Chapter 1: General Rationale for GLOBAL REPEAT HYDROGRAPHIC/CO_2/TRACER SURVEYS IN SUPPORT OF CLIVAR AND GLOBAL CARBON CYCLE OBJECTIVES

Introduction

A systematic and global re-occupation of select hydrographic sections is proposed to quantify changes in storage and transport of heat, fresh water, carbon dioxide (CO_2) and related parameters. By integrating the scientific needs of the carbon and hydrography/tracer communities, major synergies and cost savings will be achieved. The philosophy is that in addition to efficiency, a coordinated approach will produce scientific advances that exceed those of having individual programs. These advances will contribute to the following overlapping scientific objectives, which are elaborated upon in subsequent chapters:

- Data for Model Calibration and Validation
- Carbon System Studies
- Heat and Freshwater Storage and Flux Studies
- Deep and Shallow Water Mass and Ventilation Studies
- Calibration of Autonomous Sensors

The scientific objectives are important both for research programs, such as CLIVAR (Climate Variability and Prediction) and the Carbon programs, and for operational activities such as GOOS and GCOS (Global Ocean/Carbon Observing Systems). In mid-2001 the US scientific steering committees of the CLIVAR (www.clivar.org) and CCSP (Carbon Cycle Science Program) (www.carboncyclescience.gov) programs proposed the creation of a joint working group to make recommendations on a national program of observations along ocean sections to be integrated with international plans. Several community outreach programs and efforts have been implemented to seek input, such as a web site with interactive forum (www.aoml.noaa.gov/ocd/repeathydro/index.html), articles in EOS (Fine and Wanninkhof, 2001) and the JGOFS newsletter, as well as AGU and Ocean Sciences meeting community discussions. The proposed program addresses the need as discussed by Ocean-CLIVAR (San Antonio, Texas 1996), DECEN (1998), 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/CO_2 system should include periodic observations of hydrographic variables, CO_2 system parameters and tracers throughout the water column (Smith and Koblinsky, 2001; Gould *et al.*, 2001; Fine *et al.*, 2001). The large-scale observation component of the US Carbon Cycle Science Plan (Sarmiento and Wofsy, 1999; Bender *et al.*, submitted) has also defined a need for systematic observations of the invasion of anthropogenic carbon in the ocean superimposed on a variable natural background.

Earlier programs [e.g., World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Study (JGOFS) during the 1990s] have provided a full depth baseline data set that can be used for detection of future changes, and shown where atmospheric constituents are entering the oceans. The proposed measurements will reveal much about the stability of internal pathways and changing patterns in ocean properties. They will serve as a baseline to assess changes in the ocean's biogeochemical cycle in response to natural and/or anthropogenic 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 be followed through long-term measurements. Below the level of the Argo array, repeat hydrography is the only global method capable of observing these long-term trends in the ocean. The program will also provide data for sensor calibration (e.g., www.argo.ucsd.edu), and to support continuing model development that will lead to improved forecasting skill for oceans and global climate. The broader societal impacts discussed throughout the proposal include: broad and near immediate dissemination of data to enhance scientific and technological understanding; societal benefits of collection of a high quality data set, use of the data to assess climate change, and a resource for model calibration of the climate system; promotion of training and learning for graduate students, postdoctoral scientists, and new scientists.

An Integrated Sampling Strategy

The global program proposed will sustain sampling of ocean transports and inventories of climatically significant parameters on decadal time scales. The sequence and timing for the proposed sections (Fig. 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 on the Atlantic in the early years of the program and the CCSP that emphasizes constraining the carbon uptake in the Northern Hemisphere oceans in part in support of the North American Carbon program (NACP) (Wofsy and Harriss, 2002). In addition, the proposed sections are selected so that there is roughly one decade between these new occupations and the WOCE/JGOFS occupation. For the western boundary in the Atlantic, a more frequent occupation is needed to sample variability related to changes in the North Atlantic Oscillation (NAO). Ordering of sections is by basin, and coverage based on a zonal cruise in each subtropical basin and sufficient meridional cruises to calculate inventories of carbon and tracers. The observations should be considered a minimum for quantifying long-term changes. Support for observations on non-US cruises is included for CFCs, because full tracer coverage is considered an integral part of the global program. Also integral is support for carbon system parameters and tritium/^{3}He, but they have not been included here for non-US cruises due to logistics considerations. The request is for six years of funding (Table 2), although the complete occupation spans ten years. To provide flexibility to respond to changes in international commitments, schedules for out years may have to be adjusted. This proposal includes funds to collect the data and perform the quality control measures routinely carried out by providers of reference-quality data (i.e. there is no large-scale synthesis or interpretation). Post-cruise data updates, distribution, and archive will be managed by groups with separate funding. The field work is the beginning of what is hoped will be an ongoing project, integrated with a larger international effort to monitor the ocean's response to climate change.

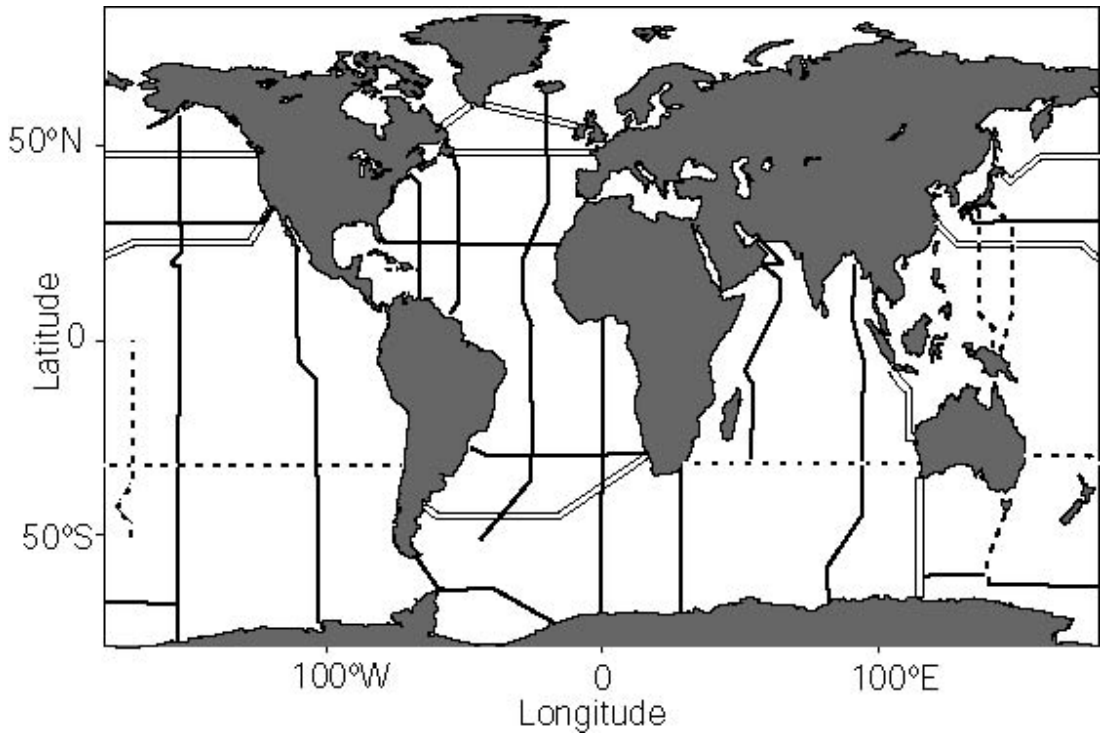


Figure 1: Map of proposed Global survey: black are proposed US lines, white are committed international, and black and white/dashed are non-US where tracers may be needed.

Table 1. Proposed 10 year US schedule for re-occupation of the Global Survey.

Section	Location	Proposed Occupation	Years between Occupations	Comment	Length (days)	# Stations
I5	32°S	2002	15/7	Tracers-UK		
A20/22	52/66°W	2003	6	full line	29/21	90/75
A16S	20-25°W	2003	12	full line	44	110
A5	24°N	2003	11/5	Tracers-UK		
P6	32°S	2003	11	Tracers-Japan		
A10	32°S	2003	11	Tracers-Japan		
A16N	20-25°W	2004	11	full line	42	135
P2, L1/2	30°N	2004	10	full line	27/39	92/127
P16N, L1/2	150°W	2005	14	full line	29/33	88/100
P10/P9	140°E/137	2005	12/11	Tracers-Japan		
P16S	150°W	2005	14	full line	40	105
S4P/P16S	67°S	2006	14	full line	51	97
P18, L1/2	105-110W	2007	13	full line	32/35	78/107
P15	170°W	2008	7	Tracers-Aus.		
I7N/I6S	55/20°E	2008	13/12	full line	47/42	156/107
I8S/I9N	90°E	2008	13	full line	38/34	81/103
P12	140°E	2008	7	Tracers[*1]Aus.		
I5 (5)	32°S	2009	22/14	full line	43	145
A13.5	0°E/W	2009	14	full line	62	162
A5	24°N	2010	12/7	full line	30	122
A21/SO4A	65°W	2010	20/14	full line	42	93
A10	32°S	2011	8	full line	29	90
A20/22	66°W	2011	8	full line	29/21	90/75

[*1] Tracers include carbon system parameters, CFCs (CFC-11, CFC-12, CFC-113), and tritium/^{3}He

Table 2a. Budgets by Measurement Type[*2a], Year, and Agency (in 1,000s of $)

		Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Total
CTD/hydro/ADCP								
J. Swift/SIO, lead								
	university	750	867	722	430	478	1,319	4,566
	NOAA	685	517	769	9	842	966	3,789
	total	1,435	1,384	1,491	439	1,320	2,285	8,355
Carbon								
R. Wanninkhof/AOML, lead								
	university	1,074	865	950	815	824	1,070	5,310
	NOAA	903	579	609	465	573	862	3,991
	total	1,977	1,444	1,559	1,280	1,397	1,932	9,589
Tracers (CFCs, He/Tr)								
R. Fine/Univ. Miami, lead								
	university	1,388	1,172	1,105	549	682	1,984	6,880
	NOAA	182	186	130	0	201	323	1,023
total (includes 2 non-US CFC cruises)		1,570	1,358	1,235	542	883	2,307	7,903
	Grand Total	4,982	4,186	4,285	2,261	3,600	6,524	25,838

Table 2b. Average cost per day by Measurement Team[*2b]

Measurement Team	Average cost (k$)/day (as proposed)	*Average cost/day (with NSF/OTS - see SIO budget discussion)*
chief scientist's party	4.23	
CTDO/S/O_2/nutrients	8.17	*15.26*
L/ADCP	1.92	
Carbon system	16.44	
CFCs (US cruises)	6.36	
Tritium/^{3}He	6.25	
Total	43.37	*50.46*

*[2a]Detailed breakdowns for Measurement Teams are available in Chapter 7. There may be insignificant budget discrepancies in the Project Description and with the official NSF budget pages due to the complexity of merging all budgets into the tables. NOAA Year 1 budgets include funds for equipment aquisions/upgrades.

*[2b]These are averages over all budget years, with no backwards adjustment to remove inter-year cost rise factors. Within each Measurement Team, budgets vary a little between PIs due to salary, etc. Work has been divided to obtain the highest efficiency, and an equitable balance of work load. One of the advantages of having more than one PI on each Measurement Team is that the members will work together to achieve the highest quality data.

Measurements are divided into three levels in order of priority (Table 3). All Level I and three Level II measurements (pH, discrete pCO_2, and CCl_4) are proposed here. Proposals for ^{14}C, ^{13}C, and Tracer Metals will be submitted separately at this time. Level I core measurements are mandatory on all cruises. The levels are also the suggested standard for international collaborators, and should be measured at highest spatial resolution practical. The rationale for classifying a measurement as Level I is based on data required to directly quantify change in ocean carbon inventory, estimate anthropogenic CO_2 empirically, characterize large-scale water mass ventilation rates, constrain horizontal heat, freshwater, carbon, nitrogen, and oxygen transports and/or net divergence, and provide an on-going basis for model evaluation. Level II measurements are highly desirable on a subset of US cruises. They may be collected on coarser station spacing and will be closely coordinated with the core effort. Level III ancillary measurements are to be done according to opportunity and space available. They should not significantly interfere with Level I or II efforts, and may be regional or specific to an individual cruise. Their focus is on upper ocean biogeochemistry processes and cycles. US measurement standards should adhere to those set by WOCE and JGOFS for CTD, hydrographic properties, tracers, and carbon system components. Certified reference materials will be used for all measurements where such standards are available.

Table 3. Measurement and Data Release Schedule[*3]

Level I: (*All data will be released in final form 6 months after the cruise except where noted*)

Dissolved inorganic carbon (DIC) ; Total Alkalinity (TAlk); CTD pressure, temperature, conductivity (salinity) (1,2); CTD oxygen (sensor) (2); Bottle salinity (2); Nutrients by standard auto analyzer (NO_3/NO_2, PO_4, SiO_3) (2); Dissolved oxygen (2); Chlorofluorocarbons (CFC-11, -12, -113) (2P); Tritium-^{3}He (4); Dissolved organic carbon; Dissolved organic nitrogen; Surface underway system (T, S, pCO_2) (1); ADCP shipboard (2); ADCP lowered (2); Underway navigation and bathymetry (2); Meteorological (1).

Level II: (*All data will be released in final form 6 months after the cruise except where noted*)

pH; discrete pCO_2; ^{14}C by AMS (3); CCl_4 and SF_6 (2P); $\partial^{13}C$ of DIC (3); Fe/trace metals; CTD Transmissometer; Surface underway system (nutrients, O_2, Chl, DIC, skin temperature).

Level III: (*All data will be released in final form within 2 years of analysis*)*

Chlorophyll; Primary production; HPLC pigments; Experimental continuous analyzers; $\partial^{15}N\ NO_3$; ^{32}Si; $\partial^{18}O$ of H_2O; NH_4; Low level nutrients; Total organic phosphorus; Upper ocean optical; isotopes of O_2; N_2, Ar, O_2; Methyl halides; DMS; ADCP (multibeam).

---

*[3]Notes
(1) Data available daily during the cruise.
(2) Data released to the relevant data management structure within 5 weeks of the cruise; (2P) in preliminary form.
(3) Data released within 6 months of shore-based analysis.
(4) Data released within 15 months of sample collection.
* As required by NSF and NOAA data release policies.

Data Policy, Management, and Scientists

The proposed program is based on the fundamental concept that data collected belong to the community, and are available to the community at large rather than being proprietary for the investigators involved in the project. The data policy proposed for this program will be stringent and geared towards rapid and open dissemination, and with a clear structure for all data to undergo thorough quality control. Such an ambitious goal requiring this degree of openness has not been tried on such a large scale. The policy includes: 1) All Level I and II observations will be made public in preliminary form through a specified data center soon after collection ("early release"), with final calibrated data provided six months after the cruise, with the exception of those data requiring on-shore analyses (see Table 3, and web site). 2). All data collected as part of the program will be submitted to a designated data management structure for quality control and dissemination for synthesis. 3) General US policy, applicable to all data collection programs, requires that post cruise inventory information be completed within 60 days of the end of the cruise. Ultimately, all data must be archived with the National Oceanographic Data Center (NODC), following timelines set by the funding agencies. The data management groups (see web site) will be responsible for making the data accessible to the community via web servers, published or online data reports, CD-ROMs, etc.

A US Oversight Committee is proposed consisting of a subset of PIs involved in the program and members of the community at large. The Committee can make recommendations on changes in lines, sequencing, measurement teams, Chief, and co-Chief scientists as required. They will make recommendations on Level III measurements as they contribute to program objectives, and ship time, berths, and seawater sample volume available for analysis. They will advocate adequate and consistent coverage of all Level I and II observations. They will ensure smooth interactions with funding agencies and individual investigators (Level III), and that adequate support is provided for the data management structures. They will serve as contact for coordinating with other national and international efforts, and coordinate with CLIVAR and Carbon program steering committees. They will oversee pre-cruise planning, data submission, and documentation.

The proposed program will serve as a community resource for training and entraining new scientists. Members of the Chief scientist's team consisting of a Chief scientist, co-Chief scientist and two graduate or post-doctoral assistants will be selected through a community wide solicitation every two years.

Chapter 2: Data for Model Calibration and Validation

The repeat survey data together with the WOCE/JGOFS data will serve as an important benchmark for improving and evaluating numerical model performance, because of their high quality, internal consistency, and reasonably comprehensive measurement suite. The new data will help refine our picture of the large-scale, climatological distributions and transports of ocean physical and chemical variables. Some of the biogeochemical data sets (e.g. DON and DOC) will be completely novel, but in many

instances, especially outside of the North Atlantic, even the most standard hydrographic data from these repeat sections will make a very significant addition (i.e doubling) to the historical record. Similarly, the underway data will contribute to our understanding of high-frequency spatial variability and the seasonal and basin-scale patterns of upper ocean physics and pCO_2. The primary utility of the repeat survey data, however, lies in the characterization of the decadal evolution of ocean physics, biogeochemistry, transient tracers, and ocean carbon storage. Modeling related applications for the repeat survey data fall into four broad categories:

- developing and testing improved model parameterizations
- prescribing initial or boundary conditions
- evaluating overall model skill
- constraining inverse and data assimilation calculations.

Ocean and climate modeling covers a diverse range of related activities with different foci and data requirements. Coarse-resolution, global and regional ocean models are now commonly used in studies of the "steady-state" physical general circulation and corresponding biogeochemical cycles, retrospective simulations for the recent historical period (1950's-present), and future projections of natural and potential human-induced climate change over the next several centuries. Such models are typically non-eddy resolving or at best eddy-permitting, and can be run either in stand-alone ocean mode or as part of a coupled ocean-atmosphere-land climate system (e.g., Blackmon *et al*., 2001). High-resolution, fully eddy-resolving simulations (1/10 deg. over a basin-scale domain) are also being conducted for approximately decadal durations to explore the dynamics and statistics of mesoscale variability.

