Global Repeat Hydrographic/CO_2/Tracer surveys in Support of CLIVAR and Global Cycle objectives: Carbon Inventories and Fluxes

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1. Project Summary

The Repeat Hydrography CO_2/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 (CO_2), chlorofluorocarbon (CFC) tracers and related parameters. It builds upon earlier programs (e.g., World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Study (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 CO_2/tracer Program 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 the thermohaline overturning, can also be documented using long-term observations throughout the water column. Below the 2000-m depth of Argo, Repeat Hydrography provides the only global measurements for observing long-term trends in the ocean (Figure 1, Table 1). 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 existing and new autonomous sensors. The data products are posted on the CLIVAR and Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/) and the Carbon dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/), and the results are used for research publications, atlases, and outreach materials. The end products are used by scientists to develop and validate models of ocean circulation changes, and models of the uptake of carbon dioxide and other anthropogenic trace gases. They are also used to access and validate models of future impacts to ocean biological ecosystems resulting from acidification, stratification, and circulation changes.

The program is co-sponsored by NOAA and the National Science Foundation and 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 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 research programs, including the focus of CLIVAR in the 2011-2014 timeframe; the SOLAS Program that emphasizes constraining the carbon uptake in the surface oceans, in part, in support of the North American Carbon Program (NACP); and the international Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) program. Emphasis during 2011 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.

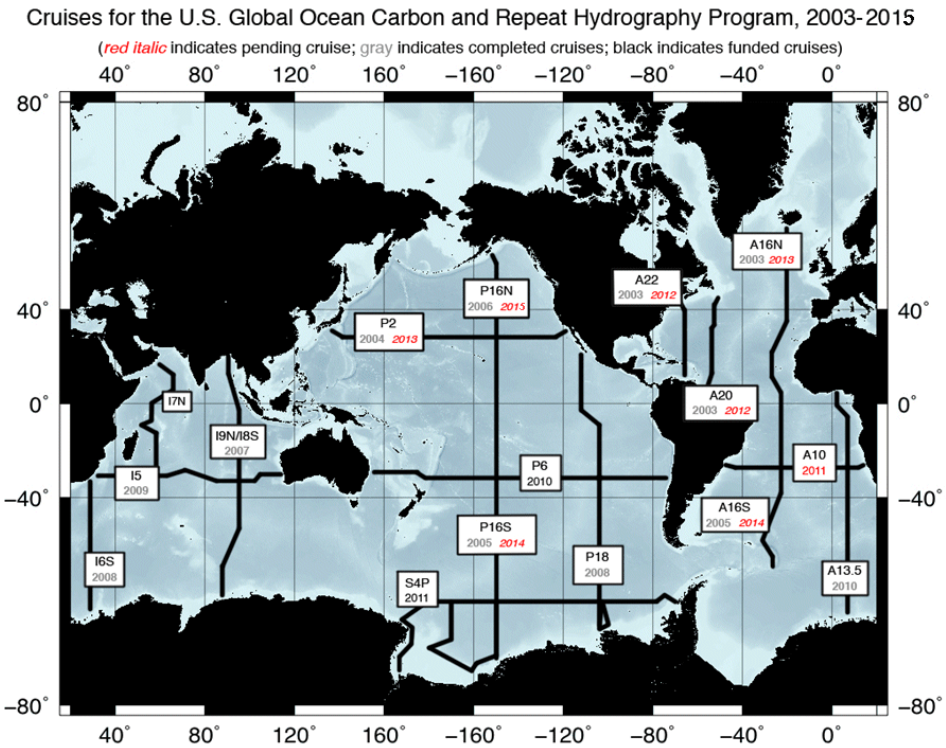

Figure 1a. Global map of U.S Repeat Hydrography CO_2/Tracer Program hydrographic sections with carbon system measurements.

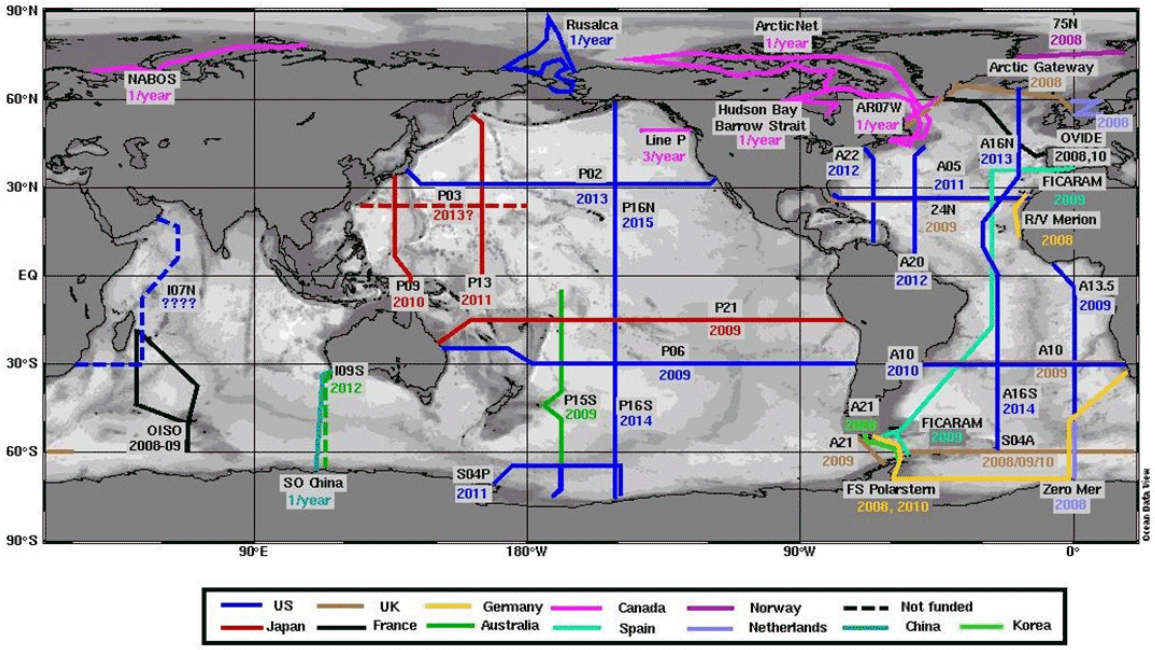

Figure 1b. Global map of international Repeat Hydrography CO_2/Tracer Program hydrographic sections with carbon system measurements. Solid lines indicate funded lines. Dashed lines indicate planned lines that are not fully funded at this time. The U.S. cruises are designated with blue lines. Section lines S4P and A10 were occupied in FY 2011.

