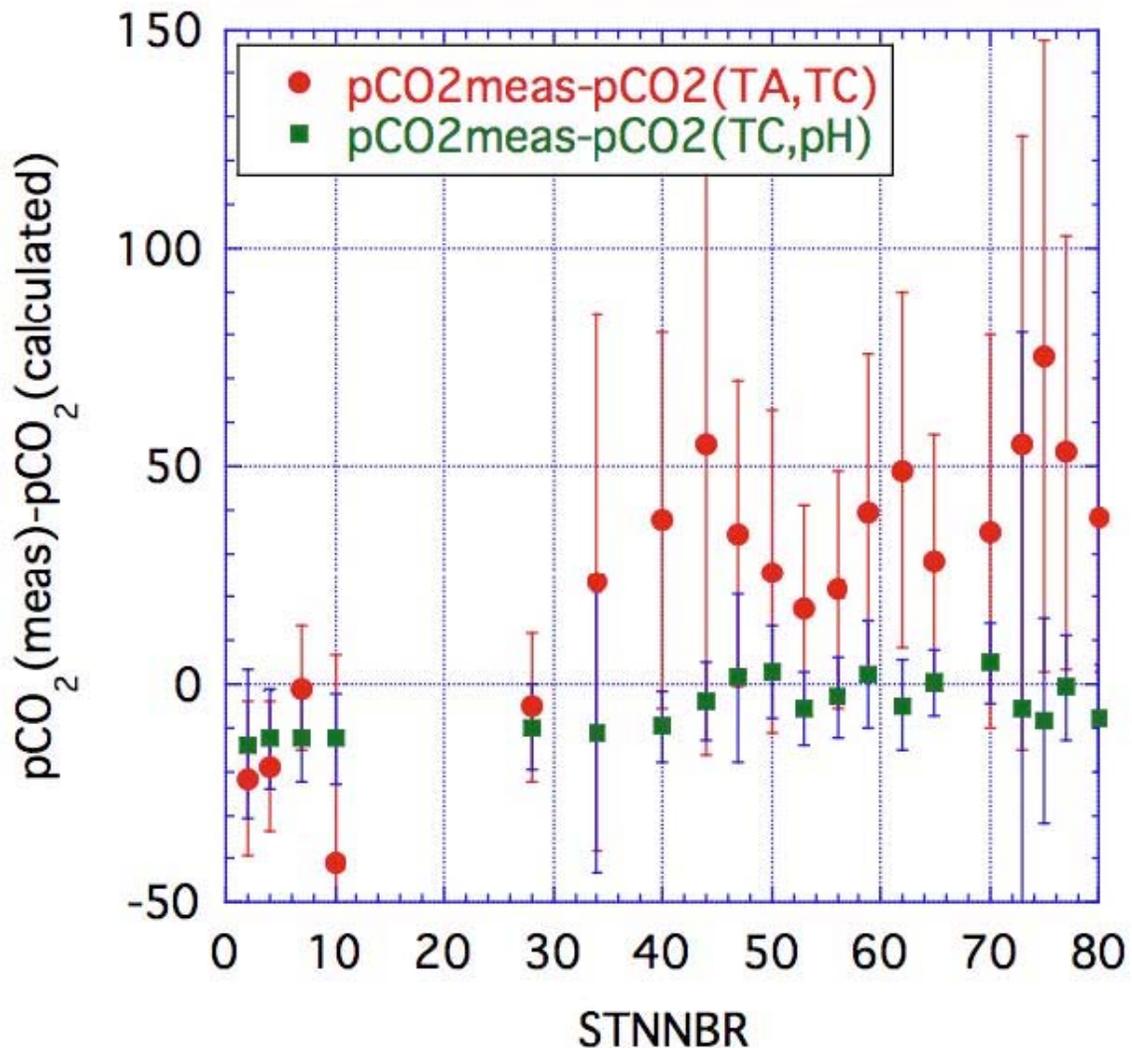


Figure 5. Station averaged ($p\text{CO}_2$ measured - $p\text{CO}_2$ calculated) versus station number (refer to Figure 2 for location). The red circles are the difference of $p\text{CO}$ measured from those calculated with TA and DIC. The green squares are the difference with $p\text{CO}$ measured from those calculated with pH and DIC. The error bars are the standard deviation of the differences for each station comprised of 25 to 35 samples.