At some level, all Earth system simulations are data driven. For example, the global, non-eddy resolving ocean models most often used for climate studies depend critically on sub-grid scale parameterizations of unresolved processes and relatively poorly known surface heat and freshwater fluxes (Large *et al*., 1997); model coefficients, therefore, must be to a degree "tuned" so that the simulations agree with the large-scale temperature and salinity fields. Focused research on improving the mechanistic basis of forward or prognostic ocean circulation models is clearly needed, which in turn requires high quality tracer data sets to differentiate between proposed numerical approaches. For example, the second phase of the international Ocean Carbon Model Intercomparison Project (OCMIP, http://www.ipsl. jussieu.fr/OCMIP/) compared a dozen ocean circulation models, revealing large differences in simulated steady-state and transient tracer fields (e.g., ^{14}C, CFCs, anthropogenic CO_2). These discrepancies result largely from uncertainties in the representation of sub-grid processes including the seasonal dynamics of the planetary boundary layer, mixing and transport by deep/intermediate water formation; flow over topography and boundary currents; heat and freshwater fluxes in sea-ice covered regions, and diapycnal and mesoscale isopycnal mixing. Oceanic transient tracer and biogeochemical constituents have source and sink distributions and lifetimes different from temperature, salinity and other traditional physical circulation parameters. The availability of a wider range of tracer data, therefore, will test the skill of general circulation models in a more comprehensive fashion (Roether and Doney, 1999).

The data requirements for ocean carbon cycle and biogeochemical models are even more demanding, because there are no fundamental relationships for biology analogous to the Navier-Stokes equations for fluid dynamics (Doney, 1999). Many of the modeling issues raised with regard to ocean physics apply to biogeochemical tracers as well, and even the most sophisticated biological and chemical simulation can not overcome a poor physical solution. The subsurface distributions of dissolved inorganic carbon, alkalinity, oxygen, and nutrients are strongly driven by the so-called "biological pump". Key issues for the current generation of models include improving surface net community production, export fluxes of dissolved and particulate organic matter and particulate inorganic matter (calcium carbonate, silicates), and subsurface remineralization. Of particular interest are the transformations occurring in the main thermocline, the so-called "twilight zone", where most of exported organic matter is remineralized. The subsurface biogeochemical data from the proposed program will provide important constraints for

developing more realistic model parameterizations for these processes, and will also provide direct information on how these processes are changing with time as a function of the downward transport of anthropogenic heat and CO_2. Observational estimates of biogeochemical tracer meridional fluxes will also be of considerable use for evaluating model behavior, much as meridional heat transport has become a key, integrated metric for physical models.

Numerical models are one of the few tools available for projecting the impacts of natural and human-induced climate change over the next several centuries. While the skill of climate projections for the end of this century are difficult to test directly, aspects of the climate sensitivity of these models can be assessed by replicating in hindcast mode the interannual to decadal variability found in historical data. The repeat survey data will extend the temporal observational record, allowing for investigation of the ability of models to capture natural climate modes (e.g., ENSO, NAO, PDO) and the predicted increasing secular climate change. Coupled ocean-atmosphere model simulations differ considerably in their details. But many simulations suggest that the effects of climate change- general warming of the upper ocean and thermocline, increased vertical stratification in both the low latitude (warming) and high latitude (freshening) surface waters, weakening of the thermohaline circulation, and reduced subsurface oxygen concentrations and anthropogenic carbon uptake-may already be evident in the observational record (e.g., Sarmiento *et al.*, 1998; Matear and Hirst, 1999).

Despite near-term advances in in-situ measurements and remote sensing, ocean observations alone will almost certainly remain too sparse to fully characterize the relevant time-space variability of the marine physics and biogeochemistry. Diagnostic modeling (inverse models up to full data assimilation systems) provides a means to generate complete, dynamically consistent ocean fields that incorporate data when and where they are available, and that provide estimates of uncertainties on the inferred quantities. These model-generated products provide the input needed for scientific and political assessments of the state of the ocean and its role in the global climate system. These products can also provide initial conditions for short-term and long-term predictions using prognostic models. Data assimilation in physical oceanography, has made significant progress over the last several years with programs initiated such as GODAE (Global Ocean Data Assimilation Experiment; http://www.bom.gov.au/bmrc/ocean /GODAE/) and ECCO (Estimating the Circulation and Climate of the Ocean; http://www.ecco.ucsd.edu). The number of biogeochemical diagnostic modeling studies using large-scale data sets is also growing (e.g., Schlitzer, 2000; Gruber *et al.*, 2002). The repeat survey data will feed into the data-stream for diagnostic and assimilation studies, providing key information on deep water properties, transient tracers, and biogeochemical variables.

Chapter 3: Carbon Dioxide Inventories and Fluxes

The long-term goals for the use of carbon parameter measurements are, first, to quantify the uptake and storage of anthropogenic CO_2 by the ocean, including its decadal-scale variability and spatial distribution, and second, to provide information for modeling the processes that control the uptake and transport of CO_2 into the ocean's interior. A detailed version of this chapter is available on the web site (www.aoml.noaa.gov/ocd/repeathydro/index.html).

Carbon dioxide is one of the most important gases in the atmosphere affecting the radiative balance of the earth. Pre-industrial atmospheric CO_2 concentrations over the past 400,000 years have oscillated around 200 to 280 ppm. Current atmospheric concentrations are now around 370 ppm as a result of industrial and agricultural activities. Over the last few decades, only half of the CO_2 released by human activity has remained in the atmosphere; on average, about 30% of the CO_2 is taken up by the ocean and about 20% by the terrestrial biosphere. In order to determine the future fate of the CO_2 that is being emitted to the atmosphere as a consequence of human activities, it is necessary to determine the changes in the carbon inventories of all three labile reservoirs in the global carbon cycle. While there is a very good observational record of the human induced atmospheric carbon changes, no such records are currently

available for the ocean, or for the terrestrial biosphere. In the past, indirect approaches were required to establish the relative roles of the ocean and terrestrial biosphere in taking up anthropogenic CO_2 from the atmosphere. In the first and second assessment report of IPCC, the method of choice was to use ocean circulation models that were either calibrated or validated with tracer observations, such as radiocarbon. More recently, a number of alternative, albeit still indirect, means of estimating anthropogenic CO_2 have been proposed. These involve efforts to balance the global budget for ^{13}C of CO_2 (Quay *et al*., 1992; Tans *et al*., 1993, Heimann and Maier-Reimer, 1996), attempts to use data based reconstructions of anthropogenic CO_2 inventories in the ocean (Gruber *et al*., 1996; Sabine *et al*., 1999) together with ocean inverse models (Gloor *et al*., 2002), or the use of the combined atmospheric oxygen and CO_2 records (Keeling and Shertz, 1992; Keeling *et al*., 1996). The latter approach has been adopted as the method of choice by the most recently published third assessment report by IPCC (Prentice *et al*., 2001).

The use of atmospheric oxygen records to differentiate between the anthropogenic CO_2 uptake by the oceans and by the terrestrial biosphere is based on the assumption that over periods longer than a few years, there is no net exchange of oxygen between the ocean and the atmosphere. This assumption has been challenged recently by several studies. They point out that the observed warming of the ocean (Levitus *et al*., 2000) likely has led to a significant outgassing of oxygen from the ocean (Bopp *et al*., 2002; Plattner *et al*., 2002). If these estimates are correct, the atmospheric oxygen based estimates of the anthropogenic CO_2 budget have to be revised significantly (several tenths of a Petagram of carbon per year or up to 10 % of the total estimated oceanic uptake) relative to the published IPCC values. Given the significant uncertainties that are associated with each of these indirect methods, it is imperative to document the time evolution of the oceanic carbon inventory directly through repeat measurements. Measurement-based constraints on the time evolution of two of the three labile reservoirs (atmosphere and oceans) will greatly improve our ability to track the fate of the emitted anthropogenic CO_2. The importance of distinguishing between the three labile reservoirs will increase in the future as nations around the world start to carbon accounting and trading of carbon credits. The determination of the anthropogenic CO_2 invasion into the ocean by direct measurements is critical considering that the ocean carbon cycle might have been affected already by climate change over the 20th century and will continue to change in the next 10 to 20 years. In such a scenario, none of the indirect methods proposed so far will work, because they are all based on the assumption that the natural carbon cycle has and will continue to operate in a steady-state. This leaves the direct determination of the temporal evolution of the oceanic carbon inventory together with the monitoring of atmospheric CO_2 as the only currently known means to assess the global redistribution of carbon in a changing climate.

The objective here is to calculate the large-scale decadal evolution of the anthropogenic CO_2 inventory to within 10% on a global and basin scale. This goal is greatly aided by the fact that, for the first time, there are a global high-quality carbon system and tracer observations in the 1990s, as part of WOCE/JGOFS. Dissolved inorganic carbon data accurate to 2 to 3 μmol/kg, which is equivalent to 2 to 3 years' uptake of anthropogenic CO_2 in near-surface waters, are now available for hydrographic transects representing most of the world's ocean (Gruber *et al*., 1996; Gruber, 1998; Feely *et al*., 1999; Sabine *et al*., 1999; Sabine *et al*., 2002; Wanninkhof *et al*., 1999). Transient tracer measurements are critical to calculate natural and anthropogenic ocean carbon concentrations. These tracers reveal mixing over the critical longer (decadal and century) time scales; and some help identify current short-term invasion rates for comparison with older data. These high-quality data, when compared with older data of much lesser quantity and quality, such as those obtained during GEOSECS, have already yielded substantial insight into carbon inventory changes over time. Sabine *et al*. (1999) and Peng *et al*. (1999) report significant changes in the carbon inventory in the Indian Ocean over the ~18 year interval between GEOSECS and WOCE, and also show that these changes agree well with those expected on the basis of ocean ventilation and the rate of increase in atmospheric CO_2. All of these approaches show very consistent patterns of long-term changes in the rate of increase in ocean carbon inventories. While these studies rely on data roughly 20 years apart, the much higher precision and accuracy of the new carbon data, and the fact that atmospheric CO_2 continues

to increase rapidly, now make it possible to detect long-term changes in the carbon inventories already over time-scales of 10 years and even less.

The benefit of the accurate determination of the spatial and temporal evolution of the oceanic carbon inventory extends substantially beyond the problem of establishing an anthropogenic CO_2 budget on the basis of direct observations. Knowledge about the space-time evolution of the ocean carbon inventory together with the accompanying tracer measurements, will provide robust constraints and validation for prognostic general circulation models that are then used for making predictions about the future. These observations will also help improve our understanding of the mechanisms responsible for the anthropogenic CO_2 uptake. To first order, the long-term oceanic uptake of anthropogenic CO_2 is regulated by water mass transport. This is very clearly the case in a steady-state ocean, but remains valid even in the case of an ocean subject to climate change. Therefore, a study with a goal of characterizing the ocean uptake of anthropogenic CO_2 would be incomplete without a component that addresses the carbon transport within the ocean's interior. For example, both model and observational studies clearly indicate that a substantial fraction of the anthropogenic CO_2 uptake occurs in the Southern Ocean south of 45°S, but very little of that uptake is being stored in this region. The anthropogenic CO_2 is transported northward and entrained into the thermocline of subtropical gyres of the southern hemisphere. It is important to find out whether the anthropogenic CO_2 uptake of the Southern Ocean has changed as a result of global climate change, (a prediction made by several coupled climate carbon models, e.g. Sarmiento *et al*., 1998; Matear *et al*., 1999). Yet, it is unlikely the changes will be seen directly in the Southern Ocean, rather substantial changes will be seen in the northward transport of anthropogenic CO_2. A joint study of the ocean carbon cycle and circulation will, therefore, help identify critical areas where potential changes in ocean circulation could have serious consequences for future anthropogenic uptake. These studies will also assist in improving monitoring for future changes.

Efforts to compute the regional and basin-scale horizontal carbon transport within the ocean using hydrographic sections and inverse techniques have been very promising. For example, Holfort *et al*. (1998) use data from three WOCE/JGOFS sections together with several pre-WOCE cruises in the South Atlantic between 10º and 30°S to estimate meridional carbon transports in this region. Notable findings by Holfort and colleagues are that the net pre-industrial carbon transport across 20°S was toward the south, but the net anthropogenic CO_2 transport is toward the north. This occurs because anthropogenic carbon is generally restricted to the upper, northward-moving waters and the southward-moving NADW contains much less anthropogenic carbon at this latitude. A study of ocean transport links the carbon flux estimates provided by the surface observation program and the ocean storage derived from the ocean interior work proposed here. The transport of oceanic carbon is a key constraint for modeling and interpreting the meridional atmospheric gradients. By studying the transports from "boxes" bound by high quality observations, the divergences in natural and anthropogenic CO_2 can also be used to pinpoint the long-term sources and sinks of CO_2. Thus, observations and transport calculations provide an independent check on the uptake estimates from models and observations of air-sea CO_2 fluxes.

Chapter 4: Oceanic storage and flux of heat and freshwater

Heat Storage

The ocean has the capacity to store heat in response to basin or sub-basin scales of decadally varying atmospheric forcing. Dominant modes of atmospheric variability having analogs in the ocean (ENSO, PDO, NAO) can produce local oceanic changes that may or may not "teleconnect" with the rest of the ocean via waves or mean currents. For example, changes in surface forcing within the subtropical gyres may have a "downstream" effect on subtropical cells, through changes in temperature or transport and thus equatorial upwelling (Federov and Philander, 2001; McPhaden and Zhang, 2002), but may have little direct influence (except via the atmosphere) on subpolar variability. It has been long recognized (Namias, 1972) that large-scale SST anomalies exist in the North Pacific. These anomalies are surface signatures of

sequestered heat, are linked to dominant spatial patterns of atmospheric variability (Davis, 1976), and persist in the ocean longer than in the atmosphere. Interannual changes in air-sea fluxes in the North Atlantic can have substantial effects upon mixed layer depths, and properties of the convectively-renewed waters of the entire North Atlantic (Dickson *et al.*, 1996). Superimposed on this large amplitude natural variability are more subtle but large-scale, greenhouse-type signals related to anthropogenic effects (eg. Levitus *et al*., 2001).

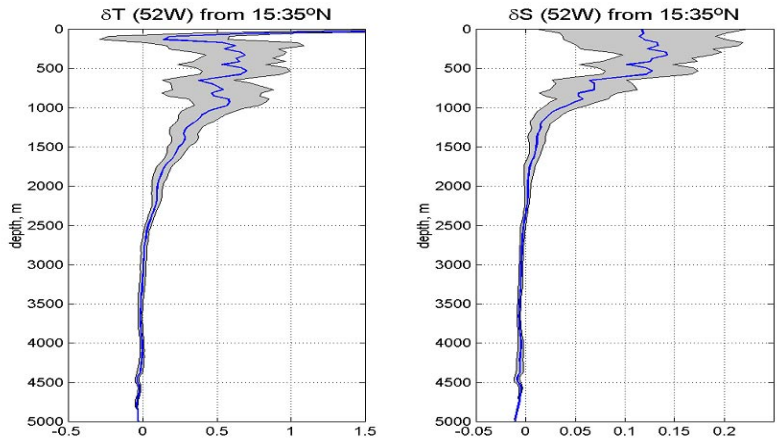
Beginning with a comparison of two pairs of zonal hydrographic sections taken some 25 years apart (Roemmich and Wunsch, 1984) in the North Atlantic, numerous examples have emerged in recent years of the changing character of the ocean from the surface to the bottom. The vertical extent of the variations clearly indicates that high latitude changes are exported via the ocean and can be detected in the tropics. In fact, Arbic and Owens (2001) suggest that dominant changes in and beneath the permanent thermocline had an origin at mid-high latitudes of the North Atlantic and could be seen south of the equator, predominantly as T/S changes on density surfaces. Temporal changes have been seen in the deep Southern Ocean (Gordon, 1982) and in the deep passages and basins of the South Atlantic (Hogg and Zenk, 1997) and the South Pacific (Johnson and Orsi, 1997; Johnson *et al*., 1994), far from bottom water formation sites. The repeat hydrographic sections will be an essential element in the study of changes in deep and bottom water formation rates and properties and their signatures as they spread out from formation regions.

Repeat hydrography will provide a multi-dimensional view of oceanic change in that other parameters such as salinity will be observed. It has been found that often changes in freshwater storage are NOT simply related to changes in thermocline depth: there is an active, variable hydrologic cycle.

Freshwater storage

With the completion of the WOCE program of global hydrography, there has begun an appreciation of the importance of changing salinity in the ocean. Wong *et al.* (1999), for example, compare WOCE era sections with climatology, and show that two principal intermediate waters formed in the North Pacific (NPIW) and Southern Oceans (AAIW) have apparently freshened by as much as 0.1 in salinity during WOCE (compared to climatology). Dickson *et al* (2002) show that both intermediate (LSW) and overflow waters have freshened by 0.05 in salinity over the past 3-4 decades to depths in excess of 2000 m. This high latitude freshening requires an addition of a layer 3 m thick of freshwater at high latitudes: this need not come from melting of sea or glacial ice, but from the subtropical oceans. The subtropical Pacific and Indian (Wong *et al.*, 1999), as well as the subtropical North Atlantic, have all seen a significant increase in upper ocean salinity over the last few decades. In the western North Atlantic subtropical gyre, there has been a significant increase in upper ocean salinity since the period of the IGY. In the western subtropical gyre (Fig. 2, next page) two hydrographic sections taken during WOCE and the IGY are compared and T/S changes estimated. These observed T/S changes have been averaged over the entire latitude extent of the gyre (15-35°N) and show a large increase in temperature and salinity in the upper km, related to changes in thermocline depth AND increase of T/S on density surfaces (Joyce *et al.*, 1999). This suggests an increase of evaporation over precipitation at mid-latitudes of the North Atlantic. It is feeding the freshwater to higher latitudes via the atmospheric bridge. In the deep water, the temperature increase persists to 2500 m, below which there is a slight salinity decrease over time. These deep changes cannot be locally generated and are signatures of changes at more northern latitudes. In fact the deep change in temperature is closely related to the type of calculation made from ocean data in the Levitus *et al*. study mentioned above. Although there has been no global assessment of freshwater storage change using hydrographic data, it is clear that multi-decadal changes in freshwater storage are occurring in the oceans of the world, that these are consistent with loss of freshwater from low latitudes, and its deposition at higher latitudes, and that these changes are communicated by ocean and atmosphere heat and freshwater fluxes across latitude bands.

For changes in the upper 2000 m, the Argo float array will provide a better temporal resolution of changing heat and freshwater storage than the repeat hydrography sections. However, T/S changes exist below 2000 m, particularly in the North Atlantic and the southern hemisphere basins, and the accuracy of the Argo salinities requires some form of in situ "calibration" (against hydrography). Thus, the repeat hydrography program not only extends the Argo sampling deeper, but provides data for referencing Argo salinities in the upper 2000 m (see Chapter 6).



Mean Temperature (left) and Salinity (right) changes from 1956 to 1997 within the subtropical N. Atlantic at 52 °W from 15 to 35 °N. A substantial heat gain can be seen from the surface to 2500m depth, while the salinity has increased above 2000m significantly and freshened at greater depths. Spatial variability is reflected in the error bars (gray) in the estimate of the mean changes over 41 years between the two hydrographic sections. Adapted from Joyce et al. (1999).