Table 1. Sequence of Repeat Hydrography CO_2/Tracer completed and planned cruises, 2003 to 2015.

Schedule of US CO2/CLIVAR Hydrography Lines (as of 11/19/10)

Dates	Cruise(for documentation and results see the Data Links page)	Days	Ports	Contact/Chief Scientist (overall coordinator: Jim Swift, SIO)	Ship
06/19/03-07/10/03	A16N, leg 1	22	Reykjavik-Madeira	Bullister, PMEL	Ron Brown
07/15/03-08/11/03	A16N, leg 2	28	Madeira - Natal, Brazil	Bullister, PMEL	Ron Brown
09/15/03-10/13/03	A20	29	WHOI - Port Of Spain	Toole, WHOI	Knorr
10/16/03-11/07/03	A22	21	Port Of Spain - WHOI	Joyce, WHOI	Knorr
06/15/04-07/25/04	P2, leg 1	41	Yokohama-Honolulu	Robbins, SIO	Melville
07/28/04-08/27/04	P2, leg 2	32	Honolulu - San Diego	Swift, SIO	Melville
01/09/05-02/22/05	P16S	45	Wellington-Tahiti	Sloyan/Swift, WHOI/SIO	Revelle
01/11/05-02/26/05	A16S	48	Punta Arenas - Fortaleza	Wanninkhof,Doney; NOAA/AOML,WHOI	Ron Brown
02/13/06-03/03/06	P16N, leg 1	18	Tahiti-Honolulu	Sabine; NOAA/PMEL	Thompson
03/10/06-03/30/06	P16N, leg 2	21	Honolulu-Kodiak	Feely; NOAA/PMEL	Thompson
02/04/07-03/17/07	I8S	38	Dunedin, NZ-Fremantle	Swift, SIO	Revelle
03/22/07-05/02/07	I9N	38	Perth-Colombo, Sri Lanka	Sprintall, SIO	Revelle
12/15/07-01/16/08	P18	32	San Diego-Easter Island	Johnson, Bullister, PMEL	Ron Brown
01/19/08-02/23/08	P18	35	Easter Island- Punta Arenas	Johnson, Bullister, PMEL	Ron Brown
02/04/08-03/17/08	I6S	43	Durban-Cape Town	Speer, FSU	Revelle
03/19/09-05/14/09	I5	57	Cape Town-Fremantle	Swift, Johnson, SIO, PMEL	Revelle
11/21/09-01/02/10	P6, leg 1	43	Brisbane - Papeete	Macdonald, WHOI	Melville
01/05/10-02/10/10	P6, leg 2	37	Papeete - Valparaiso	Curry, WHOI	Melville
03/08/10-04/17/10	A13.5	42	Cape Town-Takoradi	Bullister, PMEL	Ron Brown
02/19/11-04/28/11	S4P	60	Lyttelton-Punta Arenas	Swift, SIO	Nathaniel B. Palmer
03/11-04/11	A10	30+	Cape Town-Rio de Janeiro	Molly Baringer, AOML	Ron Brown
2012	A20/A22	59	Woods Hole-Port of Spain-Woods Hole	pending	UNOLS
2013	A16N			in NOAA program	NOAA
2014	A16S			in NOAA program	NOAA
2013	P02	68		Pending	UNOLS
2015	P16N			in NOAA program	NOAA
2014	P16S	42		Pending	UNOLS
					UNOLS
Undetermined*	I7N	51	Port Louis/Muscat		*Piracy issues prevent completion of this line

The scientific objectives are important both for the CLIVAR and the Ocean Climate and Carbon Change (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 HydrographyCO_2/Tracer Program addresses the need, as discussed by the First International Conference on Global Observations for Climate (St. Raphael, France; October 1999) and the Ocean Observations '09 Symposium (Venice, Italy), that one component of a global observing system for the physical climate/CO_2 system should include periodic observations of hydrographic variables, CO_2 system parameters and other tracers throughout the water column (Fine et al., 2001; Hood et al., 2009). 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 and NSF have 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 Program (IGBP), the World Climate Research Program (WCRP), the International Human Dimensions Program (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 CO_2/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 complementary to our program (http://www.clivar.org/carbon_hydro/index.htm). Because of these concerns, 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 CO_2/Tracer Program is being managed in accordance with the COSP Ten Climate Monitoring Principals proposed by Karl et al. (1995).

2. Scientific Accomplishments

In FY 2011, NOAA and NSF co-sponsored two CLIVAR/ Repeat Hydrography cruises in the Pacific and Atlantic sectors of the Southern Ocean, S4P and A10 (Figure 1). The UNOLS S4P cruise (19 February – 28 April) consisted of an east-west section of 140 stations nominally along 67°S from McMurdo to Punta Arenas, Chile on the Nathaniel B. Palmer. The cruise was directed by Drs. James Swift of Scripps Institution of Oceanography and Alex Orsi of Texas A&M University. Drs. Richard Feely of PMEL and Rik Wanninkhof of AOML directed the DIC and underway pCO_2 measurements on the cruise, with Nancy Williams and Kevin Sullivan as the analysts. The A10 cruise was along 30°S (26 September – 31 October) on the NOAA ship *Ronald H. Brown* from Cape Town, South Africa to Rio de Janeiro, Brazil (Figure 1). Dr. Molly Baringer of AOML was the Chief Scientist and NOAA scientists conducted the CTD/O2/LADCP, oxygen, nutrient, underway pCO_2, DIC, chlorofluorocarbon and sulfur hexafluoride measurements. Robert Castle and Charles Featherstone performed the carbon measurements.

2.1. S4P DIC and pCO_2 measurements (Feely and Wanninkhof)

PMEL and AOML scientists were responsible for DIC measurements on the S4P cruise nominally along 67˚S on the *Nathaniel B. Palmer*. A total of 3237 distinct bottle DIC values were reported. Other sampling statistics include that 320 duplicates were taken and were interspersed throughout the cruise for quality assurance. The average mean difference of the duplicates was 0.64 µmol kg^{-1}. The accuracy is determined from the analysis of the Certified Reference materials (Batch 106). The average difference from the certified value was 1.9 ± 1.8 µmol kg^{-1}.