2.5 Nutrients (Mordy and Zhang)

The major task for the nutrient group in FY-06 was the analysis of dissolved inorganic nutrients (nitrate, nitrite, phosphate and silicic acid) on the P16N cruise. This was a joint effort between nutrient laboratories at PMEL (Mordy) and AOML (Zhang), and involved several months of preparation (repairing the autoanalyzer, purchasing materials and supplies, shipping of hazmat and the autoanalyzer), several months at sea with two chemists running the autoanalyzer continuously, and several months of data reduction.

During the cruise, nutrient samples were collected from all Niskin-type bottles using 30 ml acid washed high-density polyethylene bottles that were rinsed at least three times with sample. All samples were allowed to warm to room temperature in the dark, and were analyzed within 2 hours of sample collection. Measurements were made in the temperature-controlled laboratory on the ship; nevertheless, temperatures variations were much greater ($21\pm 6^\circ\text{C}$) than on past cruises. The autoanalyzer used on P16N was a custom instrument made from various components. The reaction for phosphate was carried out using macro-sized glassware and coils from the Technicon AAI autoanalyzer. The other chemistries were carried out using micro-glassware from Alpkem. Analytical methods were from (Gordon et al., 1994), except that the reaction of phosphate occurred at 55°C with a much lower concentration of sulfuric acid (Zhang et al., 2001).

Standardization and analysis procedures specified by (Gordon et al., 1994) were closely followed, including calibration of labware (e.g. glass volumetric flasks and pipettes), preparation of primary and secondary standards, and corrections for blanks and refractive index. A mixed primary standard solution was prepared by dissolving high purity standard materials (KNO_3 , KH_2PO_4 and Na_2SiF_6) in deionized water, and this standard was stored at room temperature. Because primary nitrite standard solutions are known to be unstable, they were prepared approximately every 10 days, and were stored in the refrigerator. Working standards were freshly made at each station by diluting 20 mls of the mixed primary standard and 1 ml of the nitrite stock solutions to 500 ml with low nutrient seawater. Standardizations were performed at the beginning and end of each analytical run. Replicates were collected from the deepest Niskin bottle(s). To check for station-to-station systematic errors (i.e., errors in standard preparation), at least one replicate was stored in the refrigerator, and analyzed a second time with the subsequent station. Each analytical run and the entire data set were corrected for any drifts or offsets in standards, blanks and refractive index. To estimate the overall precision of the analysis (Table 6), we calculated the relative standard deviation of replicate samples (not including replicates used to evaluate station-to-station systematic errors).

Vertical sections of silicic acid, nitrate and phosphate are shown in Figure 6. Along most of the section, surface concentrations were depleted. Equatorial upwelling resulted in low but measurable surface nutrients between $\sim 5^{\circ}\text{S}$ - 10°N ($\sim 1500\text{km}$ to 3000km). Nutrient concentrations were also higher in the surface waters of the Alaskan Gyre as a result of deep winter mixing. Subsurface maxima of nitrate and phosphate were concomitant with the oxygen minimum in the upper 2000 m, and the distribution of these properties were a result of microbial remineralization of organic material (and to a lesser extent, processes such as denitrification and nitrogen fixation). The subsurface maximum of silicic acid was deeper than for nitrate and phosphate due to the slow dissolution of sinking siliceous material (skeletons of diatoms and radiolarians). Hydrothermal plumes rich in silicic acid emanate from Juan de Fuca Ridge, and also contributed to this maximum.

Table 6. Summary of number of nutrient samples taken and estimated precision on P16N.

| | Phosphate | Silicic Acid | Nitrate | Nitrite |
|----------------------|------------------|---------------------|----------------|----------------|
| Number of samples | 3212 | 3245 | 3145 | 3245 |
| Number of replicates | 149 | 150 | 146 | 22* |
| Percent deviation | 1.6% | 0.4% | 0.5% | 2% |

* Samples with nitrite concentrations higher than $0.05 \mu\text{M}$.