Heat and Freshwater fluxes

Hydrographic data have been essential in directly estimating the fluxes of mass, heat and freshwater as a function of depth and latitude in the ocean (see Bryden and Imawaki, 2001; Wijffels, 2001). The method of direct estimation of fluxes can be made by combination of hydrography with information about western boundary transport (eg., Hall and Bryden, 1982). Global estimates of meridional fluxes have also utilized inverse methods to constrain the "reference" velocity with hydrographic data (Macdonald and Wunsch, 1996; Ganachaud and Wunsch, 2000, heat only). Other efforts have demonstrated that inverse methods and additional velocity constraints either from directly observed velocities with a LADCP (Joyce *et al*, 2001) or non-local transport constraints (Sloyan and Rintoul, 2001) can be used to estimate fluxes, either zonal or meridional. In the latter study, a reasonable mass transport through Drake passage was obtained without any direct velocity estimates in Drake passage at all. Fluxes estimated from hydrographic data have focused on the mean circulation, rather than the variability. Thus, there is some disconnect with the ideas about variable heat and freshwater storage above. Given the errors in estimation of fluxes from hydrography, its limited resolution of decadal changes in forcing, and the prospect of a global array of Argo floats providing T/S profiles of the upper 2 km, one might expect that it would be simpler and more accurate to infer changes in heat, freshwater and mass fluxes indirectly from changes in heat, salt, and mass storage using models that assimilate observed T/S changes and estimates of air-sea fluxes (Stammer *et al.*, 2001). For the present, however, direct flux estimates are likely to play a continuing role in studies of the way the ocean redistributes various conservative and non-conservative

hydrographic properties. The repeat program will comprise the only observations that allow full-depth, coast-to-coast estimates of ocean transports of heat, freshwater, tracer and carbon in the observing system. At this time, there are very few repeat hydrographic sections outside the North Atlantic. This program should add significantly to our understanding of the error characteristics of direct flux estimates from repeat sections in different ocean basins where heat and freshwater transport are effected differently from the North Atlantic. In addition, these sections will be the only direct data useful for characterizing the role of the deep circulation in ocean flux variability.

The wide suite of physical and biogeochemical measurements on the repeat hydrography cruises will also allow analysis of coupling between physical variability (changes in ventilation rates, temperatures, and salinities) and variability of biogeochemical processes and constituents addressed in other chapters.

Chapter 5: Deep and Shallow Water Mass and Ventilation Studies

The proposed program offers an unprecedented opportunity for the study of ocean ventilation. Ventilation can be broadly defined as the penetration and sinking of waters from the surface ocean into the interior. Important characteristics of ventilation are both the physical pathways of the flow as well as the timescales for which the water is subducted (e.g., Sarmiento, 1983; Jenkins, 1987, 1998), and thus shielded from the atmosphere. Subduction of surface waters of time varying composition is central to a number of leading hypotheses about coupled ocean-atmosphere dynamics of climate variability (e.g., Gu and Philander, 1997). Characteristic timescales vary from decadal in the thermocline to centennial in the intermediate waters to millennial in the deepest abyssal waters.

Previous hydrographic programs have provided single snapshots of the ventilation of the ocean (e.g. Doney and Jenkins, 1994; Rhein *et al*., 1995; Warner *et al*., 1996; Orsi *et al.*, 1999; Fine *et al.*, 2001). The crucial remaining challenge is to measure and understand how this ventilation changes over time. Long-term time series at single stations, such as Bermuda, reveal significant changes in water mass ventilation over interannual to interdecadal time scales (e.g., Talley, 1996). Differences in repeated hydrographic sections also show notable evolution of water mass properties, which are still not fully understood. (Bryden *et al*., 1996). To what extent these represent global changes or phenomena specific to the North Atlantic cannot be understood without further global measurements of hydrographic and tracer properties.

Analysis of climatological subsurface temperature fields in the North Pacific has shown large decadal variability and apparent equatorward propagation of temperature anomalies in the thermocline (Deser *et al*., 1996). Missing from the climatological analysis are sufficient salinity observations to fully understand how the observed variability relates to surface forcing and subsurface flow. Analysis of time series north of Hawaii (Lukas, 2001) suggest that low frequency variability of the salinity field is determined by changing precipitation at the source region. In contrast, further to the east, temporal changes in salinity seem more connected to changes in ventilation and water mass formation rates (Suga *et al*., 2000). Global, high quality records of the upper ocean hydrography and tracers are required to determine a full physical understanding of the processes and mechanisms of low frequency variability in thermocline ventilation. Anthropogenic transient tracers offer a direct means of observing the ventilation of the ocean.

As transient tracers have only been present in the atmosphere since the beginning of industrial activities, their presence in seawater indicates recent contact with the atmosphere. The time that has elapsed since this contact with the ocean surface can also be estimated, especially if multiple tracers are observed. Observing the temporal penetration of these transient tracers offers the most direct and unequivocal measure of ocean ventilation. Pathways of recently ventilated water carrying signals of perturbations imprinted at the ocean surface, such as anthropogenic carbon, are clearly revealed (Weiss *at al*., 1985), and inventory calculations yield integral water mass formation rates (Smethie and Fine, 2001). Furthermore, the ages, temporal evolution of the transient tracers, and especially the tracer-tracer

relationships, contain crucial information about ventilation processes, especially the relative roles of mixing and advection (e.g., Smethie *et al.*, 2000), which are not easily diagnosed from steady-state tracers (Robbins *et al.*, 2000).

There has been an evolution in the use of transient tracers during the course of the past decades. Initial exploratory studies included a large set of such tracers (e.g., tritium, ^{3}He, ^{14}C, ^{137}Cs, and ^{90}Sr during GEOSECS; CFCs, tritium, ^{3}He, ^{14}C and ^{85}Kr during TTO; and CFCs, tritium/^{3}He, and ^{14}C during WOCE). During these studies attention has been paid to distilling the minimum set of transient tracers that will allow study of water mass formation, spreading, renewal, and facilitate model calibration from a larger set of possible measurements. The most robust combination used in recent studies is that of CFCs and tritium/^{3}He.

In order to address important issues such as age information and dilution of water masses, either separately or in combination, a set of at least two independent tracers is required. The time over which combination of several CFCs (CFC-11, CFC-12, and CFC-113) and CCl_4 will be sufficient to provide unique age and dilution information is limited. This is due to the fact that both the concentrations and practically all the ratios of these compounds either have reached or soon will reach a plateau in the surface waters. A set of tritium/^{3}He data collected on a grid that is coarser by a factor of 2 to 3 compared with the CFC sampling grid will remedy the problem created by the temporal evolution of the atmospheric concentrations of the CFCs. Uncertainties in the stability of CFC-113 and CCl_4 can be evaluated by the addition of tritium/^{3}He.

Repeated observations of the penetration of multiple transient tracers can provide important constraints on models of ocean ventilation. Transient tracers are close analogues to climate anomalies, and as dyes they are frequently used to study perturbations. Model calibrations will benefit from simultaneous use of tracers with very different boundary conditions as they represent different types of perturbations. The modeling aspects used by England and Maier-Reimer (2001) are only one view among many. Heinze *et al*. (1998), and Schlosser *et al.* (1991) discuss the details of transient tracer simulations in OGCMs and simpler models.

Chapter 6: Calibration of Autonomous Sensors

Repeat hydrography will provide accurate baseline measurements for autonomous sensors. These sensors, while potentially inexpensive and numerous, will not be sufficient to detect subtle deep and abyssal oceanic changes, which can be signatures of natural decadal variability and even sudden anthropogenic climate shifts in both physical and biogeochemical systems. The repeat hydrographic sections, with their high accuracy full-water column measurements, will provide a record of these changes and a reference for autonomous sensor arrays.

The most visible project involving autonomous ocean sensors is probably the Argo program. This array of 3000 profiling CTD floats will sample the ocean at 3° x 3° spatial and 10-day temporal resolution from the sea surface to 2000 m. These floats have a nominal lifetime of 4 years at present. Pressure sensors are expected to remain accurate to 2.4 dbar over the float life, and temperature accurate to within its present maximum reporting precision of 0.005 C. However, salinity, which is targeted for an accuracy of 0.01, may drift outside of that range because of biofouling and other problems. It is too expensive to recover the floats routinely for post-mission calibrations, so the only instrument calibrations available are usually those made before deployment.

Early profiling CTD floats experienced biofouling over a single summer season, and reported salinities freshened dramatically over time as the organisms modified the effective geometry of the CTD conductivity cells (H. Freeland, personal communication). In response an antifouling coating was applied to some float conductivity cells to prevent biological growth. This coating ablated over time, and the gradual loss of material made to the cell geometries resulted in significantly saltier readings over time (R. Davis, personal communication). Another more recent approach to the biofouling problem is to enclose the sensor in a contained and poisoned volume of seawater when not actually making measurements. This often results in stable measurements over a few years (Riser and Swift, 2002), but there have been exceptions to this stability. In some instances the poison has accidentally coated the conductivity cell after laboratory calibration, resulting in biased salinities for the first several profiles before the coating washes off (S. Riser, personal communication). In addition, this antifouling system has apparently failed on at least one recent float deployment, resulting in a significant fresh drift over time, which can be corrected by calibration using historical data (Fig. 3). Thus, while profiling float salinity stability has improved, adjustment of the salinity data are still sometimes required.

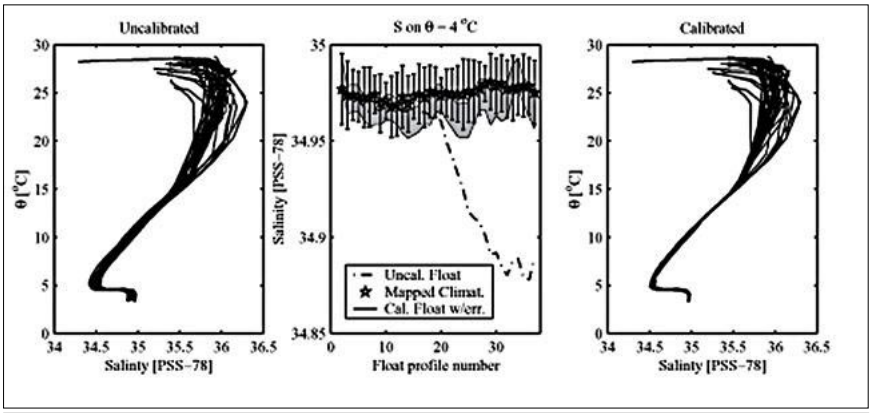


Figure 3. Argo float data from the tropical Atlantic for a rare instance in which a Seabird antifouling system apparently failed. This float was deployed in the equatorial Atlantic in January 2001 and remained there through October 2001, the period over which data are displayed. Left panel shows uncorrected theta-S curves, and right panel curves calibrated using historical data following Wong *et al*. (2002). Central panel shows salinity on theta = 4ºC including uncalibrated data (dot-dashed line), climatology with uncertainty (pentagrams with error bars) and calibrated data with uncertainties (gray shaded).

One way of dealing with drifting salinity sensors is to compare their potential temperature-salinity (theta-S) relation to that of calibrated measurements (hydrographic cruises including salinity measurements calibrated with IAPSO standard sea water). This strategy has been one driving force for the relatively deep 2000-m specification for Argo profiling depths, since the deeper one goes the more stable and uniform the theta-S relation becomes, generally. One methodology has been developed to map historical theta-S relations to float positions and use those relations to "calibrate" the float salinities (Wong *et al.*, 2002). A time-scale is included in the climatological mapping, using CFC ventilation ages (e.g. Doney *et al*., 1997). Hence, if there are hydrographic data close in space and time (relative to the ventilation age) their theta-S values dominate the climatological values with a small error, but if there are no recent and nearby data a long-term mean theta-S is used with an error comparable to the overall historical variability. Another methodology has been proposed to inter-compare floats where they approach each other in space and time, using available contemporary CTD stations as calibration anchor points (Bacon *et al*., 2001).

Both of these systems recognize that there is variability in oceanic theta-S relations from the ocean surface down to the 2000-m float profiling depth over some time-scale throughout the world ocean (Dickson *et al*., 2001). It is well known that the North Atlantic exhibits such variability. This variability is characterized by the well-sampled 0.1 in salinity variations in Labrador Sea Water over the past century (Dickson *et al*., 1996). The influence of this important component of the NADW is carried far southward via the deep western boundary current (Molinari *et al*., 1998), and significant variability is found at all depths across the entire North Atlantic (Bryden *et al*., 1996). However, it is important to recognize that, in fact such variability is global (Fig. 4), with freshening of up to 0.1 in salinity documented in the intermediate waters of the South Pacific (Wong *et al*., 1999), the intermediate waters of the South Indian Ocean (Bindoff and McDougall, 2000), and the intermediate and deep waters of the North Atlantic and South Atlantic (Arbic and Owens, 2001). In addition, the Antarctic waters such as the Weddell Sea Deep Water also exhibit substantial theta-S variability (Gordon, 1982), although the southern oceans have not been revisited nearly so often as the North Atlantic to establish a record of the changes. The presence of significant decadal intermediate and deep theta-S variability, below the 2000-m sampling limit of the Argo array in some locations, means that for the foreseeable future there will be a global need for periodic hydrographic cruises to collect high-quality calibrated measurements to which autonomous instruments such as the Argo floats can be compared and calibrated.

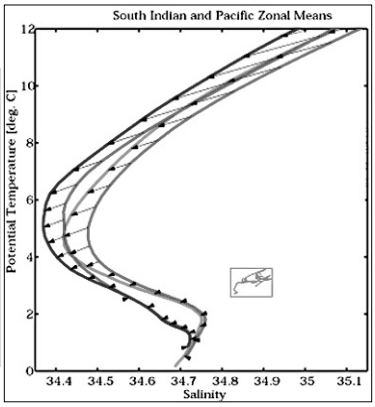


Figure 4 Zonal means of potential temperature and salinity on neutral density surfaces (arrows show directions of change along neutral densities) showing cooling and freshening over roughly 20 years along 32ºS across the South Indian Ocean (right hand curves after Bindoff and McDougall, 2000) and 35ºS in the Southwest Pacific Ocean (left-hand curves after Johnson and Orsi, 1997). Changes are large even well below the Antarctic Intermediate water salinity minimum near 5ºC. Changes are similar in magnitude to decadal changes of Labrador Sea Water properties at 1000-1500 dbar from 1928 to 1995 (line inside inset box after Dickson *et al*., 1996).

Over time the Argo array or its successors may add biogeochemical sensors to the present salinity, temperature, and pressure measurement suite. Other complementary autonomous biogeochemical sensor arrays may also be deployed (e.g., Chavez *et al*., 1999; Byrne *et al*., 2001). Imagined sensors at present include those for particulate organic carbon, particulate inorganic carbon, pCO_2, pH, alkalinity, total CO_2, or nutrients (Bishop *et al*., 2001). Clearly it is unlikely that the entire Argo array will be instrumented to sample all of these parameters, but it is possible that some subset of the array may eventually measure a subset of them. Like salinity, many of these parameters have more temporally stable and spatially uniform distributions deeper in the water column. Nevertheless, there is evidence from repeat hydrographic data in the South Indian (Bindoff and McDougall, 2000) and the North Pacific (Watanabe *et al*., 2001) for significant changes in intermediate oxygen distributions, possibly related to some combination of changes in water mass ventilation, circulation strength, and even the biological pump (Emerson *et al*., 2001). This work suggests that like temperature and salinity, intermediate and deep biogeochemical properties may vary over decadal and longer time-scales. Thus, as for salinity measurements from the Argo array, any future autonomous biogeochemical measurement system that relies on comparison to (relatively) stable deep water properties would also benefit from the repeat hydrographic sections to monitor decadal changes in those deep water properties.

Chapter 7: Implementation - Work Statements, Methodologies and Data Management

The planning group [to be supplanted after award by an Implementation Working Group (IWG)] will carefully follow the individual cruises and overall program. For efficiency and straightforward communications the coordinator for the sea program will be Dr. James H. Swift (UCSD/SIO), who will work closely with all Chief Scientists, data originators and the IWG with an annual agenda as follows:

- examine status of data from past cruises from this program and companion programs,
- assess the previous year's field work for this program,
- finalize and coordinate plans (participants, ship details) & budget for the next year's cruise(s),
- plan & revise budgets and participants for cruises two years ahead,
- review plans & first-cut revised budget and participants for cruises three years ahead, and
- review long-term plans and revisions.

The cruise plans have been well thought out, but each will be examined closely well ahead of time for any fine tuning due to scientific or logical considerations. Commitments of the science parties will be made two years prior to carrying out each cruise. These decisions will be made in close consultation (and with decision making authority as needed) from the IWG, and may result in small budget and logistical changes at least 1-2 years ahead of each cruise which can be negotiated with the agencies and vessel operators within existing agency and UNOLS funding and scheduling guidelines. Responsibility for the specific sea work and data will as usual be given to the Chief Scientist and all data originators. Thus Swift will hand off the detailed planning and execution of the work to the designated science party, meanwhile providing financial support for the academic personnel in the chief scientist's party, and also for foreign observer travel as required.

As WHPO Director Swift is also responsible for the post-cruise merging, distribution, and archive of all CTDO and bottle data parameters and documentation from the proposed program. Each Chief Scientist and most data originators will send back data to him at the conclusion of their contributions to the sea work, bringing to this program a cradle-to-grave oversight and data management support structure.

Nearly all these matters can be carried out via email and conference calls. Funds are requested, however, for the chief and co-chief scientists to attend one pre-cruise meeting at the vessel operator's institution, as per practice very strongly recommended by UNOLS. Swift will attend these meetings to help make certain that all principal planning and data management issues are fully addressed.

The sea work itself follows the approach proven successful during the 1990's hydrographic/tracer/carbon surveys: CTD/rosette stations at 55 km spacing (closer over boundaries, steep bathymetry, and across the equator; separately-proposed shallow trace metal casts at 110 km spacing can be accomodated), use of a 36-place rosette with 10/12-liter bottles proven excellent for dissolved gas sampling (there is room for a lowered-ADCP), latest-generation hardware and procedures (overseen by consortia and working groups), extensive examination and processing of data at sea (including merging disparate bottle sample data), full support of quality coding, standard community data formats, and so forth. Swift has long said that one of the legacies of the recent CO_2 surveys and WOCE Hydrographic Program work would be that we would know how to do it by the time we were done with it: Simply put, we know how to collect and manage the data which this program requires, and we are completely confident that, barring disaster, we can achieve the quality, rapid dissemination, and management goals we propose for these data.