A section of the DIC data from S4P is shown in Figure 2 (top panel). A strong west-east asymmetry was observed in the upper 3 kilometers of the water column, with DIC values that were considerably higher in the western half of the section. This large-scale DIC pattern can be directly attributed to the "age" of the waters and the pathways of the meridional overturning circulation. The waters in the Pacific Sector are much higher in DIC than in the Atlantic due to the more recent ventilation of this water mass in the Atlantic sector.

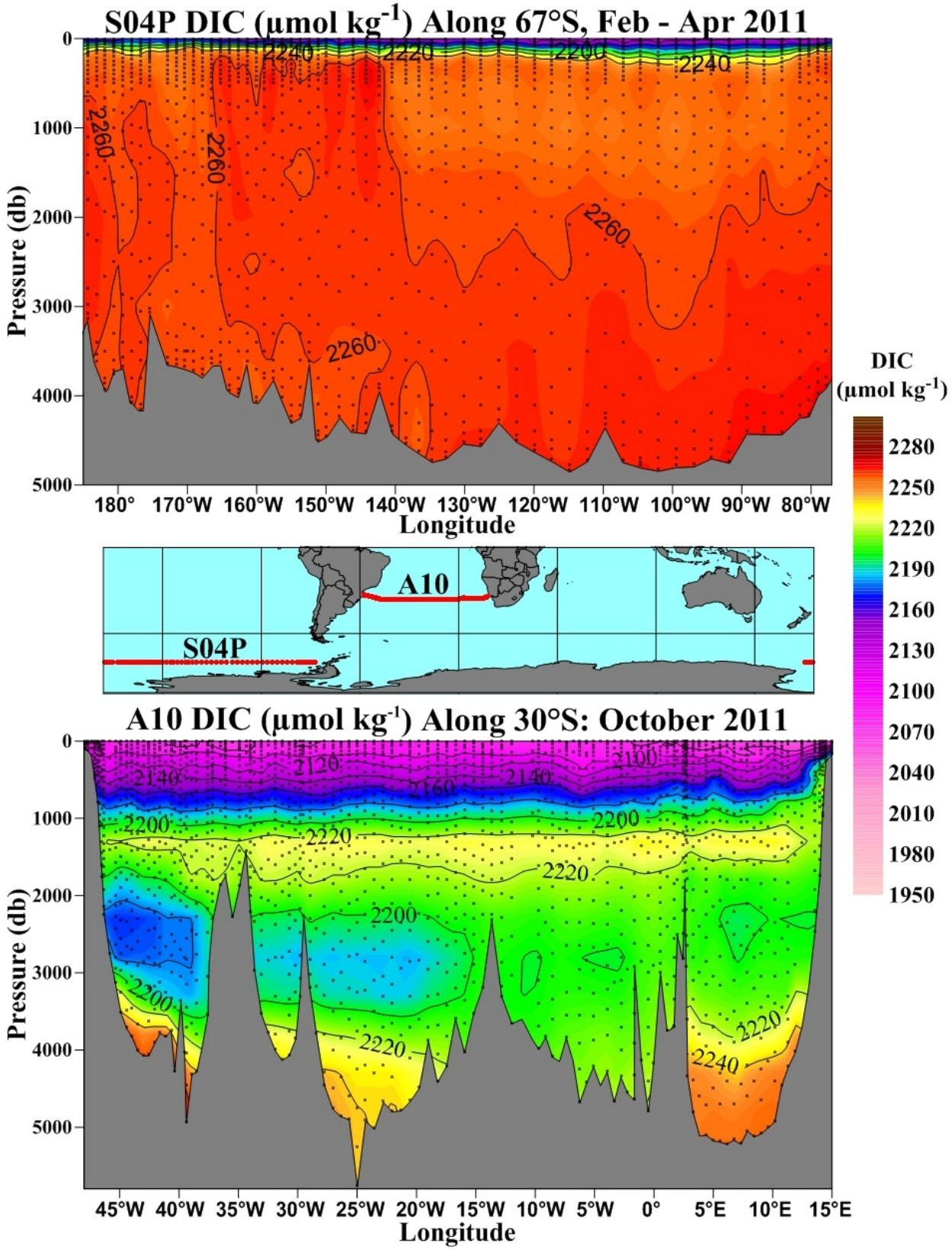

Figure 2. Sections of dissolved inorganic carbon along the S4P (top) and A10 (bottom) transects.

Underway pCO_2 data on the S4P cruise was obtained from a permanent installation on the RVIB *Nathaniel B. Palmer* overseen by the LDEO-Columbia group of Dr. T Takahashi and supported by the "pCO_2 on ships" project. A total of 23,640 surface water measurements were obtained during the cruise. A color-coded map of seawater pCO_2 is provided in Figure 3 showing large undersaturation near the ice edge and pCO_2 levels closer to saturation further from the continent. Further detail and data can be obtained from
http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/2011palmer.html
and in the 2011 annual report of the "pCO_2 on ships" project.

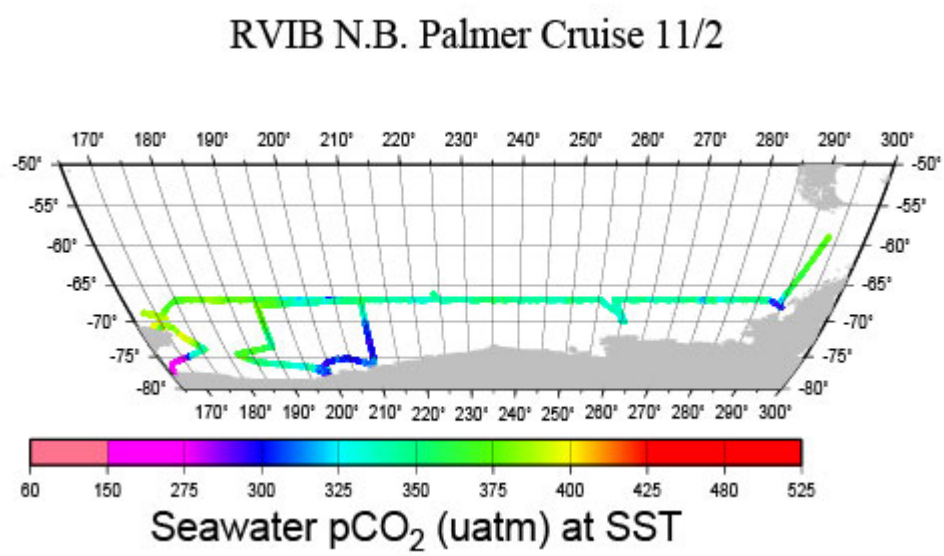

Figure 3. Seawater pCO_2 obtained from an automated pCO_2 system on the RVIB *Nathaniel B. Palmer*. As reference, air values are about 380 µatm. Figure provided by T. Takahashi of LDEO/Columbia University.