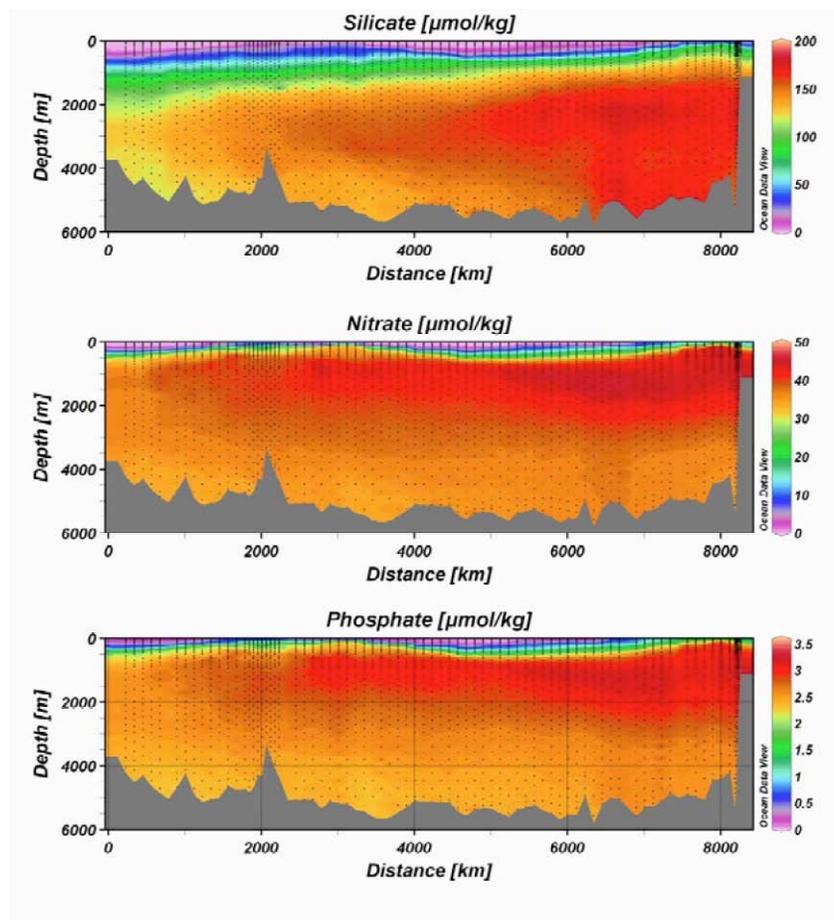


Figure 6. Vertical sections of nutrients along the P16N cruise track.

2.6 Oxygen (Langdon)

Samples were drawn from Niskin bottles into calibrated 140 ml iodine titration flasks using Tygon tubing with a Silicone adaptor that fit over the petcock to avoid contamination of DOM samples. Bottles were rinsed twice 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 $\mu\text{mol kg}^{-1}$ concentrations, and a diagnostic check of bottle integrity. One-ml of MnCl_2 and one-ml of NaOH/NaI were added using a Repipetor, and the flask was stoppered and shaken. DIW was added to the neck of each flask to create a water seal. The flasks were stored in the lab in plastic totes at room temperature for 1-2 hours before analysis. Thirty-six samples plus 1-2 duplicates were drawn from each station except the shallow coastal stations where only 15-28 samples were drawn. Total number of samples collected was 2842; total number of samples flagged after initial shipboard reduction of quality control: Questionable (QC=3) 25: Bad (QC=4) 120: Not reported (QC=5) 7.