7.1: CTDO/Salinity/Oxygen/Nutrient Measurements

The CTDO/rosette work, salinity/oxygen/nutrient analyses, and related data processing will be carried out by the Oceanographic Data Facility (ODF) at the UCSD Scripps Institution of Oceanography, the NOAA Pacific Marine Environmental Laboratory (PMEL), and the NOAA Atlantic Oceanographic and Meteorological Laboratory (AOML). James Swift and Gregory Johnson will serve as scientific overseers of this work and are ultimately responsible for the ODF and NOAA data, respectively. Data standards

and procedures will equal or improve on those of the WOCE Hydrographic Program (e.g., cf. Joyce and Corry, 1994 a/b). On every proposed cruise SIO has budgeted for a 4-person Chief Scientist's party (salary and travel for chief and co-chief scientists, and 2 grad students/post docs), the scientists' pre-cruise meeting with the vessel operator, foreign observer travel, and a bottle data expert. Beyond that, ODF will provide core CTDO, salinity, oxygen, and nutrient support for A20/22, P2, P16S, S4P, and I7N/I6S whereas NOAA/PMEL/AOML will provide this core support for A16S, A16N, P16N, P18, and I8S/I9N.

CTDO

For the CTDO measurements both groups plan to use a SeaBird 911plus CTD with dual T/C sensor packages and a SeaBird oxygen sensor, or other instruments/sensors of equivalent or improved performance. The groups have much experience with the SeaBird CTD systems, and they have developed CTD data acquisition and processing procedures which proved during WOCE to meet the data requirements for the proposed expeditions. The NOAA and ODF procedures differ in small degrees. Swift and Johnson will continue to compare and evolve procedures to improve data quality.

Both groups carry out extensive pre-cruise preparations including inventories, purchases of consumables, calibrations, software updates, and hardware tests. Test casts are performed as soon as possible at sea. Sea-Bird software is used to acquire the data. Data quality, winch and bottom parameters are monitored real-time. Meteorological and cast information are logged. Original raw data are retained. Software processing routines are run, and a CTD data analyst further processes the data at sea, including routines to check for first good surface values, and density inversions indicative of contaminated data owing to shed wakes from ship's roll not identified by Sea-Bird processing routines. WOCE flags are created and amended as needed. As sample salinity and oxygen data become available, corrections are made at sea.

All raw and processed data, plus all programs, batch files, configuration files, and forms, are returned to shore. The CTD instruments are again calibrated post-cruise. A temperature drift correction is applied if necessary, as well as any significant pressure offset. Final conductivity and oxygen calibrations are determined. Profiles are de-spiked as necessary. Posted data files will be date-stamped.

Real-world accuracy of CTD data is dependent on package configuration, electrical noise, wake effects, and local vertical gradients of the measured properties. Within those considerations, final delivered CTD data accuracy for this program should fall within ca. ±1-2 db, ±0.002 °C, and ±0.002 in salinity, limits which are appropriate for the proposed science. The CTD oxygen probe data will be corrected vis-à-vis the bottle oxygen data. In that case the data standards will be the current state of the art.

Salinity, Oxygen, and Nutrients

Salinity samples will be drawn and sealed into appropriate bottles providing very low container dissolution and sample evaporation. Salinity will be determined after a box of samples has equilibrated to laboratory temperature. The draw time and equilibration time, as well as per-sample analysis time and temperature are logged. Guildline AutoSal salinometers located in a temperature-controlled laboratory are used to measure salinities. The salinometer is standardized for each box of samples with IAPSO Standard Seawater (batch number is noted) using fresh vials. The estimated accuracy of bottle salinities run at sea is usually ≤ 0.002 relative to the standard seawater batch used. This is the WHP standard. Underway thermosalinograph data will be logged, and salinity corrections applied.

Samples are collected for dissolved oxygen analyses soon after the rosette sampler is brought on board (and after CFC and helium if they are drawn). Sample temperature is measured. The samples are generally analyzed within 4 hours of collection. Dissolved oxygen analyses are performed with an automated oxygen titrator using photometric end-point detection based on the absorption of ultra-violet light. ODF analytic methodology is based on whole-bottle modified-Winkler titration following the technique of Carpenter (1965) with modifications by Culbertson *et al*. (1991). The NOAA methodology following Friederich *et al.* (1991) is generally similar. Standardization procedures are robust and follow

WOCE protocols. The groups meet/exceed the WOCE Hydrographic Program standards. Johnson and Swift will jointly examine procedures and investigate additional steps to assure data quality, such as use of a single source of standards.

Nutrient sampling and analysis procedures follow the WOCE protocols, with analyses (phosphate, silicate, nitrate plus nitrite, and nitrite) performed via autoanalyzer, generally within a few hours after sample collection. The nutrient groups have produced WOCE data sets at the current state of the art. But the WOCE data show occasional inexplicable cruise to cruise differences, in some cases outside data quality targets. Both groups are participating in a US community nutrient analysis workshop in March 2002 to (1) document methodologies to be followed by US groups who carry out nutrient analyses for US global ocean carbon and decadal change programs, (2) establish a consortium to provide oversight of the work and recommend modifications to the approved protocols, (3) provide a report, and (4) establish priorities for future activities aimed at improving the accuracy and precision of reference-quality seawater nutrient analyses. The groups are also exploring use of common sources of standards for these cruises.

Data Management and Discussion

All CTD/rosette data acquired through the proposed program will be indexed by cruise, station, cast, and sample/bottle (the last category is for bottle data only). All sub-sampler serial numbers (e.g., salinity bottle, oxygen flask number, etc.) will be logged. All groups will have access on board and later to files combining the index parameters, CTDO values corresponding to bottle closures, plus the bottle data. Tracer, CO_2, and biogeochemical data will be merged at sea. The WOCE Hydrographic Program Office will promptly (< 30 days) merge data ashore. The merged data are jointly examined at sea for reasonableness and to note doubtful data. Cast data logs summarize all data comments and actions.

Except for rare and unusual problems, the bottle data are expected to be in very close to final form before the end of a cruise. Final CTD data (typically little changed from shipboard processed data, but with much-improved documentation) are expected within several months of the post-cruise CTD calibrations.

There are additional considerations which affect the relationship of a measured seawater characteristic to the value for that parameter which obtains at the sampled level in the original seawater water column. Not much is published about them. These deal partly with the realities of sampling from a water column from a moving ship, partly with sample drawing and analytic realities, and partly with data management. In 1994 Swift drafted a document "Data Evaluation and Quality Control for Routine CTD/Hydrographic Data". For completeness, Swift has placed a PDF file ("data_eval.pdf") of the 1998 version of the cited document in the ftp directory <ftp://odf.ucsd.edu/pub/jswift>.

The standard methodologies do not contain explicit statements about the use of replicates. This issue was debated during the 1970s and 1980s but not so much during WOCE because for salinity, oxygen, and nutrients it has been shown that repeated sampling over many stations in low-variability portions of the water column provides a more effective measure of replication ability than analyzing classical replicates from a single sample, which only gets at a part of the real-world issues affecting total precision.

The budget includes substantial data processing services at sea so that the bottle S, O_2, and nutrient data can be point checked at sea, and also so that the CTDO data can be run through the processing sequence, including matching at sea to pre-cruise CTD calibration and onboard salinity and analyses. In nearly every case these data are in terms of science use nearly indistinguishable from so-called "final" data.

Final CTD processing must await the return of the CTD to the calibration laboratory for its post-cruise check. A substantial measure of final data processing lies in documentation, which adds greatly to the value of the data. There are many elements to the documentation, but in terms of value to data users, the data quality codes and the text record made of the reason for every issuance of a "non-good" quality code are especially valuable.

Our data management includes multiple redundancies and backups, thorough tracking, and version documentation and control. All records, raw data, and processed data are held for at least 10 years, with most documentation and processed data archived for 20 years or longer. (Primary documentation is never discarded.) As in WOCE, the data group at SIO will submit complete data/documentation files to the archive at NODC for each cruise, along with the data. The submissions to NODC will be citable.

Reviewers should note that the sea work portion of the budget for ODF shipboard data acquisition is handled through NSF's Oceanographic Technical Services Program, and thus is not charged to the science budget. This results from changes in mechanisms for such technical support made at NSF which allow "specialized instrument support" items to be supported transparently to research proposals. Present NSF policy permits ODF to supply these services via this mechanism at the costs shown. NSF policy requires that ODF's shore data processing and documentation services be part of the proposed science budget. NOAA Year 1 budgets include funds for equipment aquisions/upgrades.

Work and Budget Summary for the CTDO, Salinity, Oxygen, and Nutrient Program (costs in 1000s of $):

YEAR	PURPOSE	PMEL/AOML	CIMAS	SIO/SWIFT	TOTAL THIS PROPOSAL	*SIO/ODF (NSF OTS)*	*GRAND TOTAL*
2003	A16S	517	167	192	876	*57*	*933*
	A20/22			377	377	*563*	*940*
2004	A16N	372	146	188	706	*58*	*764*
	P2			442	442	*765*	*1,207*
2005	P16N	565	203	262	1,031	*91*	*1,122*
	P16S			279	279	*506*	*785*
2006	*data*	9			9		*9*
	S4P			319	319	*658*	*976*
2007	P18	618	224	351	1,193	*104*	*1,297*
2008	I6S/I7N			671	671	*1,210*	*1,881*
	I8S/I9N	713	253	343	1,309	*123*	*1,431*
TOTAL		2,794	994	3,423	7,211	*4,134*	*11,345*

7.2: Direct Velocity Measurements

During the WOCE Hydrographic Program (WHP), direct velocity measurements from Acoustic Doppler Current Profilers (ADCP) became a standard complement to the hydrographic sections. ADCP technology, its strengths and weaknesses, and its applications in WOCE are reviewed by King et al., (2001); only a brief overview will be given here. The two methods used extensively in the WHP, and proposed here, are shipboard (SADCP), in which a hull-mounted sonar transducer profiles currents in the upper several hundred meters continuously along the ship track, and lowered (LADCP), in which one or two self-contained Doppler sonars are mounted on the CTD package, yielding a full-depth velocity profile at each station (Fischer and Visbeck, 1993; Firing, 1998).

ADCP measurements have contributed to our image and our understanding of the ocean on scales from basin-wide down to finestructure. For example, at low latitudes the wind driven Ekman transport and its vertical distribution (with implications for meridional heat flux) have been measured in the Atlantic (Chereskin and Roemmich, 1991), the Pacific (Wijffels et al., 1995), and the Indian Ocean (Chereskin et al., 1997). The absence of a level of no motion-the tendency of the near-bottom flow to resemble a weaker version of the shallow currents-has been demonstrated in many high-latitude regions such as the Subantarctic Front in the Pacific (Donohue et al, 2001). ADCP measurements have revealed previously unsuspected currents, leading to substantial revision of basin-wide meridional transport estimates (Beal

and Bryden, 1999; Donohue et al., 2000). Aided by bottom tracking, LADCP measurements have revealed in detail the bottom-intensified outflows from the Weddell Sea (Gordon et al., 2000). Polzin et al. (2002) have shown that the finestructure in LADCP profiles can be used to estimate diapycnal mixing.

LADCP and SADCP methods are highly complementary to each other as well as to hydrographic measurements--the combination of all three provides the highest ratio of information to cruise dollars. Both LADCP and SADCP can be used to reference geostrophic current estimates (and in quantifying ageostrophic parts of the current field), but they have different strengths and weaknesses. SADCP sampling (continuous between stations) matches the geostrophic calculation (which is an average between stations), but covers only the upper part of the water column. LADCP sampling (full-depth profiles on station) doesn't match the geostrophic calculation in the horizontal, but it provides an accurate measurement of the barotropic velocity at each station. It can resolve complex velocity structure near bottom topography, and near the equator where synoptic geostrophic calculations are useless.

We hope and expect that much or all of the proposed work will be done on ships with lower frequency SADCP installations than the standard 150-kHz of the WOCE era. These newer systems, reaching depths of 600-700 m (e.g., 75 kHz) or even 1000-1200 m (38 kHz), will improve the accuracy of geostrophic referencing from SADCP data; averaging over a larger vertical interval, and including a smaller fraction of upper ocean, reduces the contribution from internal waves (especially the near-inertial part of the spectrum). Even these lower-frequency sonars, however, leave 80% or so of the water column unmeasured-the LADCP is still essential to complete the picture.

*Shipboard ADC**P***

Firing will be responsible for shipboard ADCP (SADCP) data collection, processing, and archiving on all cruises. This will be done with no additional at-sea personnel, under the assumption that basic responsibility for maintaining a working SADCP resides with a shipboard technicians' group for each ship. The person from our group whose primary responsibility will be to operate the lowered system during a cruise will assist in monitoring the SADCP. A second major assumption is that the NODC Joint Archive for Shipboard ADCP (JASADCP) (http://ilikai.soest.hawaii.edu/sadcp/) will remain at UH, and will retain sufficient NODC support to serve as the primary long-term archiver and distributor of the processed data sets, as it has been for the WHP SADCP data.

Pre-cruise activities include corresponding with the shipboard tech group to verify that a suitable system of hardware and software including high quality navigation devices are in place and will be operational for the cruise. Recent data samples will be requested and inspected. A suitable member of the science party (preferably ADCP personnel in charge of the LADCP) will be identified as the onboard SADCP representative. Instructions for instrument setup and monitoring will be provided to the representative and to the ship's tech group. Particularly prior to the first use of a given ship in this project, it may be necessary for an SADCP expert to work on the ship's ADCP system in port before the cruise.

During each cruise, email contact with the ship will be maintained to help resolve any questions or problems that may arise. If an ADCP representative is aboard, that person may perform preliminary processing of the data during the cruise to ensure that the system is fully operational. Alternatively, we hope that by the time of these cruises most or all of the ships will be using a system similar to the one we have developed for the NB Palmer and the LM Gould (http://currents.soest.hawaii.edu/antarctic/). This system logs complete raw data sets, performs preliminary processing at frequent intervals, makes both raw and processed data available to the science party onboard via a web server, and emails a daily system status report to shore. Funds for installing this system are, however, not being requested here.

Following each cruise, data will be processed using the public software developed primarily at UH beginning in 1985 (Firing, E., 1991; King, B. A., E. Firing, and T. M. Joyce 2001). The software has undergone frequent refinement and extension, most recently to improve the editing facilities and to support the data formats coming from RDI's present generation of ADCPs (Ocean Surveyor phased

arrays; http://currents.soest.hawaii.edu/reports/endeavor_report/os_eval_jtech.pdf) and data acquisition system (VMDAS). Software maintenance and evolutionary improvement will continue as a small but essential part of this project. Major additional work may be required by circumstances beyond our control, such as the use of an unfamiliar data acquisition on a particular ship.

Processed data will be provided to the JASADCP for archiving and distribution, but will also be made available on our UH web site via a page dedicated to the project, with plots for browsing and downloading, and downloadable data sets within 6 month after the cruise.

Lowered ADCP

Visbeck will have overall responsibility for lowered ADCP (LADCP) data collection, processing, and archiving on all cruises. However, the at-sea ADCP personnel support will be shared by Firing and Visbeck. Consistent with our usual practice on WHP cruises, we will provide one LADCP person per cruise, under the assumption that for the remaining watches one or two additional members of the scientific party will be designated to perform the routine LADCP setup immediately before each cast, and to download the data immediately after the cast. A second assumption is that the NODC Joint Archive for Shipboard ADCP (JALADCP) (http://ilikai.soest.hawaii.edu/ladcp/) will remain at UH, and will retain sufficient NODC support to serve as the primary long-term archiver and distributor of the processed LADCP data set. The burden is about an order of magnitude less for LADCP data compared to SADCP data if only the final profile is archived.

Pre-cruise activities include corresponding with the shipboard tech group to verify that the CTD system is prepared to accommodate the LADCP hardware. At present two types of LADCP systems are in common use, one based on one down-looking RDI BB150 ADCP and one based on a dual RDI WH300 ADCP system with one unit looking upward and one looking downward. Both types record internally but use an external battery pack; cabling and battery requirements for the two types are different, unfortunately. We anticipate that most of the cruises will employ the dual WH300 system, since the BB-150 is no longer manufactured. (The dual WH300 system has the advantage of much smaller size and weight, for lower shipping cost and greater ease of handling.) In the first years we are requesting resources to build up an LADCP instrument pool consisting of two complete systems. (Two per cruise is essential for reliability.) This can be supplemented occasionally by one existing LADCP system at LDEO and UH respectively.

During each cruise the ADCP person will operate the LADCP system on one watch, train and supervise the designated watch standers from the opposite watch(es), and perform a preliminary processing and backup of the data. High-resolution GPS fixes throughout the cast are an essential ancillary data set; presumably they will be logged routinely by the ship's data acquisition system, and probably by the SADCP system as well.

Following each cruise, data will be processed using the public software developed primarily at LDEO beginning in 1996. The software has undergone frequent refinement and extension (Visbeck 2002; http://www.ldeo.columbia.edu/~visbeck/ladcp). Software maintenance and evolutionary improvement will continue as a small but essential part of this project. Algorithms from other LADCP data processing software packages, such as the UH system, may be used in the final data processing.

Processed data will be provided to the JALADCP for archiving and distribution, but will also be made available on our LDEO web site via a page dedicated to the project, with plots for browsing and downloading, and downloadable data sets within 6 month after the cruise.