2.2. A10 Dissolved inorganic carbon (DIC) and underway pCO_2 data acquisition and reduction (Wanninkhof and Feely)

During the A10 cruise described in detail in section 2.3, R. Castle and C. Featherstone of AOML performed dissolved inorganic carbon (DIC) measurements that are tier 1 core measurements in the CLIVAR/CO_2 repeat hydrography effort. A total of 2300 Niskin bottles were sampled, and considered "good" after initial on board quality control. Approximately 260 duplicate samples were taken to assess precision. Final quantitative assessment of accuracy and precision will occur during shore-based quality control in 2012. R. Castle along with the ship's survey technician maintained the underway pCO_2 system.

Two automated DICE (Dissolved inorganic carbon extractors) were used during the cruise. While both systems worked well, they both had unusually high blanks. Normally the blank is less than 20 counts per minute, but we were forced to run them with blanks in the 40-70 range. As reference, a count of 200 equals about 1 µmol kg^{-1} and this is the magnitude of correction for a typical coulometric titration run of 10 minutes. Extensive tests were performed to determine

the cause of the high blanks. No leaks or sources of CO_2 could be found to account for the problem. The most likely cause was the use of 2-year-old anode solution. Since the high blanks were not caused by leaks in the system and remained relative stable throughout an 8 to 12 hour operation of a cell, the values computed should be accurate. The mean difference between duplicate samples was 1.4 +- 1.1 µmol kg^{-1} (n=124) for the unit called DICE3 and 2.0 +- 1.5 µmol kg^{-1} (n=134, two pairs omitted) for DICE 4. Comparison of the deep water values (below 2000 meters) with those obtained on the 2003 A10 cruise do not show a significant difference (see Figure 4 below) confirming that there were no major biases in the analyses. However, the data will require a careful post-cruise quality control check prior to submission to CDIAC and CCHDO databases.

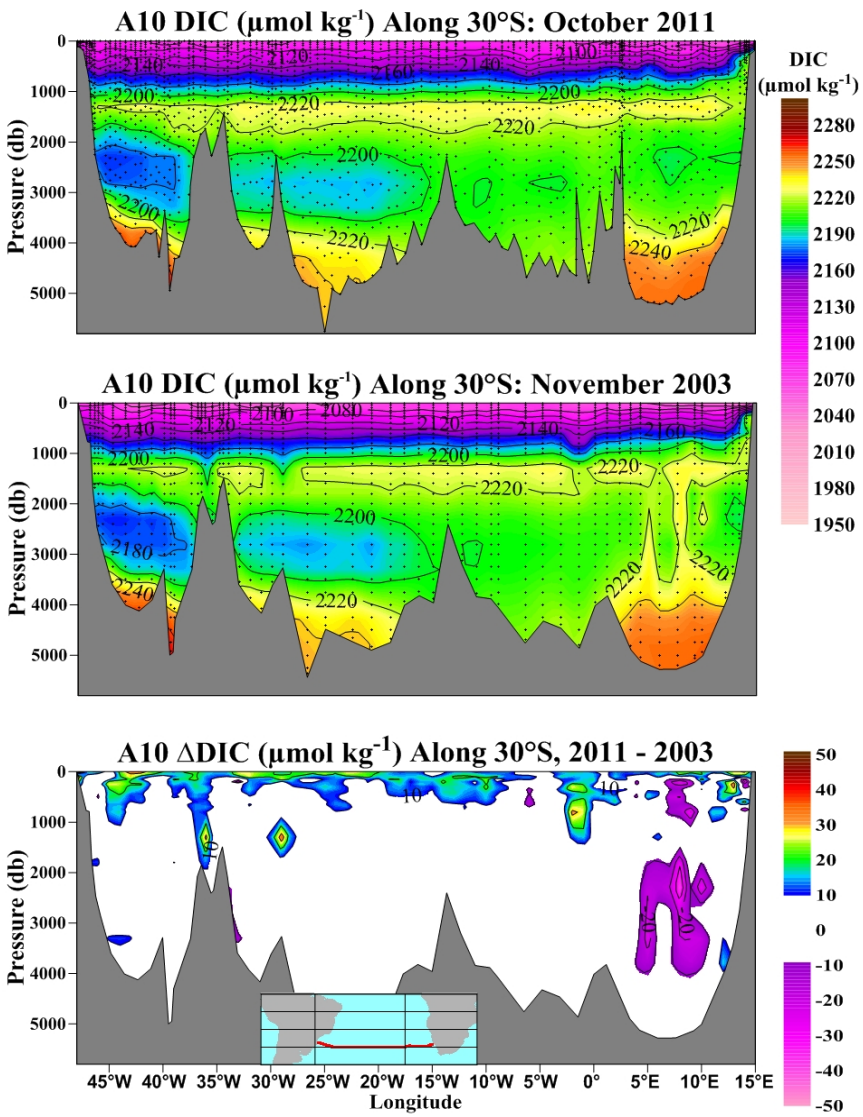

Figure 4. Cross-section of preliminary DIC values for the CLIVAR/CO_2 A10 cruise in 2011 (top) and the cruise along the same transect in 2003 (middle).The difference is shown in the bottom panel. Near surface values are predominantly positive as expected due to anthropogenic CO_2 input, while the differences below 1000 m are very small suggesting no significant accuracy issues with the 2011 DIC values. The negative anomalies at depth in the Eastern basin in the bottom panel bear closer inspection but appear to be data issues with the earlier data. (Figure courtesy of D. Greeley, NOAA, PMEL).

The underway pCO_2 system ran well during the cruise with no major issues. Approximately 15,000 surface water CO_2 measurements and 1,300 air CO_2 measurements were performed with an automated underway CO_2 system and reduced (Pierrot et al. 2009). The data shown in Figure 5 shows the South Atlantic as undersaturated with respect to the atmosphere in October, 2011with strong draw downs in the Eastern and Western regions.