Dissolved oxygen analyses were performed with a MBARI-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365 nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by a 386 PC running the Oxygen program written by Gernot Friedrich. Thiosulfate was dispensed by a Dosimat 665 fitted with a 5.0 ml buret. The whole-bottle titration technique of (Carpenter, 1965) with modifications by (Culberson and Knapp, 1991) was used, but with a more dilute solution of thiosulfate (10 g L^{-1}). Standard curves were run each day. The reagent blank was taken to be the intercept of the standard curve and compared to the reagent blank determined by the convention two titration method. The autotitrator and Dosimat generally performed well. Endpoints were noted to be noisy during periods of particularly bad weather. Thiosulfate molarities were calculated from titration of the standard iodate solution dispensed using a calibrated Wheaton bottle top dispenser and corrected to 20°C. The 20°C molarities were plotted versus time and were reviewed for possible problems. Blank volumes and thiosulfate molarities were smoothed (linear fits) at the end of the cruise and the oxygen values recalculated. Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at AOML and corrected for the buoyancy factor. The Dosimat and Wheaton positive displacement dispenser used for dispensing the KIO_3 were calibrated in the same way. Liquid potassium iodate standard solution with a normality of 0.0100 was prepared and bottled at AOML prior to the cruise. A single batch was used during the cruise.

In addition to the photometric end-point technique, samples from several stations during leg 2 were analyzed using an amperometric detection method (Culberson and Huang, 1987) for comparison. This was done to test amperometric detection method for future standard use. The difference between the two techniques was on average $<1 \mu\text{mol kg}^{-1}$.

2.7 Chlorofluorocarbons (Bullister)

Samples for the analysis of dissolved CFC-11 and CFC-12 were drawn from ~1835 of the water samples collected during the P16N expedition. Efforts were made to sample CFCs from the same bottles sampled for carbon parameters (DIC, alkalinity, pCO_2 and pH) and other tracers. Twelve liter water sample bottles, specially designed to minimize CFC contamination, were used on the cruise. When taken, water samples for CFC analysis were the first samples drawn from the 12-liter bottles. Care was taken to coordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, CFC, helium-3, dissolved oxygen, DIC, alkalinity and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 12-liter bottles into 100 ml precision glass syringes. The syringes were immersed in a holding bath of fresh water until analyzed.

For air sampling, a ~100 meter length of 3/8" OD Dekaron tubing was run from

the laboratory to the bow of the ship.

Concentrations of CFC-11 and CFC-12 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). For seawater analyses, water was transferred from a glass syringe to a fixed volume chamber (~30 ml). The contents of the chamber were then injected into a glass sparging chamber. The dissolved gases in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber and were concentrated on a cold-trap. The trap was then heated and its contents injected onto a pre-column and the main analytical column. The analytical systems were calibrated frequently using a standard gas of known CFC composition. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of 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 or blank samples was ~10.5 minutes.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et al., 2000). 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 per kilogram seawater (pmol kg^{-1}). 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 working standard. The response of the detector to the range of moles of CFC-12 and CFC-11 passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at intervals of 10 days during the cruise. These were supplemented with occasional injections of multiple aliquots of the standard gas at more frequent time intervals. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity. The precisions of measurements of the standard gas in the fixed volume ($n=395$) were $\pm 0.44\%$ for CFC-12, and 0.56% for CFC-11.

The efficiency of the purging process was evaluated periodically by re-stripping high concentration surface water samples and comparing the residual concentrations to initial values. These re-strip values were approximately $<1\%$ for all 3 compounds.

The average atmospheric concentrations determined during the cruise (based on sets of 5 air analyses made daily, $n=23$) were 252.9 ± 4.4 parts per trillion (ppt) for CFC-11 and 547.2 ± 5.0 ppt for CFC-12.

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

| Table 7. Summary of number of CFC-11 samples taken and the estimated precision for the P16 cruise | |
|--|--|
| | CFC-11 |
| Number of samples | 1835 |
| Number of replicates | 38 |
| Average standard deviation | 0.004 pmol kg ⁻¹ (or 0.45%), whichever is greater |

| Table 8. Summary of number of CFC-12 samples taken and the estimated precision for the P16 cruise | |
|--|--|
| | CFC-12 |
| Number of samples | 1835 |
| Number of replicates | 38 |
| Average standard deviation | 0.003 pmol kg ⁻¹ (or 0.36%), whichever is greater |

A small number of water samples had anomalously high CFC 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 during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the preliminary data, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples that were drawn from the rosette but never analyzed due to a variety of reasons (e.g. power outage during analysis).