Cruise plan and per-cruise cost

The following table gives the cruise schedule with the approximate average cost per cruise for the direct velocity measurements, and the person responsible for LADCP staffing (Σ = 581 days; $1120k):

Year	Cruise	# stations	days	$K	Responsible	Ports
2003	A20	90	29	63 V/F	Visbeck	WHOI - Port of Spain
	A22	75	21	46 V/F	Visbeck	Port of Spain - WHOI
	A16S	110	44	72 F/V	Firing	Montevideo -Fortaleza
2004	A16N	135	42	91V/F	Visbeck	Fortaleza - Reykjavik
	P2/1	92	27	59 V/F	Visbeck	San Diego - Honolulu
	P2/2	127	39	63 F/V	Firing	Yokohama - HI
2005	P16N/1	92	27	44 F/V	Firing	HI - Tahiti
	P16N/2	100	33	72 V/F	Visbeck	Honolulu -Kodiak
	P16S	105	40	65 F/V	Firing	New Zealand -Tahiti
2006	S4P/P16S	97	51	111V/F	Visbeck	Wellington - Perth
2007	P18/1	78	32	52 F/V	Firing	Punta Arenas - Easter Island
	P18/2	107	35	76 V/F	Visbeck	Easter Island- San Diego
2008	I7N	156	47	102V/F	Visbeck	Port Louis - Muscat
	I6S	96	42	68 F/V	Firing	Capetown - Capetown
	I8S/I9N/1	81	38	62 F/V	Firing	Perth - Perth
	I8S/I9N/2	103	34	74 V/F	Visbeck	Perth - Calcutta

7.3: Chlorofluorocarbon Measurements

The CFCs will contribute to the overall scientific objectives as discussed in the overview. They will be used to identify newly ventilated water masses (*e.g.*, Weiss *et al.*, 1985; Fine and Molinari, 1988; Smethie, 1993), and their inventories used to calculate rates of formation (Smethie and Fine, 2000), and rates of ventilation and subduction (*e.g.,* Warner *et al.*, 1996; Fine *et al*., 2001). CFC ages are also used to constrain biogeochemical processes, such as calculation of anthropogenic CO_2 inventory (Gruber *et al*., 1996), and time integration of models (*e.g.,* England and Maier-Reimer, 2001, Gray and Haine, 2001).

Distributions of the anthropogenic chlorofluorocarbons in both seawater and the atmosphere will be measured on all proposed sections. Four U.S.-based CFC analytical laboratories have agreed to share the workload as detailed in the table below.

Table - Proposed CFC Measurement Plan for U.S. Repeat Hydrography[1]

Section	Year	Length (days)	CFC System	CFC Personnel	No. of CFC Analysts	Final Data Provider
A20	2003	29	Smethie	Smethie	4	Smethie
A22	2003	21	Smethie	Fine	4	Fine
A16S	2003	44	Bullister	Bullister/Warner	3	Warner
A16N	2004	42	Bullister	Bullister/Warner	3	Bullister
P2-1	2004	27	Fine	Smethie	2	Smethie
P2-2	2004	39	Fine	Fine	2	Fine
P16N-1	2005	29	Bullister	Warner	3	Warner
P16N-2	2005	33	Bullister	Bullister	3	Bullister
P16S-1	2005	40	Fine/ Smethie	Fine	3	Fine
S4P	2006	51	Smethie	Smethie	3	Smethie
P18-1	2007	32	Bullister	Bullister	3	Bullister
P18-2	2007	35	Bullister	Warner	3	Warner
I7N	2008	47	Fine	Fine	3	Fine
I6S	2008	42	Fine	Warner	3	Warner
I8/9-1	2008	38	Bullister	Bullister	3	Bullister
I8/9-2	2008	34	Bullister	Smethie	3	Smethie

[1] Warner and Bullister will also share responsibility for CFC measurements and data processing for repeats of P12 (45 days) and P15S (45 days) aboard Australian research vessels in the 2007-2009 time frame.

Table – Proposed Budget for the CFC Measurement Program[1] (costs in 1000s of $)

PI (Institution)	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Total
Bullister(NOAA)	182	186	130	0	201	323	1,023
Fine [2](U Miami)	231	262	307	25	26	407	1,257
Smethie(LDEO)	196	134	40	252	14	214	849
Warner(U.Wash.)	173	57	194	25	199	432	1,080
University total	*599*	*452*	*542*	*302*	*239*	*1,053*	*3,186*
Total	781	638	672	302	440	1,376	4,209

[1]Cost of standard calibration by R.F. Weiss is included in SIO budget.
[2]Fine is the lead PI for the CFC measurement team.

We have agreed upon a series of protocols detailed below to assure the data are of the highest quality and to eliminate potential systematic differences in reported concentrations between laboratories.

Analytical Methods

Concentrations of CFC-11, CFC-12 and CFC-113 in seawater and air will be measured by shipboard electron-capture gas chromatography, based on techniques described in Bullister and Weiss (1988). Since there will be insufficient time for shipment between some cruises, two complete CFC analytical systems will be used during this program, one provided and maintained by PMEL and one by LDEO or RSMAS (Table 1). Specially designed laboratory vans will be used when possible to minimize possible contamination by sources of CFCs used on the ships. Water samples (which should be drawn first from the rosette bottle) will be collected in 100-cc precision glass syringes and ~30-cc aliquots will be measured using standard purge-and-trap techniques and electron capture gas chromatography. Gas standards, prepared and stored in high pressure cylinders, will be run frequently to check for the stability of the analytical system. Peak areas and heights will be determined by digital integration, and the nonlinear response of the detector calibrated by injecting known amounts of a standard gas. These calibration curves will be run at regular intervals. The digital chromatograms will be stored for future reanalysis, should it be necessary.

Clean ambient air samples, drawn from a continuously pumped sampling line at the bow of the ship, will be analyzed on a daily basis to compare with expected atmospheric levels of CFC-11, CFC-12, and CFC-113 and to provide information on the degree of saturation of surface waters with the overlying atmosphere.

Standards

Two types of CFC standards will be used at sea; one consisting of clean, dry compressed air with CFC concentrations close to modern atmospheric levels and one of clean, dry compressed air which has been spiked with CFCs so that the amounts injected in a small volume (approximately 3 cc) of standard gas are in the same range a those in ~30 cc of surface seawater. Both types of standards will be prepared and checked for initial uniformity at PMEL. Two cylinders of each type will be sent on each cruise. One of each pair will be used as a working standard for routine calibration of the CFC system at sea, and the second cylinder of each pair will be used as a backup, and to check at regular intervals for possible drift in CFC concentrations in the working standards.

Absolute calibration of the CFC concentrations in the standards will be performed by the SIO CFC group. All CFC concentrations in air and water samples will be referenced to the SIO-1998 calibration scale (Prinn *et al.,* 2000), which has an estimated absolute accuracy of 1% for the species we measure. We anticipate the overall precision of the air and seawater CFC measurements will meet or exceed WOCE

standards (Joyce and Corry, 1994). We will also offer to assist our international collaborators with calibration of their standards.

Time Scales

CFC-11 and CFC-12 will continue to be the mainstays of oceanographic research because of their high concentrations and their inertness. CFC-113 is easily measured as part of the CFC-11 and CFC-12 analyses, and provides useful information, especially for waters exposed to the atmosphere in the 1980s and early 1990s when atmospheric CFC-113 was rising much more steeply than these other compounds. However, we must qualify the use of these CFC-113 data to account for its slow degradation in upper ocean waters (Roether *et al*., 2001).

We propose also to measure carbon tetrachloride (CCl_4) in air and seawater samples on selected cruises . CCl_4 has a significantly longer atmospheric history than CFC-11, CFC-12 and CFC-113 (Walker *et al*., 2000). In some regions of the ocean, CCl_4 may provide information on circulation and mixing processes extending back several decades earlier than the CFCs, and in some cases may be a better analog for anthropogenic CO_2 (Wallace *et al*., 1994). Although CCl_4 is non-conservative in the ocean in warm, near-surface waters (Wallace *et al*., 1994), it may be nearly conservative in cold, subsurface waters (Huhn *et al*., 2001). We see potential value in measuring dissolved CCl_4 in deep waters in regions which may have very low CFC-11 and CFC-12 concentration but which may have undergone some ventilation during the past century. The sections selected for CCl_4 measurements (A20, A22, A16S, A16N, P16S, S4P, P18-1, I6S, I8S, P12, and P15S) include those where we anticipate a deep or abyssal CCl_4 signal may be present. CCl_4 analysis will be done using a separate extraction system in order not to interfere with the through-put of the CFC measurements. We anticipate sampling for CCl_4 in regions of interest at a resolution of about 25% of that for the CFCs.

We also encourage the inclusion of measurements of other anthropogenic tracers, especially the highly-inert perfluorinated compounds, into the measurement program as the analytical techniques develop. For example, levels of dissolved atmospheric SF_6 have already been measured (Law and Watson, 2001; Vollmer and Weiss, 2002). It is probable that, during the next six years, this technique will be refined for routine shipboard use. It is important to develop measurement techniques for these new tracers; their measurement will enhance the information provided by the CFCs because these compounds are currently increasing in the atmosphere while CFCs are nearly constant or slowly decreasing.

Data

Preliminary CFC concentrations will be calculated automatically after each analysis, and the CFC data will be merged with other hydrographic parameters on a daily basis at sea and checked for consistency. We anticipate that a near-final CFC data set will be available at the completion of the cruise, within the five-week release time for preliminary data. Final data processing and data quality evaluation will be completed by the lead analytical group soon after the completion of each cruise. This processing will include examination of air measurements, near-surface CFC saturations, the consistency of CFC concentrations and ratios in vertical profiles and between adjacent stations, and comparison of the CFCs with other hydrographic parameters. The final data will be sent to the appropriate data acquisition center (*i.e.* WHPO or its successor) within six months of completion of the expedition.

Sampling Strategy

It is recommended that the CFC sampling be closely coordinated with the sampling for total CO_2 and alkalinity. CFCs should be sampled from top to bottom at as many stations as possible. An effort was made on the 2001 repeat of P12 to coordinate the sampling between the CFC and CO_2 groups. In general the CO_2 group was more interested in the upper ocean where the bulk of the anthropogenic CO_2 is found, while the CFC group was more interested in the deep ocean where the signal of newly-formed bottom waters was found. Approximately 80% of the CFC samples coincided with the depths of CO_2 sampling.

An effort was made to resolve the sharp vertical gradients of both properties through the upper thermocline. It is recommended that a 36-position rosette be used to facilitate these differences in sampling strategy.

During WOCE, between 50 to 60 samples per day could be analyzed for CFCs. In general, this does not reflect the limits of the analytical instrument, but is instead primarily due to time loss for sampling the rosette. One way to increase this number would be to add a third analyst. The analytical system could then be run continuously during sampling. On a few sections, the desired sampling required to resolve sharp concentration gradients exceeds the capacity of the analytical system. In this case, we recommend that four analysts and two CFC systems be used.

Consortium Oversight

This consortium of CFC analytical laboratories will meet in Years 1, 3, and 6 of the grant period to evaluate our efforts. We will discuss any analytical difficulties, assess the success of the sampling program, and evaluate our abilities to continue the proposed work (Table 1). If we think it beneficial, we will meet with the CO_2 measurement consortium to refine the sampling strategy or with other measurement consortia to enhance coordination, and sort out problems that may arise.

7.4: Tritium/^{3}He Measurements

Background

Tritium/^{3}He measurements are part of the core measurements for the repeat hydrography/carbon plan and they will contribute to the overall goals of this program as discussed in the main proposal text. The tritium/^{3}He program is tightly linked to the CFC program. The main purpose is to have independent transient tracer information available for studies of (1) pathways of surface perturbations, including the anthropogenic CO_2 signal, into the interior of the ocean (Jenkins and Rhines, 1980; Doney and Jenkins, 1995; Schlosser et al., 2001), (2) estimates of time scales for spreading of specific water masses and mean residence times using hydrographic data,, tracer data, as well as current measurements (Jenkins, 1998), and (3) calibration of models of low (e.g., Mensch et al., 1996; Heinze et al., 1988) to high complexity (e.g., Heinze et al., 1998). There are solid base line observations for tritium/^{3}He from previous programs, especially the WOCE Hydrographic Program and the tritium and ^{3}He signals are still well pronounced in the younger water masses of the oceans. It has been shown that even low Southern Ocean tritium concentrations can be measured and effectively interpreted (Bayer and Schlosser, 1991; Mensch et al., 1996).Results from the WOCE program are summarized at the following www sites: http://hil.whoi.edu/ , http://www.ldeo.columbia.edu/~etg/woce, and http://www.pmel.noaa.gov/vents/lupton/helpage.html.

Besides providing significant information in its own right, the addition of tritium/^{3}He to the CFCs will contribute to eliminating expected ambiguities in the CFC distributions that are caused by the plateaus in the atmospheric concentrations of the CFCs, as well as of some of the CFC ratios. The tritium/^{3}He program will be shared between the WHOI and LDEO groups as outlined in the tables below.

Methods

The methods for measurement of helium isotopes and tritium by the ^{3}He ingrowth method have been firmly established at WHOI and LDEO. Below we briefly summarize the methods used for this project Descriptions of the methods are available in the literature (e.g., Lott and Jenkins, 1984, 1998; Ludin et al., 1998) and at http://www.ldeo.columbia.edu/~etg/ms_ms/Ludin_et_al_MS_Paper.html.

Sample collection: Tritium samples will be collected in 1-liter glass bottles and shipped to either WHOI or LDEO for onshore preparation for mass spectrometric measurement. The helium isotope samples will be extracted at sea and the ampoules with the helium gas are shipped back to LDEO and

WHOI for measurement. Two seagoing extraction units will be available for the helium extraction work at sea to ensure that one system is always available for shipment. The extraction units are designed following the concept used during the WOCE field program (Lott and Jenkins, 1998). We plan to collect samples on all US cruises. Sampling on foreign cruises could not fully be firmed up and will be proposed as the program develops. The division of cruises between LDEO and WHOI is summarized in Table 1.

ON AVERAGE, samples will be collected on every fifth hydrographic station. On the basis of a station spacing of ca. 50 km this will provide one tritium/helium station every 250 km or ca. 2.5 degrees latitude. This resolution is similar to the WOCE station spacing for tritium/helium. ON AVERAGE, we will collect samples from 20 depth levels. The detailed sampling grid will be guided by the CFC sampling and will be adjusted according to the features detected in the CFC distributions. At low latitude, we will achieve higher resolution in the upper water column to resolve the strong transient tracer gradients. At high latitudes we will collect samples throughout the water column at a lower vertical resolution.

As with the WOCE program, the WHOI group will be responsible for provision of the at-sea gas extraction systems. Due to extensive use, the original van-laboratories are no longer serviceable. A more cost-effective approach will be adopted by using systems that will be mounted in the ship's main lab. Thus additional costs will be incurred by the WHOI group for their initial construction (year 1) and subsequently their set-up, and maintenance of the systems during fieldwork.

Sample preparation

Tritium: Samples are prepared for mass spectrometric tritium measurement by quantitative extraction of all dissolved gases from a water sample (efficiency > 99.95 to 99.995% for helium) followed by flame sealing of the gas-free water in a pre-treated glass bulb with low helium permeability (e.g., Ludin et al., 1998; Lott and Jenkins, 1998). The preparation of tritium samples for measurement will be performed in the helium isotopes laboratories at WHOI and LDEO. The glass bulbs with the helium-free water are then stored for 3 to 6 months for in-growth at low temperature to minimize the diffusion of helium from the glass into the water sample. After storage times of three to 6 months, the samples will be measured by extracting and purifying the ^{3}He grown in from tritium decay will be extracted from the water sample and measured in a dedicated helium isotope mass spectrometer.

Helium: For measurement of helium isotopes all gases will be extracted from the water samples at sea and stored in glass ampoules with low helium permeability. We use water vapor as carrier gas for transporting the gases extracted from the water sample into the glass ampoules. The ampoules can be stored at room temperature for extended periods of time.

Sample measurement

Tritium: For measurement of tritium the tritiogenic ^{3}He is extracted from the glass bulbs and measured in a dedicated helium isotope mass spectrometer. The mass spectrometer is computer controlled and all steps of sample inlet, purification and measurement are fully automated (e.g., Ludin et al., 1998; Lott and Jenkins, 1984, 1998). Air standards are measured between samples to ensure linearity and stability of the mass spectrometer. The expected precision of the tritium measurements is ±1 to 2 %. Detection limits of 0.005 TU (1 TU stands for a tritium to hydrogen ratio of 10^{-18}) can be achieved.

Helium: For measurement of helium isotopes, the helium and neon fractions are separated from the permanent gases and water vapor. A cryogenic cold trap filled with activated charcoal is then used to separate helium from neon. Helium isotopes are measured in a dedicated helium isotope mass spectrometer, neon is measured simultaneously in a quadrupole mass spectrometer (e.g., Ludin et al., 1998; Lott and Jenkins, 1984). Helium isotope data are reported in the ∂-notation, where ∂^3He is the deviation of the measured ^{3}He/^{4}He ratio from that measured in air ($\partial^3 He = ([^3He/^4He]_{sample}/[^3He/^4He]_{air} -1 *$

100%). Precision of the helium isotope measurements are ±0.2% or better for ∂^3He and ca. ±0.5% or better for the absolute helium and neon concentrations.

Quality control and calibration

There will be routine intercalibrations between the two laboratories by exchanging working standards and measuring samples from the same Niskin bottle. Additionally, the laboratories are calibrated against external standards (e.g., IAEA standard). The final data quality control will be done by section and handled by the laboratory that is responsible for sample collection on the respective section.

Consortium concept and turnaround time

Between WHOI and LDEO, we have available 3 dedicated mass spectrometers for measurement of tritium and helium isotopes (LDEO: one helium isotope and one tritium mass spectrometer; WHOI: one tritium/He isotope mass spectrometer). We will coordinate the flow of samples through the laboratories to take advantage of the availability of the three mass spectrometers. For example, sample sets for tritium and helium isotopes can be swapped between the two laboratories if the stability of the individual mass spectrometers is out of synch with the required type of measurement. By allocating samples between the two laboratories according to the availability of mass spectrometer time, we anticipate to speed up the turnaround time for the tritium/helium isotope measurements proposed as part of the repeat hydrography program. We anticipate finishing the sample sets from individual cruises within approximately 12 to 15 months from the time of sampling. The LDEO group is presently running hydrological samples that are delivered within this time line.

Data release

As stated above we anticipate speeding up the data production time by using three dedicated mass spectrometers in a consortium type concept. Once the data have been produced they will be controlled for quality and released to the community via a www site, as well as via submission of data lists to the appropriate data centers. These data will be publicly available. In case of partial data set availability we will release such partial data sets if the quality of the data can be assured.

Table: Planned division of cruises (only US cruises are listed). The calculations of the number of samples are based on an average sampling density of every 5th station at a vertical resolution of 20 depth levels.

Prop Year	Section	Year	Institution	T/He stations WHOI	T/He stations LDEO	Samples WHOI	Samples LDEO
1	A20/A22	2003	WHOI	33		660	
1	A16S	2003	LDEO		22		440
2	A16N	2004	LDEO		27		540
2	P2	2004	WHOI	43		876	
3	P16N/1	2005	LDEO		18		352
3	P16N/2	2005	WHOI	20		400	
3	P16S	2005	LDEO		21		420
4	S4/P16S	2006	LDEO		20		388
5	P18/1	2007	WHOI	16		312	
5	P18/2	2007	LDEO		21		428
6	I7N/I6S	2008	WHOI	50		1008	
6	I8S/I9N	2008	LDEO		37		736
Total				**162**	**166**	**3256**	**3304**

Table: Tritium/^{3}He measurements: Annual costs by institution in 1000s of $.