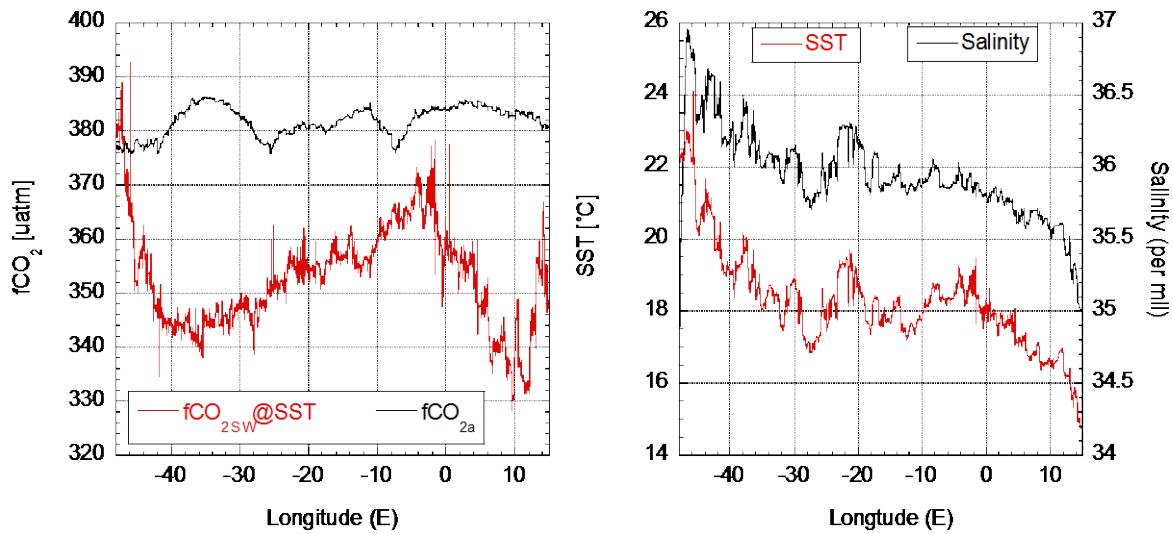

Figure 5. Surface water (red line) and air (black line) levels of fugacity of CO_2 (fCO_2) along the transect occupied during the CLIVAR/CO_2 A10 cruise (left). Temperature (red line) and salinity (black line) are shown in the right panel.

2.3. A10 CTD/O_2 and Bottle Salinity (Baringer and Johnson)

In FY2011 we finalized the CTD/$O_2$and bottle salinity data from the meridional WOCE Section A13.5, comprised of 129 full-depth stations along 0ºE occupied in boreal spring 2010 from about 54°S (the Antarctic Circumpolar Current) to 4.7°N (the African continental shelf). These finalized data have been delivered to the CCHDO where they are made available online at http://cchdo.ucsd.edu/data_access/show_cruise?ExpoCode=33RO20100308. They have also been submitted to NODC for archiving and distribution. These data were our primary deliverable for FY2011.

We also continued preparations for what was originally scheduled as a boreal spring 2011 reoccupation of WOCE Section A10. We completed pre-cruise instrument calibrations, bought materials and supplies, packed them and the rest the science gear, and loaded it all on the NOAA Ship *Ronald H. Brown* in Charleston. The cruise was rescheduled to start on 28 August 2011, but owing to mechanical difficulties with the ship, the cruise dates were actually 26 September – 31 October 2011. For the PMEL contribution to the CTD/O_2 work, Kristene McTaggart served as the lead CTD/O_2 technician. For the AOML contribution, Molly Baringer served as chief scientist, Kyle Seaton and Andrew Stefanick ran salinities and the LADCP, and James Hooper stood a CTD watch. In addition to leaving port nearly a month late, the ship's winches were problematic. Nonetheless, the science party, ship's officers, and crew came together to collect data on 120 full-depth stations along the cruise track, largely meeting the cruise objectives.

Since the bulk of A10 was completed in FY2012, the cruise results will be summarized more fully in next year's report. Finalizing and submitting data from that cruise will be a primary deliverable for FY2012. However, as a preview, we note that the cruise crossed the Vema Channel, affording a look at changing properties in the Antarctic Bottom Water as it moves north from the Argentine Basin to the Brazil Basin. The cruise data show the temperature of this water has increased steadily over the last few decades, warming by about 0.1ºC since 1980 (Figure 6). This change is astonishingly large. Monitoring changes like these is important in studying how the ocean circulation is changing, how much heat the oceans are gaining, and how much this heat gain is contributing to sea level rise. All of these topics are key to understanding the Earth's changing climate.

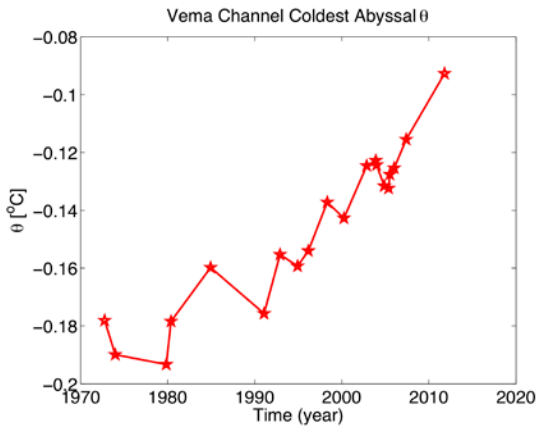

Figure 6. Coldest bottom temperatures in the Vema Channel, after Zenk and Morozov (2007, *Geophys. Res. Lett.*), updated using data from the Sept. – Oct. 2011 reoccupation of WOCE Section A10 on the NOAA Ship *Ronald H. Brown*.

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 FY2011 are summarized here. We published papers on ocean density contributions to sea level rise (Johnson and Wijffels, 2011) and recent global abyssal ocean warming (Purkey and Johnson, 2010). The latter study uses repeat hydrographic data to show that the Antarctic Bottom Water around the world and in the deep Southern Ocean has warmed sufficiently over the past two decades to account for roughly a tenth of the energy estimated to be building up the in Earth's climate system. As of September 2011 we had in press manuscript on roles of the Pacific Equatorial Undercurrent in climate models (Karnauskas et al., 2011), Antarctic Intermediate Water warming over the past century (Schmidtko and Johnson, 2011), and a forced annual Rossby wave in the deep southern tropical Indian Ocean (Johnson, 2011). The latter was published in early FY2012. In the North Atlantic several papers were published including an update of the meridional overturning circulation (MOC) array along 26°N from the Rapid/MOC/MOCHA/WBTS program (Baringer et al., 2011; Rayner et al., 2011), an extension of the MOC time series near 26°N using historical data (Longworth et al., 2011) and a paper tracing Labrador Sea Water pathways (van Sebille et al., 2012). In the South Atlantic, inter-ocean exchange variability was described using a combination of in situ data and numerical models (Dong, et al, 2011). Numerical models were

also used to show that inter-ocean exchanges in the South Atlantic are needed to explain the model-observed multi-decadal variability of the MOC and heat transport in the Atlantic; local air-sea forcing is insufficient to explain the variability (Lee et al., 2011).