A composite section of CFC-12 concentrations along P16S in 2005 and P16N in 2006 is shown in Figure 7. The strong latitudinal gradient in surface CFC-12 concentrations primarily reflects the latitudinal gradient in surface temperature, since the solubility of CFCs is greater at cold temperatures. CFC-12 concentrations in general decrease with depth, reflecting the relative isolation of deeper waters from recent exchange with the atmosphere. There especially strong penetration of CFC-12 in mode and intermediate waters in the southern hemisphere south of 40° S, indicating the potential of this region to take up atmospheric gases, including CO₂.

Figure 8 shows the concentration of dissolved sulfur hexafluoride (SF₆) along P16N in 2006 (SF₆ measurements were not made on P16S in 2005). The spatial resolution for SF₆ measurements was relatively coarse in this pilot study on P16N, with at

total of ~130 SF₆ samples analyzed during the expedition. Atmospheric concentrations of SF₆ have been increasing rapidly in the atmosphere during the past 2 decades. Along with the CFCs, this compound has the potential to be an extremely useful tracer of ocean circulation and mixing processes, for estimating anthropogenic CO₂ uptake and for multi-tracer dating of water masses (Bullister et al., 2006). At present, typical concentrations of dissolved SF₆ in surface waters are ~1000 times lower than CFC-12. We hope to develop our analytical techniques to make SF₆ measurement more routine on future repeat hydrography cruises.

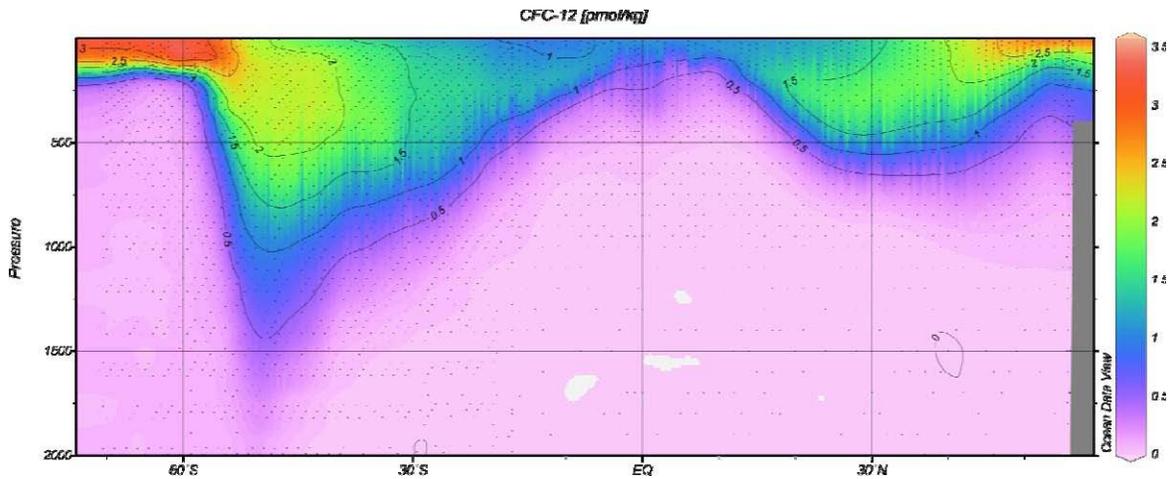


Figure 7. CFC-12 concentrations along P16S in 2005 and P16N in 2006.