Institution	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Total
LDEO	278	251	337	226	250	360	1,702
WHOI	461	469	226	21	193	571	1,942

7.5: Carbon System Parameter Measurements

Dissolved inorganic carbon (DIC); total alkalinity (TAlk); pH; partial pressure of CO_2 (pCO_2); dissolved organic carbon (DOC); dissolved organic nitrogen (DON); and surface water pCO_2.

To implement the Carbon Inventories and Transport component of the program, measurements of several organic and inorganic carbon system parameters are included in the core proposal. The overall scientific justification is outlined in Chapter 3; here we describe some of the logistic details. DIC is the main parameter we wish to follow over time. TAlk provides us with a sensitive indicator of calcium carbonate dissolution and therefore quantifies the increase in DIC in the water column by dissolution. Although certified reference materials (CRMs) are available for DIC and TAlk [*Dickson et al*., 2002 a, b] the extreme accuracy necessary to discern changes over 10-year time intervals warrants over-determination of the inorganic carbon system on select lines. We propose this over-determination on the cruise lines that had four inorganic carbon system parameters measured (DIC, TAlk, pH, & pCO_2) as part of the NOAA OACES program in the 1990s. The relative changes in pCO_2 and pH are greater than the corresponding changes in DIC and TAlk [*Wanninkhof and Feely, 1998*], thus pH and pCO_2 changes will be extremely sensitive indicators of anthropogenic and/or natural change throughout the water column.

The oceanic DOC pool is estimated to be 685 Pg C [*Hansell and Carlson*, 1998] which is about 2 % of the total oceanic carbon pool. It is a critical parameter to elucidate the large scale workings of the biological pump as much of the transformation from living organic matter in the ocean to inorganic constituents is believed to pass through the DOC pool. With precisions of 1 micromole/kg achieved in the past 10 years, small (14 micromole C) but systematic large-scale water column increases have been measured between the Atlantic and Pacific oceans [*Hansell and Carlson*, 1998]. Recently, reference materials have been produced to assure long-term precision (and possible accuracy) of the measurements [*Hansell*, 2001]. The measurements have also been instrumental in determining regional carbon mass balances and remineralization patterns [*Hansell and Carlson*, 2001; *Hansell and Feely*, 2000]. DON represents 6-7% of fixed marine dissolved nitrogen. The pool serves as a new nutrient sink in productive environments and as a new nutrient source for export production in oligotrophic waters. Its global scale distribution remains weakly resolved.

Surface water pCO_2 measurements are now being performed routinely in a highly automated fashion. These measurements provide an important link between the oceanic and atmospheric carbon reservoirs in that pCO_2 is controlled by the (sub) surface carbon cycling. Surface water pCO_2 in turn determines the CO_2 fluxes to and from the atmosphere.

Measurement details

Dissolved Inorganic Carbon (DIC)

The groups of Feely of NOAA/PMEL, Sabine of JISAO/UW, and Wanninkhof NOAA/AOML will perform DIC measurements on all cruises as outlined in the Table below. These three groups have extensive experience in the measurements as important contributors to the OACES and WOCE/WHP carbon efforts in the 1990s. By running two automated DIC analyzers, SOMMAs [*Johnson et al*, 1998] simultaneously a sample throughput of about 70 samples per day can be achieved making it possible to sample about 1/2 of all the sample bottles brought to the surface. The measurement methodology that will be followed is detailed in the "Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water" [DOE, 1994]. Certified reference materials CRMs will be used on

all cruises with approximately 1 CRM for each 20 samples. Roughly 10-15 % of the sample depths will be run in duplicate to assure good statistics on reproducibility. One highly experienced and one less experienced SOMMA operator will be on each cruise. Quality control will occur in two steps; one on the cruise and one immediately post cruise. The post-cruise quality control will include comparison with other carbon system parameters and multi-elemental multi-linear regressions taking advantage of close interdependencies between hydrographic (T, S, NO_3, SiO_4, and PO_4) and carbon parameters. Data will be provided in accord with the data release policies described in Chapter 1. The final QC will occur with close interaction between all the team members.

Discrete pCO_2

A composite team of AOML and PMEL operators will perform discrete partial pressure of CO_2, pCO_2 measurements with equipment maintained and provided by AOML. The system will be run around the clock with a sample throughput of about 50 a day. Measurements will be performed on 500 ml subsurface samples at fixed temperature (20 ˚C). Six compressed gas standards with mole fractions ranging from 200 to 2000 ppm, that bracket the samples, are used after 8 to 10 samples to calibrate the system. The methodology is outlined in Wanninkhof and Thoning [1993]. The primary purpose will be to assess the internal consistency of the inorganic carbon system. The data will also be used in conjunction with DIC or TAlk to verify decadal changes, and causes of changes, in TAlk and DIC in the water column. The utility of the over determination is outlined in several papers [see e.g. *Millero et al*, 1995; *Lee et al*, 2000]. Currently, there are some instrumental and standardization issues for samples containing pCO_2 levels greater than 1000 microatm. These will be addressed with careful laboratory tests and recalibration of our compressed gas standards in the 1000 to 2000 ppm range. Moreover, we plan to analyze some samples at two different temperatures (20 and 4˚C) so as to analyze samples closer to in situ temperatures.

Underway pCO_2, UW pCO_2

Underway pCO_2 measurements will be shared among the groups of Feely (PMEL), Wanninkhof (AOML) and Weiss (SIO) (see Table). The first two groups operate similar instruments using an infrared analyzer (IR) [*Feely et al.*, 1998]. The SIO group uses a gas chromatograph that measures N_2O and CH_4 as well as CO_2 [*Weiss*, 1981]. This capability will be particularly useful to identify upwelling areas that have a ubiquitous N_2O signal. On the cross-equatorial P16N cruise both an IR and a GC system will be deployed, in part to compare these systems and to determine if there are any systematic biases in the IR analysis due to compositional changes in the headspace gas. Additionally, the P16N line will reoccupy earlier transects using the same GC system that were made during FGGE in 1979-80 and WOCE in 1991. For all systems, seawater is pumped continuously from the bow intake into an air/water equilibrator. The headspace gas in the equilibrator is then analyzed automatically. Compressed gas standards containing CO_2 levels traceable to the WMO scale will be used to calibrate the instruments at frequent intervals. The underway systems will be routinely checked and maintained by the analysts responsible for the DIC, CFC or discrete pCO_2 measurements, and will not require an additional person aboard ship. The different systems have been used extensively [*Weiss et al*, 1992] and intercompared with good results during the WOCE/WHP Indian Ocean cruises in 1995 [*Sabine et al.*, 2000]. Data obtained from the cruises will be available through a live access server at CDIAC (supported by a separate Hankin, Kozyr, *et al.* proposal to NOAA/OGP/GCC).

pH and Total Alkalinity, TAlk

The Miami (Millero) and Scripps (Dickson) groups will be responsible for all of the total alkalinity (TAlk) and pH measurements. The groups will share equipment and CO_2 analysts. Both groups have years of experience in making these measurements on WOCE, JGOFS and NOAA cruises [*Lee et al.*, 1997; *Millero et al*., 1998]. TAlk will be measured on all of the cruises and pH on the few cruises where both pCO_2 and DIC are measured. This will also allow a detailed examination of the internal consistency of the field measurements [e.g. *Lee et al*., 1996]. The methods are described in detail in the DOE [1994]

handbook. TAlk will be measured using closed cell titration systems used in earlier studies [*Millero et al.*, 1993] or using a newly developed open cell approach if it is deemed suitable [*Dickson et al.*, 2002b]. Two systems will be used to complete the daily sample load (~70/day). The precision is 2 -micromole kg^{-1}. The performance of the titration systems will be monitored using CRMs [*Dickson*, 1997]. The precision of the pH measurements is 0.0005. The pH system will be monitored using TRIS buffers [*DeValls and Dickson*, 1998].

Dissolved Organic Carbon, DOC and Dissolved Organic Nitrogen, DON

DOC and DON concentrations will be determined at sea by the Hansell (RSMAS) and Carlson (UCSB) groups. Sample throughput will match that of the DIC and TAlk measurements. DOC will be measured by high temperature combustion (HTC) using a Shimadzu TOC-VN with auto injection (CV of 1.5-2.5%). DON is calculated as the difference between total dissolved nitrogen concentrations and dissolved inorganic nitrogen, (measured by the hydrographic team). DOC and total dissolved nitrogen, TDN will be measured simultaneously by placing the 2 detectors (NDIR and chemiluminescence) in series with the Shimadzu HTC instrument. Four point standard curves using KHP for C and KNO_3 for N will be run daily to calibrate the response of the high temperature combustion systems. Both measurements will be quality controlled using reference materials distributed to the international community by the Hansell laboratory [*Hansell*, 2001]. The RMs will be analyzed at regular intervals during each analytical day. Low C/N reference water (LCW) will be prepared prior to the cruise and employed to determine system blanks. For each cruise, one senior technician with expertise on both the C and N systems will be joined by 2 junior analysts. Project management will primarily be the responsibility of Mr. Charlie Farmer at RSMAS. Data will be provided in accord with data release policies described in Chapter 1.

Summary of costs per line (in $ K) and PIs with lead PI listed first

Line	Year	Discrete DIC	Discrete pCO_2	U/W pCO	DOC	DON	Discrete TALK	Discrete pH
Equipment	2003	287 F/W	35 W	72F/W	190 H/C	18 H/C	41 D/M	41 D/M
A16S	2003	183 W	156 W/F	14 W	192 H/C	5 H/C	66 M	66 M
A20	2003	127 F/S		35 We	96 H/C	3 H/C	67 D	
A22	2003	93 S		26 We	96 H/C	3 H/C	132 M	
A16N	2004	127 F/S	158 W/F	14 F	201 H/C	5 H/C	137 M	137 M
P2, Leg 1	2004	117 S		33 We	101 H/C	3 H/C	41 D	
P2, Leg 2	2004	163 W		48 We	101 H/C	3 H/C	60 D	
P16S	2005	163 W		49 We	213 H/C	5 H/C	90 D	
P16N, L1	2005	105 F/S	103 W/F	51WeF	107 H/C	3 H/C	74 M	74 M
P16N, L2	2005	105 F/S	105 W/F	54WeF	107 H/C	3 H/C	74 M	74 M
S4P	2006	286 W/F/S	164 W/F	15 W	425 H/C	5 H/C	385 D/M	
P18, L 1	2007	203 F/S	88 W/F	14 F	218 H/C	3 H/C	82 D	75 M
P18, L 2	2007	164 W	130 W/F	13 F	218 H/C	3 H/C	150 M	75 M
17N	2008	178 F/S		57 We	110 H/C	1 H/C	71 D	
I6S	2008	140 S		51 We	110 H/C	1 H/C	162 M	
I8S	2008	146 W	115 W/F	14 W	110 H/C	1 H/C	65 D	60 D
I9N	2008	143 W	113 W/F	13 W	110 H/C	1 H/C	80 M	80 M
Total		2,730 F/S/W	1,128 W/F	573We/F/W	2,705 H/C	43 H/C	1,786 D/M	682 D/M

C = Carlson, F = Feely , D = Dickson , H = Hansell , M = Millero, S = Sabine, W = Wanninkhof , We = Weiss

Note: Per agency guidance, costs are spread over the duration of the proposal, insofar as possible, leading to occasional anomalous per cruise cost estimates.

RESULTS FROM PRIOR NSF SUPPORT: Most references for PIs included in Reference list.

A.G. Dickson (**NSF OCE98-19007 -** *The Quality Control of Oceanic Carbon Dioxide Measurements: Preparation and Distribution of Reference Materials*): This work, which has been funded by NSF since 1989, provides the underpinning for high-quality measurements of oceanic carbon dioxide properties. Surface sea water is sterilized and bottled; samples from each batch are then analyzed using reference methods for total dissolved inorganic carbon and for total alkalinity developed to provide accurate certification of the batches of sea water. The remaining bottles are then distributed (at cost) to laboratories around the world as certified reference materials. The work has been described in a series of three manuscripts (Dickson *et al*., 2002a,b; Keeling *et al*., *in prep*.). As a result of the widespread availability of these reference materials, there has been a significant improvement in the quality of oceanic carbon dioxide measurements allowing, for the first time, data from different cruises to be used to produce a consistent and accurate data set – even when the cruises are by different investigators. This has been documented in a number of publications (e.g. Johnson *et al*., 1998; Millero *et al*., 1998; Lamb *et al*., 2002 – the full citations are in my Biographical Sketch). Work is still in progress to characterize the accuracy of methods for the measurement of pH, $p(CO_2)$ and the $^{13}C/^{12}C$ ratio of dissolved inorganic carbon so as to extend the usefulness of our reference materials to these parameters.

Dickson, A. G., Anderson, G. C. & Afghan, J. D., 2002a. Reference materials for oceanic CO_2 analysis: 1. A method for the certification of total alkalinity. *Mar. Chem.* (submitted).

Dickson, A. G., Afghan, J. D. & Anderson, G. C., 2002b. Reference materials for oceanic CO_2 analysis: 2. A method for the certification of total alkalinity. *Mar. Chem.* (submitted).

Keeling, C. D., Guenther, P. R., Emanuele, G., Lueker, T. J. & Dickson, A. G., Reference materials for oceanic CO_2 analysis: 3. A method for the certification of total dissolved inorganic carbon. *Manuscript in preparation.*

S.C. Doney is a Co-PI on *Collaborative Research: Oceanic N_2 Fixation and Global Climate*; (NSF/NCAR 9820037, 2000-2004). The overall goal of this collaborative, biocomplexity project is to investigate the potential interactions and coupling of atmospheric dust production and deposition, marine nitrogen fixation, ocean carbon sequestration, and the global climate system. The NCAR component involves exploring the dust--N_2 fixation--ocean CO_2 storage dynamics using global numerical models. In the first two years of the project, we have developed and validated a nitrogen fixation scheme (with iron, phosphorus, and temperature controls) within a new global mixed layer marine ecosystem model (Moore et al. 2002a; 2002b). The simulated spp. Trichodesmium distributions agree well with in situ estimates, with highest fixation rates in the Caribbean, subtropical North Pacific, South Pacific, and Australia and Indonesia. We are presently midway through the exercise of coupling the ecosystem model with a new version of the NCAR ocean general circulation model with active biogeochemistry and CO_2 dynamics. We plan to complete development and testing by the end of 2002 and to conduct sensitivity experiments, retrospective historical simulations and future climate change projections.

Moore, J.K., S.C. Doney, J.A. Kleypas, D.M. Glover, and I.Y. Fung, 2002a: An intermediate complexity marine ecosystem model for the global domain. *Deep-Sea Res., II, 49,* 403-462.

Moore, J.K., S.C. Doney, D.M. Glover, and I.Y. Fung, 2002b: Iron cycling and nutrient limitation patterns in surface waters of the world ocean. Deep-Sea Res., II, 49, 463-507.

R.A Fine (**OCE94-13222** - *WOCE Sections I7N, I9N, I10 and I5W/I4 in the Indian Ocean: CFC Measurements*; 11/1/94 – 10/31/97; $950,000): Two chlorofluorocarbons (CFC-11 and CFC-12) were measured on WOCE sections I7N, I9N, I10 and I5W/I4 in the Indian Ocean. We consistently analyzed samples at 85-90% of the stations, and met WOCE standards for precision of <1% for CFC-11, <1.4% for CFC-12. All of our data have been submitted to the WOCE data office. So far eight manuscripts have resulted: Haines, M.A., M.E. Luther and R.A. Fine, 1997, Model-validated parameterization for air-sea gas transfer in the North Indian Ocean, *Geophys. Res. Letts*., 24: 2545-2548. Howell, E.A., S.C. Doney,

R.A. Fine and D.B. Olson, 1997, Geochemical estimates of denitrification in the Arabian Sea and the Bay of Bengal during WOCE, *Geophys. Res. Letts*., 24: 2549-2552. Aydin, M., Z Top, R.A. Fine and D.B. Olson, 1998, Modification of waters in the northeastern subpolar Pacific, *J. Geophys. Res*., 103: 30,923-30,940. Haines, M.A., R.A. Fine, M.E. Luther and Z. Ji, 1999, Particle trajectories in an Indian Ocean model and sensitivity to seasonal forcing, *J. Phys. Oceanogr*., 29: 584-598. Plahn, O., M. Rhein, R.A. Fine and K.F. Sullivan, 1999, Pollutants from the Gulf War serve as water mass tracer in the Arabian Sea, *Geophys. Res. Letts*., 26: 71-74. Smethie, W.M., Jr. and R.A. Fine, 2001, Rates of North Atlantic Deep Water formation calculated from chlorofluorocarbon inventories, *Deep-Sea Res*., 48: 189-215. Fine, R.A., K.A. Maillet, K.F. Sullivan, and D. Willey, 2001, Circulation and ventilation flux of the Pacific Ocean *J. Geophys. Res*., 106: 22159-22178. O'Connor, B.M., R.A. Fine, K.A. Maillet and D.B. Olson, 2001, Formation rates of subtropical underwater in the Pacific Ocean, re-submitted to *Deep-Sea Res*., also in 1998 U.S. WOCE Annual Report.

E. Firing (**OCE-9531885** - *High Resolution Velocity Sections in the Northeast Atlantic,* 10/01/1996-09/30/2001, $360,000. PIs: Eric Firing and Peter Hacker. Effective co-PI: Kathleen Donohue): Shipboard and Lowered ADCP data were collected on three WHP cruises of the Knorr to the eastern subpolar gyre of the North Atlantic during 1996 and 1997. The complete shipboard ADCP data set is available from NODC and the LADCP data are available on request. Relevant publications are Polzin *et al*. (2002) and King *et al*. (2001).

N. Gruber received his first NSF grant as a PI last year to investigate Interannual to Decadal Variability in the Ocean Carbon Cycle of the Subtropical and Subpolar Gyres} (OCE-0097337, 4/01 - 3/04). The goal of this project is to investigate how the carbon cycle in the mid- and high latitudes has responded to past variations in meteorological forcing. This project combines the analysis of observations with hindcast simulations using a state-of-the-art coupled biogeochemical/physical model. The long-term aim is to develop a quantitative understanding of how the ocean carbon cycle might react to possible future climate change. Publications to date include Gruber *et al*. (2001) and Gruber *et al*. (2002).