2.4. CFC Tracers (Bullister)

A primary deliverable was to make high precision measurements of dissolved chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) on the A10 CLIVAR Repeat Hydrography section in the South Atlantic Ocean. We were successful in reaching our goals. Concentrations of CFC-11, CFC-12 and SF_6 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). D. Wisegarver from NOAA-PMEL coordinated preparing the CFC/SF_6 equipment for the cruise. He was the lead analyst for the CFCs/SF_6 measurements, and is working with the PI in the processing and calibrating of the data sets and in maintaining and upgrading the instruments.

Samples for the analysis of dissolved CFC-11, CFC-12 and SF_6 were drawn from ~2592 of the 2816 water samples collected during the A10 expedition. Efforts were made to sample CFCs and SF_6 from the same bottles sampled for key carbon system parameters (DIC, alkalinity, pCO_2 and pH) and other tracers. The cruise was completed in October 2011 and preliminary data collected on this cruise are publicly available at:
http://cchdo.ucsd.edu/data_access/show_cruise?ExpoCode=33RO20110926
Final processing of the data is underway and will be completed and archived at this website by March 2012.

The estimated precisions for the CFC-11, CFC-12 and SF_6 seawater analyses are shown in the following tables. These fully meet international 'WOCE' quality standards for these measurements.

Table 2. Summary of CFC and SF6 information for the CLIVAR A10 cruise.

Summary of number of CFC-11 samples taken and the estimated precision for the CLIVAR A13.5 cruise	
Number of samples	2592
Number of replicates	464
Average standard deviation	0.003 pmol kg^{-1} (or 1.0%), whichever is greater
Summary of number of CFC-12 samples taken and the estimated precision for the CLIVAR A13.5 cruise	
Number of samples	2592
Number of replicates	462
Average standard deviation	0.003 pmol kg^{-1} (or 1%), whichever is greater
Summary of number of SF_6 samples taken and the estimated precision for the CLIVAR A13.5 cruise	
Number of samples	2592
Number of replicates	461
Average standard deviation	0.02 fmol kg^{-1} (or 2.0%), whichever is greater

CFC concentrations along the A10 section (Figure 7) are highest in the upper 1000 meters of the water column, indicating the potential of this region to rapidly take up atmospheric gases (including CO_2) on decadal time scales. CFC concentrations in the water column generally decrease in the depth range from about 1000-2000 meters, reflecting the relative isolation of deeper waters from recent exchange with the atmosphere. Our improved analytical techniques now allow greater sensitivity to CFCs and SF_6 at extraordinarily low concentrations and we can now reliably measure dissolved CFC-11 and CFC-12 at concentrations below 0.0025 pmol per kilogram seawater (pmol/kg), where 1 pmol = 1 picomole =10^{-12} mole) and SF6 at 0.02 fmol/kg (where 1 fmol = 1 femtomole =10^{-15} mole). In 2011 there were detectible levels of CFC-11 and CFC-12 throughout the deep and abyssal waters along the A10 section, with a strong maximum centered at about 2200 meter depth along the western boundary, reflecting the transport of North Atlantic Deep Water and deeper, near-bottom maxima reflecting northward transport of abyssal Antarctic Bottom Water (AABW). The near-bottom AABW signal is strongest near the deep western boundary of the section at about 40°W, but can also be detected in the deep Brazil Basin (~15°W – 30°W) and in the deep Cape Basin (~5°EW – 15°E). On decades-to century timescales, the deep ocean will be a major reservoir for anthropogenic CO_2 and climate warming signals. The CFC signals can provide valuable information on the rates and pathways by which surface-derived climate signals (e.g. anthropogenic CO_2 and warming) can be carried into this region of the deep ocean.

The A10 section was also occupied on 1993 as part of the WOCE program. Differences in CFCs over decadal time intervals, gathered as part of the CLIVAR Repeat Hydrography Program, can be used to test ocean circulation models and help detect and quantify changes and variability in water formation and ventilation rates, which is of great relevance to ongoing climate studies.

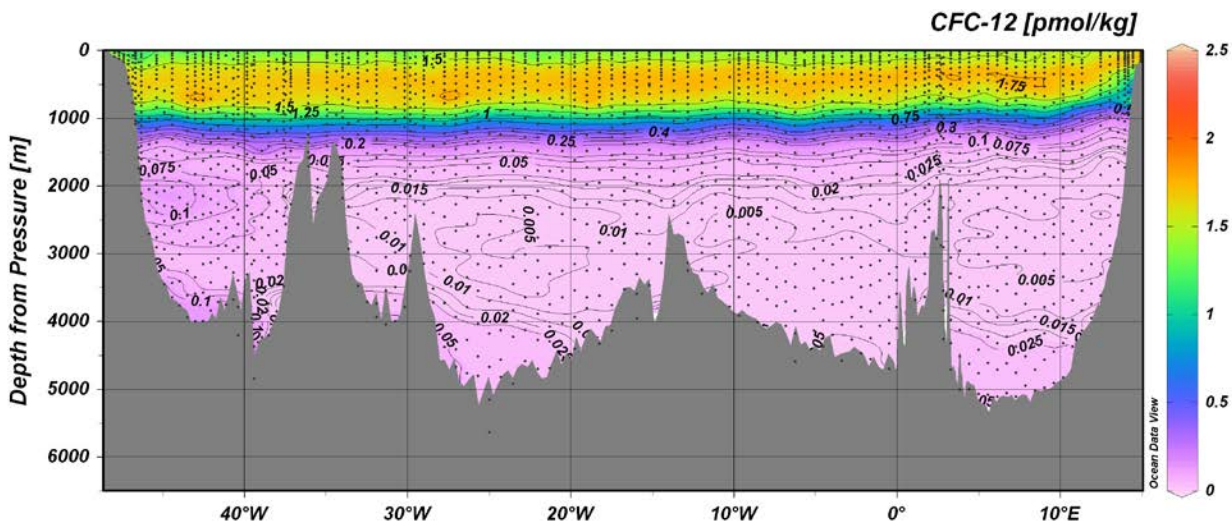

Figure 7. A section of CFC-12 concentrations along the CLIVAR A10 section in 2011. Dots indicate locations where individual water samples were collected and analyzed for CFCs and SF_6.