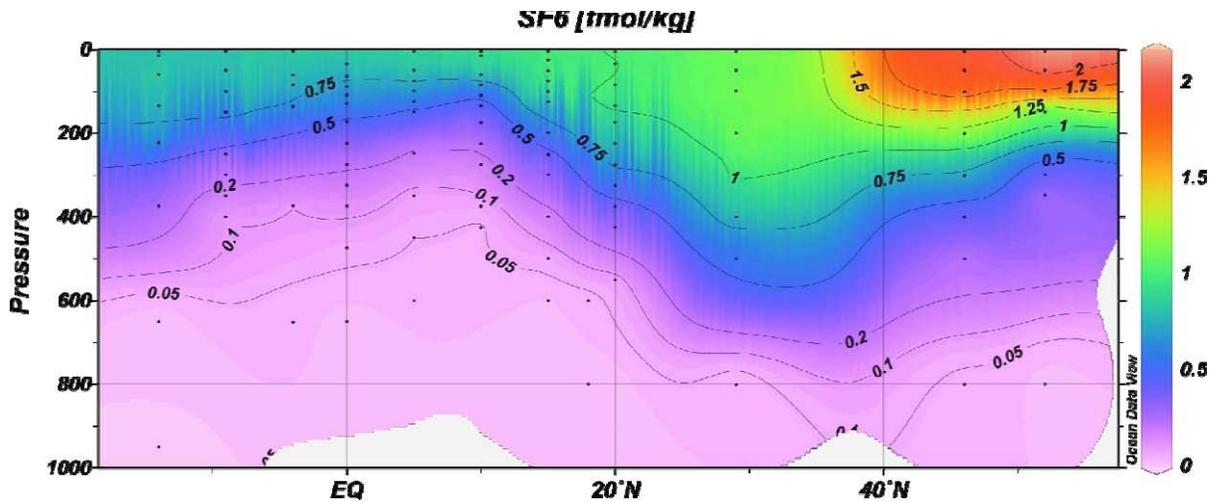


Figure 8. Concentration of dissolved sulfur hexafluoride (SF₆) along P16N in 2006

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- Arrigo, K., H. Bange, R. Feely, N. Gruber, D. Hansell, G. Herndl, K. Lee, T. Johannessen, K. Johnson, A. Körtzinger, N. Metz, T. Saino, and B. Stephens (2006): Joint SOLAS-IMBER Ocean Carbon Research: Implementation Plan. IMBER Report No. 1/SOLAS Report, International Council for Science, Scientific Committee on Oceanic Research, 45 pp.
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Relevant Meetings and Presentations in FY06

Sabine:

- IOCCP SSG Meeting, Broomfield, CO, October 1, 2005 (organizer and chair of meeting)
- Geological Society of America Annual Meeting, Salt Lake City, UT, Oct. 17-18, 2005 (invited talk: The CaCO₃ Cycle and its Role in Global Climate Change)
- IOCCP/CLIVAR Repeat Hydrography Workshop, Shonan Village, Japan, Nov. 14-16, 2005 (co-organizer and discussion session leader)
- PICES section on Carbon and Climate meeting, Shonan Village, Japan, Nov. 17, 2005
- Guest lecture at Art Institute of Seattle, Seattle, WA, April 19, 2006 (talk on global climate change and ocean acidification).
- OCO annual review, Silver Spring, MD, May 10-12, 2006 (invited talk: The Global Ocean Carbon Cycle: Inventories, Sources and Sinks)
- NACP Science Steering Group Meeting, Silver Spring, MD, May 18-19, 2006 (report to SSG on ocean carbon components)
- North Atlantic Synthesis Meeting, Laugarvatn, Iceland, June 26-July 2, 2006
- Ocean Carbon and Climate Change Scientific Workshop, Woods Hole, MA, July 10-12, 2006
- OCCC and Ocean Carbon and Biogeochemistry SSG meeting, Woods Hole, MA, July 13, 2006
- Global Carbon Project SSG meeting, Mexico City, Mexico, Aug. 30-Sept. 4, 2006

Feely:

- IOCCP SSG Meeting, Broomfield, CO, October 1, 2005
- IOCCP/CLIVAR Repeat Hydrography Workshop, Shonan Village, Japan, Nov. 14-16, 2005
- PICES section on Carbon and Climate meeting, Shonan Village, Japan, Nov. 17, 2005
- Ocean Sciences Meeting, Honolulu, HI February 2006 - Decadal Variations in Ocean Interior
- Circulation and Biogeochemistry: Results From the CLIVAR/CO₂ Repeat Hydrography Program, Feely and Talley co-chairs.
- OCO annual review, Silver Spring, MD, May 10-12, 2006 (poster: The Repeat Hydrography CO₂/Tracer Program) Ocean Carbon and Climate Change Scientific Workshop, Woods Hole, MA, July 10-12, 2006
- North Atlantic Synthesis Meeting, Laugarvatn, Iceland, June 26-July 2, 2006

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