Gruber, N., N. Bates, C. D. Keeling and C. LeQuere, Interannual variability in the extra-tropical ocean carbon cycle: The role of the North Atlantic, Proceedings of the 6th International CO_2 conference, OB16, 677-680, Sendai, Japan, 2001.

Gruber, N., C.D. Keeling and N. Bates, 2002. Influence of the North Atlantic Oscillation on the interannual variability of the carbon cycle in the North Atlantic, Nature, submitted.

D.A. Hansell and C.A. Carlson have worked together on the US JGOFS BATS and AESOPS programs. Together they were supported by NSF/OPP from 1994-1998 on two consecutive studies in the Ross Sea (**OPP-9317200** and **OCE-9530845**). During AESOPS, the PI's were responsible for investigations of dissolved organic carbon and nitrogen during five cruises to the Ross Sea and the Antarctic Polar Front region. The majority of the research focused on the cycling of carbon and nitrogen through DOM in the Ross Sea polynya in a *Phaeocystis sp*. dominated system. The rather surprising results were that modest accumulation of DOC (~15 µM) occurred during the *Phaeocystis* blooms compared to the magnitude of total organic matter production, rather than large accumulations of DOC (~mM levels) suggested by earlier work. Approximately 10 - 15% of net community production accumulated as DOC. In addition, the freshly produced DOM had a C:N ratio essentially at the Redfield ratio. The semi-labile DOM that accumulated in the Ross Sea was produced and removed within a six-month period, thus supporting very little vertical export as DOC. The work conducted under these two grants resulted in 17 publications and at least 12 presentations at international meetings. These grants supported undergraduate students A. Ritchie, J.B. Cullen, and T. Tredennick.

W.J. Jenkins (**OCE89-11657** - 3/15/89 – 4/30/94; $270,000; Estimation of Air-Sea Exchange, Nutrient Transport And New Primary Production in the Subtropical Ocean Using Time Series Tracer Data): The work focused on the use of time series tracer data to constrain upper ocean processes, primary production,

and biogeochemical cycling at an oligotrophic ocean site (BATS). It involved consideration of both transient and conventional hydrographic properties. The principal investigator has made significant contributions to the development and use of tritium-^{3}He dating in the oceans. Using this technique, I have determined rates of water mass renewal (e.g., Jenkins, 1982a, 1987), oxygen utilization rates and primary production (Jenkins, 1987, 1988b; Jenkins and Wallace, 1992), oxygen production rates (Jenkins and Goldman, 1985; Musgrave *et al*., 1988; Spitzer and Jenkins, 1989), diapycnal and isopycnal mixing rates (Jenkins, 1980, 1991, 1997), climatic changes in water mass renewal rates (Jenkins, 1982b), subduction rates (Jenkins, 1987, 1996), tracer granularity (Jenkins, 1987; Joyce and Jenkins, 1993), and vertical nutrient transport (Jenkins, 1988a, 1997). I have improved tritium detection limits by more than an order of magnitude (Jenkins *et. al*., 1983) and used tritium to study abyssal ventilation and deep western boundary currents (Jenkins and Rhines, 1980; Jenkins et al, 1983; Doney and Jenkins, 1994).

Using a 15-year time series of tritium and ^{3}He measurements in the Sargasso Sea, I have a direct visualization of vertical advection in the main thermocline: the downward movement of the bomb-tritium maximum can be determined to be 17±3 m/y. The long-term evolution of tritium and ^{3}He inventories in the main thermocline places an additional constraint on basin scale new production by providing an estimate of the rate of nitrate efflux from the main thermocline (Jenkins, 1998). Also, using observations of the three-dimensional distributions of oxygen, mass, salinity, and tritium-helium age, I have been able to compute absolute velocities to order 0.1 cm/s accuracy, isopycnal diffusivities, subduction rates, and oxygen consumption rates in the eastern subtropical North Atlantic (Jenkins, 1998).

The P.I. has not recently held any NSF grants, as he has been working in the U.K. since 1998. Five papers arising from the above program, along with the references cited, appear in the Reference list.

T.M. Joyce (**OCE-98-18465** - *Decadal variability of Subtropical Mode Water, Gulf Stream separation, and large-scale atmospheric fields in the N. Atlantic Ocean from 1954-1999*; 3/01/1999-8/31/2002; $330,000): This grant examines the variability of Eighteen Degree Water at Bermuda in terms of atmospheric forcing (Joyce *et al*., 2000), and relates these to large-scale changes in Gulf Stream path. The latter was further studied using more recent data, including that from the TOPEX/Poseidon altimeter in Frankignoul *et al*. (2002, in press). Wintertime climate variability on longer time scales going back to the later 1800's was examined for the eastern US and Sargasso Sea (Joyce, 2002, in press), where it was found that their relation to the NAO has changed significantly over time to where it is now the most important single climate index for wintertime climate variability in the region. However, this was not always the case. Finally, the results from a WOCE hydrographic section at 66W in the N. Atlantic were published (Joyce *et al*., 2001), where we used hydrographic, tracer and LADCP data with an inverse model to obtain absolute zonal transport across the section.

Joyce, T. M., C. Deser, and M. A. Spall, 2000. The relation between decadal variability of subtropical mode water and the North Atlantic Oscillation. *J. Clim., 13*, 2550-2569.

Frankignoul, C., G. de Coetlogon, T. M. Joyce, and S. Dong, 2002. Gulf Stream variability and ocean-atmosphere interactions. *J. Phys. Oceanogr*., in press.

Joyce, T. M., 2002. One hundred plus years of wintertime climate variability in teh Eastern US. *J. Clim*., in press.

Joyce, T. M., A. Hernandez-Guerra, and W. M. Smethie Jr., 2001. Zonal circulation in the NW Atlantic and Caribbean from a meridional WOCE hydrographic section at 66W. *J. Geophys. Res., 106*, 22,095-22,113.

F.J. Millero (OCE0000365 - *Southern Ocean Iron Experiments (SOFEX) Collaborative Research*; $297,178; 2/01 to 1/03; and **OCE-8800411** - *JGOFS: The Carbon Dioxide System in the Southern Oceans*; $477,047; 11/94 to 10/97: During the last five years we have received support from NSF to study the carbon dioxide system in the Southern Ocean as part of the JGOFS process study and the SOFEX experiment. Some of the recent papers concerned with CO_2 are listed below. Other publications can be found on: http://www.rsmas.miami.edu/groups/mpc/

Sabine, *et al*. (1999) 13, 179-198.

Wanninkhof *et al*. (1999) Mar. Chem., 65, 291-301.
Peng, et al. (1999) Tellus, 51B, 531-540.
Gordon, *et al*. (2000) Deep Sea Res. II, 47 (15-16), 3095-3117.
Lee, et al. (2000) Geophys. Res. Lett., 27, 229-232.
Lee, *et al*. (2000) Biogeochem. Cycles, 25, 979-994.
Gordon, *et al*. (2000) Deep Sea Res. II, 47 (15-16), 3095-3117.
Sweeney, *et al*. (2000) Deep Sea Res. II, 47 (15-16), 3369-3394.
Sweeney, *et al*. (2000) Deep Sea Res. II, 47 (15-16), 3395-3421.
Sabine, *et al*. (2000) Mar. Chem., 72(1) 33-53.
Morrison, *et al*. (2001) Deep Sea Res., 48(19-20) 3943-3972.
Lamb et al. (2002) Deep-Sea Res. II, 49, 21-58.
M.S., Ph.D. and undergraduates participate in this research program. During 30 years of NSF support, the participants in research publications include 10 high school students, 25 undergraduate students, 43 graduate students and 19 postdoctoral associates.

P. Robbins (**OCE-9819244** - *An assessment of Anthropogenic carbon in the Pacific Ocean with Specific Application to Diagnostic Inverse Models of the Circulation*; 03/01/99-02/28/02): This collaborative Study with Andrew Dickson is part of the JGOFS synthesis and modeling program. The central objective is to examine methods for separating observed inorganic carbon measurements into anthropogenic and natural components with specific regard to errors introduced into oceanic transport calculations of carbon.

Robbins, P.E. On the use of salinity normalizations for the calculation of oceanic property transports, *J. Geophys. Res*., 106, 30,939-30,946, 2001.

Robbins, P.E. Estimates of anthropogenic carbon in the ocean based on chloroflourocarbon measurements: Applying generalized aged distributions to ocean ventilation, in preparation.

Robbins, P.E., and S.E. Zedler, Anthropogenic carbon inventory in the Indian Ocean based on chloroflourocarbon measurements and generalized aged distributions, in preparation.

C. Sabine (**OCE-0095960** - *Temporal Evolution of Chlorofluorocarbons and Inorganic Carbon in the Southern and Southwestern Pacific Oceans*; M. Warner, C. Sabine, J. Bullister; 4/1/2001 – 3/31/2004; $326,474): Although this project is less than a year old, we have already completed a 50-day cruise along 170°W and a 46-day cruise south of Tasmania along 140°E. In collaboration with the Australians, over 2100 samples were collected and analyzed for TCO_2 and alkalinity. Estimated accuracy for these measurements is better than ±2 μmol kg^{-1} based on the at-sea analysis of Certified Reference Materials and preliminary quality assessment procedures. Early results from these cruises indicate significant increases in both CFC and TCO_2 concentrations since these lines were last occupied approximately 6 years ago. Sabine's other NSF contracts, some of which are ending and others that are expected to start in the next few months, are all part of the JGOFS Synthesis and Modeling Project. These grants involve the synthesis and interpretation of the WOCE/JGOFS Global CO_2 survey conducted in the 1990's, in which Sabine was an active participant. These contracts have resulted in numerous scientific publications and publicly available synthesis data sets (see JGOFS SMP web site).

P. Schlosser - We received support for measurement of ca. 9000 samples (3500 tritium and 5500 helium isotope samples) as part of the WOCE Hydrographic Program one-time survey (6 grants: 5 for measurement; one for synthesis. Example: WOCE WHP line P17S: OCE 91-16474: 'Tritium, He Isotope and AMS ^{14}C Measurements on WOCE WHP Line P17S': 10/15/92 - 9/30/95; $314,000). All WOCE samples have been measured and the synthesis of the data is underway and coming close to completion. Whereas the WOCE funding was more or less completely for data production and synthesis, we did obtain first results that have been used in publications or are being summarized in manuscripts. For example, the Pacific S4 results contributed to the assessment of the input of glacial meltwater into the South Pacific (Hohmann *et al*., in press). This was the first time that such an assessment could be done independently from evaluation of the mass balance of the Antarctic Ice Sheet. The Indian Ocean helium

data have been synthesized and used to map a major helium plume that suggests a southwesterly spreading of intermediate waters (ca. 2500 m depth) in the central Indian Ocean. This spreading is dominated by mixing rather than advection (Hohmann *et al*., to be submitted). Again, this is the first determination of the extent of the Mid-Ocean-Ridge plume in the Indian Ocean and we expect significant new information from these observation. The potential of a variety of tracers measured during WOCE has been summarized in a chapter of the book 'Ocean circulation & climate' (Schlosser *et al*., 2001. Results from the time series along AR7W are in press (Khatiwala *et al*., 2002). More results are emerging and we expect to write up the major findings from the WOCE survey within the next two years.

Publications based on results from the WOCE survey: Schlosser *et al*., 2001; Hohmann *et al*., 2002; Khatiwala *et al*., 2002; for details, see reference list of proposal.

W.M. Smethie, Jr. (**OCE 95-31864** - *CFC Measurements along the ACCE 52 and 66°W Lines*, 3/15/97-2/28/01, $439,000): During July and August of 1997, hydrographic/tracer sections were run along 52° and 66° W in the western subtropical Atlantic. Three subsurface maxima of CFCs 11, 12, and 113 were present in the DWBC along the northern continental slope: an upper maximum associated with Upper Labrador Sea Water (ULSW), a middle maximum associated with Classical Labrador Sea Water (CLSW) and a deep maximum associated with overflow water from Denmark Strait and the Iceland-Scotland Ridge. The upper two maxima merge into a single maximum that extends southward across the entire basin with concentration generally decreasing and then increasing in the DWBC at the southern boundary. Relatively high CFC concentrations extend to 35°S, well seaward of the DWBC indicating substantial recirculation from the boundary. Isolated lobes of high CFC water near 31°N also appear to be a recirculation feature, but it is too far south to be part of the Gulf Stream recirculation. A well defined salinity minimum in the theta/S plot for the northern ends of the sections associated with the upper CFC maximum indicates the presence of CLSW that formed during the early 1990s. The deep CFC maximum has a similar pattern to the upper maximum but it does not extend across the entire basin along 52°W, indicating the presence of older deep and bottom water of southern origin. As for the upper maximum, relatively high CFC concentrations in the deep maximum extend from the northern end of the sections to about 35°N indicating substantial recirculation from the western boundary. Low CFC concentrations in the deep water of the Caribbean Sea indicate that a mixture of ULSW and CLSW sinks to the bottom after flowing over the sill. Interpretation of the data is still in progress. Publications and scientific presentations to date, which are included in the reference list, are: Smethie (1998), Smethie (1999a), Smethie (1999b), Schlosser *et al*. (2001) and Joyce *et al*. (2001).

J.H. Swift (**OPP-9709130** - *Hydrography of the Canada Basin***;** 09/01/97-08/31/00; $317,239): OPP-9709130 funded Swift's participation on the 1997 section from the Canadian icebreaker *Louis S. St-Laurent* across the waters of the southern Canada Basin of the Arctic Ocean. This determined the surface-to-bottom distributions of the physical and chemical characteristics along a closely-spaced section of measurements extending from the Beaufort shelf to the deep Canada Basin site selected for the year-long SHEBA ice camp. The measurements identify the structure and spatial limits of the boundary regime, and relate that to the hydrographic structure of the interior of the Canada Basin. This program included CTDO, salinity, oxygen, and nutrients. Measurements from other programs with separate funding include CFCs, CO_2 parameters, He/Tr, ^{18}O, barium, ^{129}I, ^{137}Cs, TOC, TON, and the pesticide "HCH". No prior reference-quality data of similar scope and completeness existed from this domain. Results have been presented at national scientific meetings and journal publications on the propagation of Pacific-origin water along the North American continental margin have been published (cf., Vitae). Other results include the absence of the recent Atlantic layer warming signal from any part of the section, evidence of deep silicate enrichment from boundary regions, and evidence that ventilation signals present at mid-depth in the Chukchi boundary region of the Canada Basin are not transmitted into the Beaufort boundary region or into the southern Canada Basin interior. The 1997 results fit well with the handful of sections across the other Arctic Ocean basins, which also show the relative isolation of much of the interior of the

Arctic Ocean from the shelf seas. Swift is preparing a monograph integrating Arctic Ocean and Nordic Seas data, "Dissolved Oxygen in the Arctic Ocean and Nordic Seas", for journal submission.

L.D. Talley (**OCE-9712209 -** *Pacific Circulation Based on WOCE Observations; Pacific WOCE Hydrographic Programme Atlas*; 11/1/1997-9/30/2002; $410,000): This supports Pacific WOCE data analysis and the Pacific WHP Atlas (in progress: http://gyre.ucsd.edu/whp_atlas). Global heat transports (Talley, 1999a, 2002) were computed and decomposed into portions associated with shallow, subducting circulation, intermediate water formation and deep water formation, based on Reid's (1994, 1997) velocities. Global meridional overturning streamfunctions were computed (Talley *et al*., in preparation). A theoretical paper (Talley, 1999b) provides a simple framework for coupled ocean-atmosphere mid-latitude modes and was motivated by the Antarctic Circumpolar Wave and North Pacific mid-latitude decadal modes. Global mode waters, with some information on intermediate waters, were reviewed, with some new perspectives (Hanawa and Talley, 2001). WOCE data synthesis was reviewed (Talley *et al*., 2001). The roles of cabbeling and double diffusion in altering the density of the NPIW salinity minimum were explored (Talley and Yun, 2001). South Pacific gyre variability was studied using WOCE XBT data from 30°S (McCarthy *et al*., 1999), revealing large-scale interannual fluctuations of the thermocline and transport associated with variations in Sverdrup transport. Other current NSF grants are relevant to the proposed AAIW work – a study of dense shelf water formation through brine rejection in the Okhotsk Sea, contributing to new North Pacific Intermediate Water, and a study of Japan Sea winter convection and brine rejection. Reference that does not appear in my CV: Talley, L.D., D. Stammer and I. Fukumori, 2001: The WOCE Synthesis. Ocean Circulation and Climate, G. Siedler and J. Church (eds), International Geophysics Series, Academic Press, pp. 525-546.

M. Visbeck (**NSF-OCE -** *Studies of Boundary Current Dynamics*, H. Ou and M. Visbeck, 09/01/00-08/31/03, $360,000): The project is well on its way with M. Visbeck supervising the numerical modeling experiments of this study. We have the first set of numerical results at hand and are currently analysing those and refining some of the experimental setup.

(NSF-ATM - *The climate impact of the Southern Hemispheric Annular Mode*, A. Hall and M. Visbeck, 11/15/00-10/31/03, $238,131): Good progress has been made in diagnosing the impact of the Annular Mode in the GFDL coupled climate model. We have identified a significant impact on both the oceans circulation as well as the sea ice abundance. A first paper has been submitted and is currently under revision.

(NSS-OPP - *Circumpolar Deep Water and the West Antarctic Ice Sheet*, S. Jacobs and M. Visbeck, 3/1/98-2/28/02, $297,018): We have successfully collected ~150 CTD stations and my responsibility was making direct velocity measurements using the LADCP system. The data have all been processed and are now incorporated in the scientific analysis of the whole data set. The lowered ADCP allowed for the first time to measure currents directly in front of some of the smaller ice shelves and gave insight in to the distribution of barotropic and baroclinic energy.

M.J. Warner (**OCE-9819192** – *Interpretation of the Subsurface CFC Maxima in the North Pacific*; $145,000; 03/1/99-02/28/02): This study is a synthesis of the CFC and hydrography data collected during the WOCE Hydrographic Program and during two University of Washington student cruises. The goal of the proposed data synthesis and modeling study was to investigate the ventilation of the North Pacific subtropical thermocline and specifically the processes which resulted in the formation of a shallow CFC concentration maxima. It had been suggested that the CFC maxima was related to the presence of mode waters. The results of the data synthesis (Mecking and Warner, 2001, see Biographical Sketch for reference) show that the CFC maxima were collocated with the potential vorticity minima which characterize subtropical mode water in the western North Pacific during the WOCE period. However, the CFC maxima were found to be deepening to below the Central Mode Waters during the late 1990s. Both these observations and a steady-state age model suggest that the CFC maxima are transient features which

are currently deepening with time due to the decrease in the rate of increase of these compounds in the atmosphere.