Sulfur hexafluoride (SF_6) is rapidly increasing in the atmosphere and has the potential to be a valuable time-dependent tracer of ocean circulation and mixing processes. The PMEL group pioneered the routine measurement of SF_6 as part of the CLIVAR Repeat Hydrography program,

and measurements of this compound have been included on all subsequent CLIVAR cruises. On the A10 section we also included (for the first time on a CLIVAR Repeat Hydrography section) measurements of dissolved nitrous oxide (N_2O) (see Figure 8). N_2O is an important greenhouse gas and plays a role in a variety of chemical processes in the atmosphere. Large scale studies of dissolved N_2O in the ocean will improve understanding of the role of the compound in the nitrogen cycle in the ocean and of the ocean's contribution to the global N_2O budget.

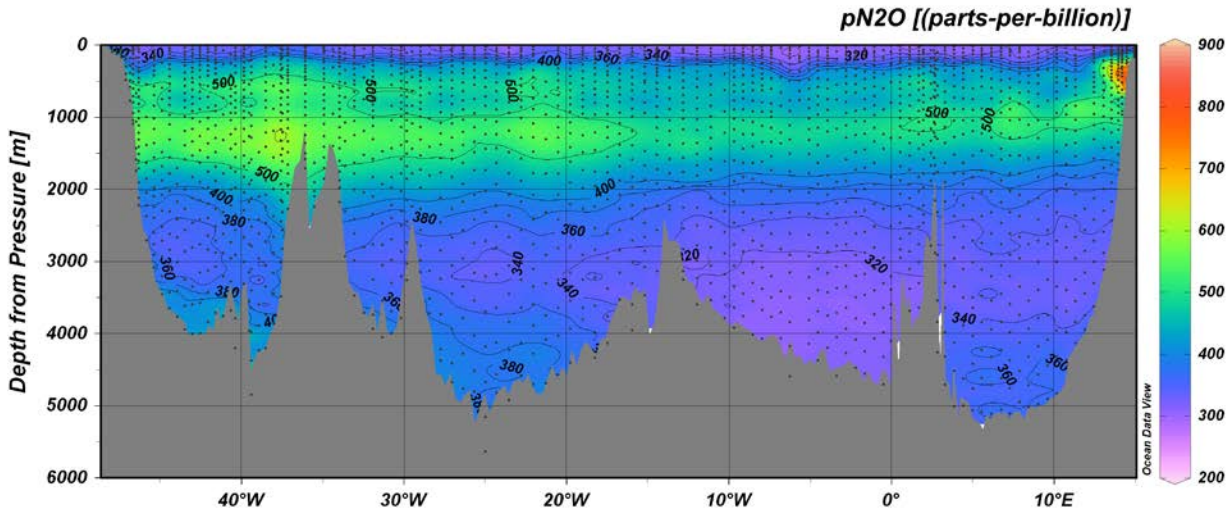

Figure 8. A section of the partial pressure (in parts-per-billion) of dissolved N_2O (pN_2O) along the CLIVAR A10 section in 2011. Dots indicate locations where individual water samples were collected and analyzed for N_2O. The present atmospheric pN_2O is approximately 320 ppb. The strong sub-surface pN_2O maximum along the section indicates in-situ production of this gas and net loss of N_2O to the atmosphere by air-sea gas exchange.

2.5. Nutrients (Mordy and Zhang)

The primary task of the nutrient group was to collect nutrient data on the A10 repeat hydrographic section in the Atlantic Ocean. On the A10 cruise, P. Proctor and C. Fischer conducted high precision shipboard analysis of phosphate, nitrate, nitrite and silicic acid on 2736 samples collected from the CTD rosette at discrete depths. 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. (1993) and recent updated manual by Hydes et al. (2010) including calibration of labware, preparation of primary and secondary standards, and corrections for blanks and refractive index. Newly available reference standards prepared by the Japanese Meteorological Institute were analyzed at each station. Mordy and Zhang will be responsible final data processing and quality control.

The precision of nutrient analysis on A10 is shown in Table 3. The precision of all nutrient species meet international quality standards for these measurements. Data collected on this cruise are available and archived at:
http://cchdo.ucsd.edu/data_access/show_cruise?ExpoCode=33RO20110926

Table 3. Precision of nutrient measurements on the A10 repeat hydrographic cruise determined from replicate analysis of deep water samples (>10 µmol kg^{-1} nitrate).

	Phosphate	Silicic Acid	Nitrate
Total number of replicates	323	323	319
Standard deviation (□M)	0.013	0.23	0.32
Relative standard deviation	0.54%	0.46%	0.70%

Sections of the major nutrients from the A10 cruise are shown in Figure 9. Major features include low nutrient concentrations in surface waters; an intense sub-surface (~1000-1500m) nitrate maximum resulting from remineralization of sinking organic matter; and lower concentrations in North Atlantic Deep Water that reside above nutrient-rich Antarctic Bottom Water. These results will be used to explore decadal changes in nutrient and oxygen content in the oceans, and examine to what extent such changes might be coupled to carbon inventory changes, all of which are similarly forced by ocean circulation, biological productivity and biogeochemical cycles.

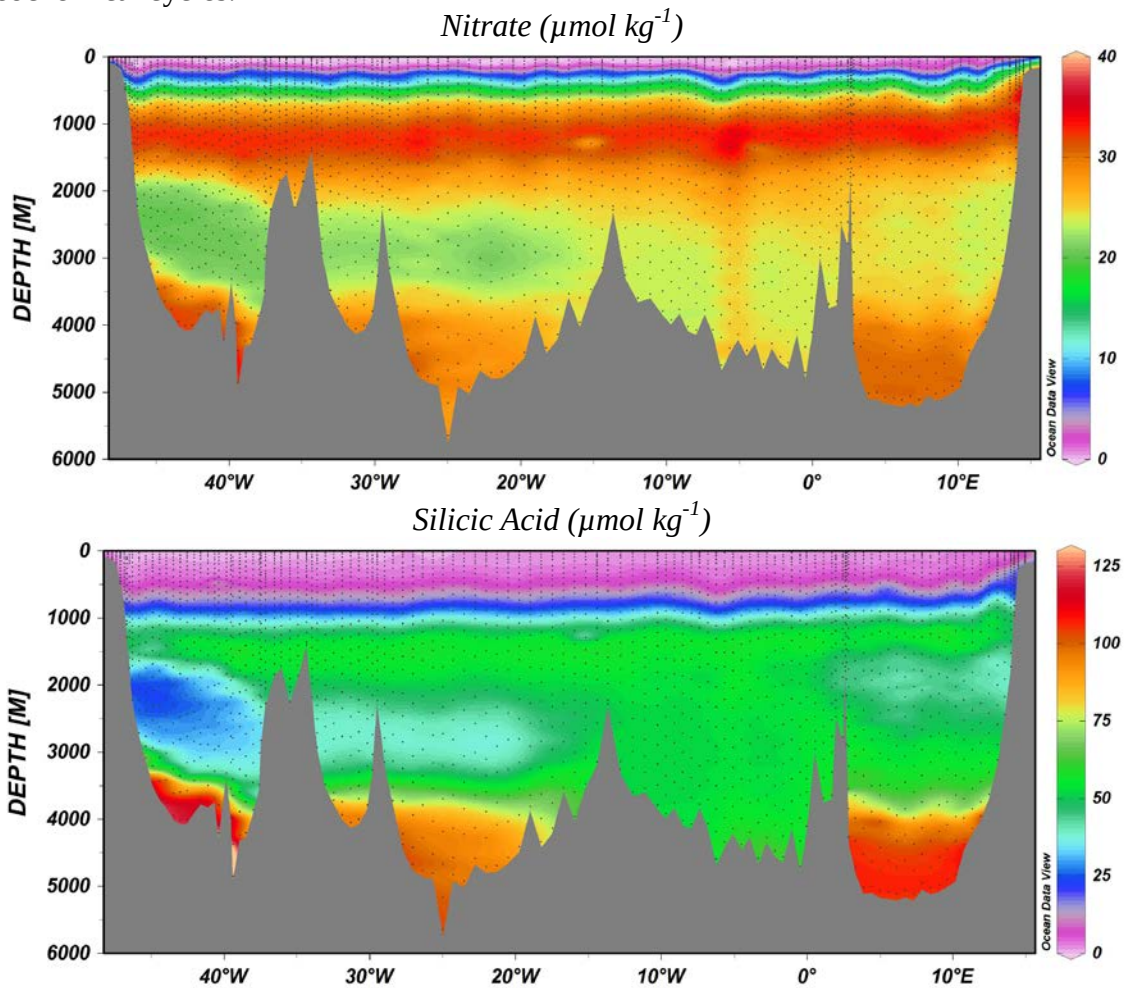

Figure 9. Preliminary sections of nitrate and silicic acid along the A10 cruise track.

2.6. Discrete Oxygen (Baringer and Langdon)

An additional task of the nutrient group was to collect oxygen data on the A10 repeat hydrographic section in the Atlantic Ocean. On the A10 cruise, C. Langdon and G. Berberian conducted high precision shipboard analysis of dissolved oxygen performed with an automated titrator using amperometric end-point detection [Langdon, 2010] on all Niskin bottle samples taken during the cruise. Sample titration, data logging, and graphical display were performed with a PC running a LabView program written by Ulises Rivero of AOML. The analysis was completed using standard high-quality methods as appropriate for the WOCE and Repeat Hydrography programs [Dickson, 2005]

A total of 232 sets of duplicates were run, two for each station. The average standard deviation of all sets was 0.2 umol/kg. Eight oxygen flasks were removed and replaced with different flasks during the cruise, after it was noted that the stoppers did not fit tightly. The following flasks were replaced 6, 7, 9, 14, 47, 48, 49, 54.

2.7. Education and Outreach

Dr. Feely, Sabine and Wanninkhof are contributors to the Intergovernmental Panel on Climate Change Fifth Assessment Report. Dr. Sabine is the corresponding lead author to Chapter 6: Carbon and Biogeochemical Cycles and Dr. Feely is a lead author of for Chatper 3: Observations: Oceans for Climate Change 2013: The Physical Science Basis. Dr. Wanninkhof is a contribution author for Chapter 3. Drs. Feely, Sabine and Wanninkhof also participated in the planning and implementation of the Regional Carbon Cycle Assessment and Processes (RECCAP; http://www.globalcarbon project.org/recap) to establish the mean carbon balance and change over the period 1990-2009. Drs Feely, Sabine and Wanninkhof have presented several invited talks at National meetings and University Seminars on there global carbon work. Drs. Feely and Sabine are the supervisors one NRC post-doctoral fellow, Dr. Adrienne Sutton and two graduate students from the University of Washington, Ms. Andrea Fassbender and Ms. Nancy Williams.

R. Wanninkhof currently hosts Dr. Leticia Barbero, a post doctoral fellow from Spain working on methods to interpolate sparse carbon data in time and space. He is the ocean carbon co-lead (with Dr. T. Tanhua of U. Kiel) of the deep ocean observation strategy group developing innovative means of observing changes in the deep ocean.

G. Johnson is serving as a lead author for Chapter 3: Observations: Oceans for Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Intergovernmental Panel on Climate Change Fifth Assessment Report,and M. Baringer is a contributing author. Johnson is currently advising U. of Washington School of Oceanography graduate student S. Purkey, who is working with him on quantifying and understanding global abyssal temperature changes and their contributions to global heat and sea level budgets. In FY2011 S. Purkey also worked on developing classroom modules for a high school curriculum on climate and climate change as part of the UW in the high school program (http://www.uwhs.washington.edu/uwhs/courses/sci.asp). G. Johnson and S. Purkey engaged with the public news media this year for stories on deep ocean warming

(http://www.ouramazingplanet.com/1993-ocean-deep-mysteries-exploration.html; http://www.reportingclimatescience.com/this-issue/oceans-and-polar/deep-ocean-warming-contributes-to-sea-level-rise.html). G. Johnson also advised NRC postdoctoral fellow S. Schmidtko (now a Senior Research Associate at U. of East Anglia), working on global observational analyses of Southern Ocean water mass formation and variability, as well as constructing a global temperature and salinity climatology, using Argo and historical hydrographic data. Baringer co-authored a recently accepted paper with postdoctoral fellow Eric van Sebille (supported under the MOCHA/Rapid/WBTS program) looking at the propagation pathways of Labrador Sea Water in the North Atlantic,

J. Bullister participated in the 2011 NOAA Summer Science Camp at PMEL and as part of this worked with middle-school students on environmental science projects. Two graduate students participated at sea on the CLIVAR A10 expedition as part of the CFC team and were involved on all aspects of the CFC program.

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4. Publications and Reports

4.1. Publications led by Principal Investigators

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