A diagnostic model was developed using flow fields derived from Levitus climatolgy for isopycnal surfaces which outcrop in the North Pacific in order to study the effects of mixing on the derived tracer ages. During the student cruises, which repeated portions of WOCE sections P16N and P2, the pCFC ages increased at most depths. The goal of this effort was to determine if this "aging" is due to mixing or whether it reflects a change in physical processes. Two manuscripts are in preparation based upon this work.

R.F. Weiss has a long-standing involvement with NSF-sponsored research on CFCs as tracers of ocean circulation and on the study of carbon dioxide (CO_2) and nitrous oxide (N_2O) distributions in the surface waters of the world oceans, both areas of research that are represented in this proposal. Under NSF support he carried out some of the first CFC studies of deep-ocean mixing rates (Bullister and Weiss, 1983), of western boundary transport (Weiss *et al*., 1885), and of ventilation rates in deep lakes (Weiss *et al*., 1991). He also improved the technology for making accurate low-level CFC measurements (Bullister and Weiss, 1988), and trained several of the present-day leaders in this field. He has published large data sets of oceanic CFC distributions which have been used extensively in the numerical modeling community (e.g. Weiss *et al*., 1993). More recently, under NASA support, he has played a major role in the study of CFCs in the global atmosphere (Prinn *et al*., 2000), which has benefited the use of CFCs as ocean tracers (Walker *et al*., 2000). NSF support was also instrumental in the development of the "Weiss equilibrator" and automated gas chromatographic system for underway measurement of surface ocean pCO_2 and pN_2O distributions (Weiss, 1981a; Weiss *et al*., 1992). This work has contributed, with support from the NSF and the DOE, the largest and most widely distributed data sets for the study of the air-sea fluxes of CO_2 (Takahashi *et al*., 1996) and N_2O (Nevison *et al*., 1995). Under NSF support Weiss also discovered the global increase in atmospheric N_2O (Weiss, 1981b), and determined the solubilities of CO_2 (Weiss, 1974) and N_2O (Weiss and Price, 1980) in water and seawater. (References appear in the Reference list.)

References

Arbic, B.K, and W.B. Owens. 2001. Climatic warming of Atlantic Intermediate Waters. *J. Clim., 14*, 4091-4108.

Bacon, S., L.R. Centurioni, and W.J. Gould. 2001. The evaluation of salinity measurements from PALACE floats. *J. Atmos. Ocean. Technol., 18*, 1258-1266.

Bayer, R. and P. Schlosser. 1991. Tritium profiles in the Weddell Sea. *Mar. Chem., 35*, 123-136.

Beal, L.M., and H.L. Bryden. 1997. Observations of an Agulhas undercurrent. *Deep-Sea Res., Part I, 44*, 1715-1724.

Bender, M. *et al*. 2002. A. U.S. Large-CO_2 Observing Plan: Oceans and Atmosphere. Report for the U.S. Carbon Cycle Science Interagency Working Group, Washington D.C. U.S. Global Change Research Program, submitted for publication. (Available at: http://www.ogp.noaa.gov/mpe/gcc/co2/observingp/an/toc.htm)

Bindoff, N.L., and T.J. McDougall. 2000. Decadal changes along an Indian Ocean Section at 32°S and their interpretation. *J. Phys. Oceanogr., 30*, 1207-1222.

Bishop, J.K.B., C.K. Guay, J.T. Sherman, C. Moore, and R.E. Davis. 2001. Prospectus for A "C-Argo": A new approach for exploring ocean carbon system variability. Extended abstract 01-07, International Workshop on Autonomous Measurements of Biogeochemical Parameters in the Ocean, Honolulu, February 20-22, 2001.

Blackmon, M., B. Boville, F. Bryan, R. Dickinson, P. Gent, K. Kiehl, R. Moritz, D. Randall, J. Shukla, S. Solomon, G. Bonan, S. Doney, I. Fung, J. Hack, E. Hunke, J. Hurrell, J. Kutzbach, J. Meehl, B. Otto-Bliesner, R. Saravanan, E.K. Schneider, L.Sloan, M. Spall, K. Taylor, J. Tribbia, and W. Washington. 2001. The Community Climate System Model. *Bull. Amer. Meteorol. Soc., 82*, 2357-2376.

Bopp, L., C. LeQuere, M. Heimann, A. Manning, and P. Monfray. 2002. Climate induced oceanic oxygen fluxes: implications for the contemporary carbon budget. *J. Geophys. Res.*, submitted.

Bryden, H.L., M.J. Griffiths, A.M. Lavin, R. C. Millard, G. Parilla, and W.M. Smethie. 1996. Decadal changes in water mass characteristics at 24ºN in the Subtropical North Atlantic Ocean. *J. Clim., 9*, 3162-3186.

Bryden, H.L., and S. Imawaki. 2001, Ocean heat transport. In *Ocean Circulation and Climate: Observing and Modelling the Global Ocean*, G. Siedler, J.Church, and J. Gould (Eds), Academic Press, London, 715 pp.

Bullister, J. L., and R. F. Weiss. 1983. Anthropogenic chlorofluoromethanes in the Greenland and Norwegian Seas. *Science, 221*, 265-268.

Bullister, J. L., and R. F. Weiss. 1988. Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep-Sea Res., 35*, 839-853.

Carpenter J.H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnology and Oceanography, 10*, 141-143.

Chavez, F.P., P.G. Strutton, G.E. Friederich, R.A. Feely, G.C. Feldman, D.G. Foley, and M.J. McPhaden. 1999. Biological and chemical response of the equatorial Pacific Ocean to the 1997-98 El Nino. *Science, 286*, 2126-2131.

Chereskin, T.K., and D. Roemmich. 1991. A comparison of measured and wind-derived Ekman transport at 11ºN in the Atlantic Ocean. *J. Phys. Oceanogr., 21*, 869-878.

Chereskin, T.K., W. D. Wilson, H. L. Bryden, A. Ffield, and J. Morrison. 1997. Observations of the Ekman balance at 8º30'N in the Arabian Sea during the 1995 southwest monsoon. *Geophys. Res. Lett., 24(21)*, 2541-2544, 1997.

Culbertson, C.H., G. Knapp, M. Stalcup, R.T. Williams, and F. Zemlyak. 1991. A comparison of methods for the determination of dissolved oxygen in seawater. Report WHPO 91–2, WOCE Hydrographic Programme Office.

Davis, R.E. 1976. Predictability of sea surface temperature and sea level pressure anomailies over the North Pacific Ocean. *J. Phys. Oceanogr., 6*, 249-266.

DECEN. 1998. Decade-to-Century-Scale Climate Variability and Change. A Science Strategy. Panel on Climate Variability on Decade-to-Century Time Scales, Board on Atmospheric Sciences and Climate, Commission on Geosciences, Environment, and Resources, National Research Council, National Academy Press, Washington, D.C., 142 pp.

Deser, C., M.A. Alexander, and M.S. Timlin. 1996. Upper- ocean thermal variations in the North Pacific during 1970- 1991. *J. Climate, 9*, 1840-1855.

DeValls, T.A., and A.G. Dickson. 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ("tris") in synthetic seawater. *Deep-Sea Res., 45*, 1541-1554.

Dickson, A. G., and C. Goyet (Eds). 1994. ORNL/CDIAC-74, DOE, *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2*.

Dickson, R.R., J. Lazier, J. Meinke, P. Rhines, and J. Swift. 1996. Long-term coordinated changes in the convective activity of the North Atlantic. *Prog. Oceanogr., 38*, 241-295.

Dickson, A.G., G.C. Anderson, and J.D. Afgan. 2002a. Reference materials for oceanic CO_2 analysis: 1. Preparation, distribution, and use. *Mar. Chem*., submitted.

Dickson, A.G., J.D. Afgan, and G.C. Anderson. 2002b. Reference materials for oceanic CO_2 analysis: 2. A method for the certification of total alkalinity. *Mar. Chem.*, submitted.

Dickson, B., J. Hurrell, N. Bindoff, A. Wong, B. Arbic, B. Owens, S. Imawaki, and I. Yashayaev. 2001. The World during WOCE, in *Ocean Circulation and Climate: Observing and Modelling the Global Ocean*, G. Siedler, J. Church, and J. Gould (Eds). Academic Press, London, 715 pp.

Dickson, R., I. Yashayaev, J. Meincke, W. Turrell, S. Dye, and J. Holfort. 2002. Rapid freshening of the deep North Atlantic over the past four decades. *Nature*, submitted.

DOE. 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2*. Dickson, A. G., and C. Goyet (Eds.), ORNL/CDIAC-74.

Doney, S.C., and W.J. Jenkins. 1988. The effect of boundary conditions on tracer estimates of thermocline ventilation rates. *J. Mar. Res., 46*, 947-965.

Doney, S.C., W.J. Jenkins, and H.G. Ostlund. 1993. A tritium budget for the North Atlantic. *J. Geophys. Res., 98*, 18,096-18,081.

Doney, S.C., and W.J. Jenkins. 1994. Ventilation of the Deep Western Boundary Current and abyssal western North Atlantic: estimates from tritium and excess ^{3}He distributions. *J. Phys. Oceanogr., 24*, 638-659.

Doney, S.C., and W.J. Jenkins. 1995. Ventilation of the deep western boundary current and abyssal western North Atlantic - estimates from tritium and ^{3}He distributions. *J. Phys. Oceanogr., 24*, 638-659.

Doney, S.C., W.J. Jenkins, and J.L. Bullister. 1997. A comparison of ocean tracer dating techniques on a meridional section in the eastern North Atlantic. *Deep-Sea Res. I, 44*, 603-626.

Doney, S.C. 1999. Major challenges confronting marine biogeochemical modeling. *Global Biogeochem. Cycles, 13*, 705-714.

Donohue, K.A., E. Firing, and L. Beal. 2000. Comparison of three velocity sections of the Agulhas current and Agulhas undercurrent. *J. Geophys. Res., 105*, 28585-28593.

Emerson, S., S. Mecking, and J. Abell. 2001. The biological pump in the subtropical North Pacific Ocean: Nutrient sources, Redfield ratios, and recent changes. *Global Biogeochem. Cycles, 15*, 535-554.

England, M.H., and E. Maier-Reimer. 2001. Using chemical tracers to assess ocean models. *Rev. Geophys., 39*, 29-70.

Federov, A.V., and S.G.H. Philander. 2000. Is El Nino Changing? *Science 288*, 1997-2002.

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy. 1998. A new automated underway system for making high precision pCO_2 measurements onboard research ships. *Analytica Chim. Acta, 377*, 185-191.

Feely, R.A., C.L. Sabine, R.M. Key, and T.-H. Peng. 1999. CO_2 survey synthesis results: Estimating the anthropogenic carbon dioxide sink in the Pacific Ocean. *U.S. JGOFS News, 9(4)*, February 1999, pp. 1-4.

Fine, R.A., and R.L. Molinari. 1988. A continuous deep western boundary current between Abaco (26.5°N) and Barbados (13°). *Deep-Sea Res., 35*, 1441-1450.

Fine, R.A., K.A. Maillet, K.F. Sullivan, and D. Willey. 2001. Circulation and ventilation flux of the Pacific Ocean. *J. Geophys. Res.-Oceans, 106(10)*, 22,159-22,178.

Firing, E. 1991. Acoustic Doppler current profiling methods and navigation. WOCE Hydrographic Program Operations and Methods Manual, WHP Office Report WHPO 91-1; WOCE Report No. 68/91; US WHP Office, SIO, La Jolla, CA. http://whpo.ucsd.edu/manuals/pdf/91_1/firadcp.pdf.

Firing, E. 1998. Lowered ADCP and use in WOCE. *International WOCE Newsletter*, pp. 10-15.

Fischer, J., and M. Visbeck, 1993. Deep velocity profiling with self-contained ADCPs, *J. Atmosph. and Oceanic Technol., 10*, 764-773.

Friederich G.E., L.A. Codispoti, and C.M. Sakamoto. 1991. An Easy-to-Construct Automated Winkler Titration System. MBARI Technical Report N0 91-6, 33pp.

Ganachaud, A., and C. Wunsch. 2000. Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data. *Nature, 408*, 453-457.

Gloor, M, N. Gruber, J. L. Sarmiento, C.S. Sabine, R. Feely, and C. Rödenbeck. 2002. A first estimate of present and pre-industrial air-sea CO_2 flux pattern based on ocean carbon measurements, *Science*, submitted.

Gordon, A.L. 1982. Weddell Deep Water variability. *J. Mar. Res., 40*, 199-217.

Gordon, A., M. Visbeck and B. Huber. 2001. Export of Weddell Sea Deep and Bottom Water. *J. Geophys. Res., 106*, 9005-9017.

Gray, S.L., and T.W.N. Haine. 2001. Constraining a North Atlantic general circulation model with chlorofluorocarbon observations. *J. Phys. Oceanogr., 31*, 1157-1181.

Gruber, N. and J.L. Sarmiento, and T.F. Stocker. 1996. An Improved Method for Detecting Anthropogenic CO_2 in the Oceans. *Global Biogeochem. Cycles, 10*, 809-837.

Gruber N. 1998. Anthropogenic CO_2 in the Atlantic Ocean. *Global Biogeochem. Cycles, 10*, 809-837.

Gruber, N., E. Gloor, T.M.C. Hughes, and J.L. Sarmiento. 2002. Air-sea flux of oxygen estimated from bulk data: Implications for the marine and atmospheric oxygen cycle. *Global Biogeochem. Cycles*, in press.

Hall, M.N., and H.T. Bryden. 1982. Direct estimates and mechanisims of ocean heat transport. *Deep-Sea Res., 29*, 3339-359.

Hansell, D.A., and C.A. Carlson. 1998. Deep ocean gradients in dissolved organic carbon concentrations. *Nature 395*, 263-266.

Hansell, D.A., and R.A. Feely. 2000. Atmospheric intertropical convergence impacts surface ocean carbon and nitrogen biogeochemistry in the western tropical Pacific. *Geophys. Res. Let., 27*, 1013-1016.

Hansell, D.A. 2001. The good, the bad and the ugly: Are my DOC results any good? *U.S. JGOFS Newsletter, 11*(2), 14-15.

Hansell, D.A., and C.A. Carlson. 2001. Biogeochemistry of total organic carbon and nitrogen in the Sargasso Sea: control by convective overturn. *Deep-Sea Res. II, 48*, 1649-1667.

Heimann, M., and E. Maier-Reimer. 1996. On the relations between the oceanic uptake of CO_2 and its carbon isotopes. *Global Biogeochem. Cycles, 10(1)*, 89-110.

Heinze, C., P. Schlosser, K.P. Koltermann, and J. Meincke. 1990. A tracer study of the deep water renewal in the European Polar Seas. *Deep Sea Res., 37*, 1425-1453.

Heinze, C., E. Maier-Reimer, and P. Schlosser. 1998. Transient tracers in a global OGCM: Source functions and simulated distributions. *J. Geophys. Res., 103*, 15,903-15,922.

Hogg, N.G., and W. Zenk. 1997. Long-period changes in bottom water flowing through Vema Channel. *J. Geophys. Res., 102*, 15,639-15,646.

Holfort J, K.M. Johnson, B. Schneider, G. Siedler, and D.W.R. Wallace. 1998. Meridional transport of dissolved inorganic carbon in the South Atlantic Ocean. *Global Biogeochem. Cycles 12*, 479-499.

Huhn, O., W. Roether, P. Beining, and H. Rose. 2001. Validity limits of carbon tetrachloride as an ocean tracer. *Deep-Sea Res., 48(9),* 2025-2049.

Jenkins, W.J. 1980. Tritium and ^{3}He in the Sargasso Sea. *J. Mar. Res., 38,* 533-569.

Jenkins, W.J. and P.B. Rhines. 1980. Tritium in the Deep North Atlantic Ocean. *Nature, 286,* 5776, 877-880.

Jenkins, W.J., and J.C. Goldman. 1985. Seasonal oxygen cycling and primary production in the Sargasso Sea. *J. Mar. Res., 43,* 465-491.

Jenkins, W.J. 1987. ^{3}H and ^{3}He in the Beta triangle: observations of gyre ventilation and oxygen utilization rates. *J. Phys. Oceanogr., 17,* 763-783.

Jenkins, W.J. 1988. Using anthropogenic tritium and ^{3}He to study subtropical gyre ventilation and circulation. *Philosophical Transactions of the Royal Society (London), A325,* 43-61.

Jenkins, W.J. 1991. Determination of isopycnal diffusivity in the Sargasso Sea. *J. Phys. Oceanogr., 21,* 1058-1061.

Jenkins, W.J., and D.W.R. Wallace. 1992. Tracer based inferences of new primary production in the sea. In *Primary Production and Biogeochemical Cycles in the Sea,* P.G. Falkowski and A.D. Woodhead (Eds.), Plenum, New York, pp. 299-316.

Jenkins, W.J. 1998. Studying thermocline ventilation and circulation using tritium and ^{3}He. *J. Geophys. Res., 103,* 15,817-15,831.

Johnson, G.C., D.L. Rudnick, and B.A. Taft. 1994. Bottom water variability in the Samoa Passage. *J. Mar. Res., 52,* 177-196.

Johnson, G.C. and, A.H. Orsi. 1997. Southwest Pacific Ocean water-mass changes between 1968/69 and 1990/91. *J. Clim., 10,* 306-316.

Johnson, K.M., *et al*. 1998. Coulometric total carbon dioxide analysis for marine studies: Assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean CO_2 survey 1994-1996. *Mar. Chem., 63,* 21-37.

Joyce, T., and C. Corry (Eds). 1994. Requirements for WOCE Hydrographic Programme Data Reporting. WHPO Publication 90-1 Revision 2, WOCE Report 67/91, Woods Hole, Mass., USA, May 1994, 144 pp.

Joyce, T., and C. Corry (Eds). 1994 WOCE Operations Manual, Volume 3: The Observational Programme, Section 3.1: WOCE Hydrographic Programme, Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1, WOCE Report No. 68/91, Revision 1, Woods Hole, Mass., USA, November 1994.

Joyce, T.M., R.S. Pickart, and R.C. Millard. 1999. Long-term hydrographic changes at 52 and 66°W in the North Atlantic subtropical gyre and Caribbean. *Deep-Sea Res. II, 46,* 245-278.

Joyce, T.M., A. Hernandez-Guerra, and W.M. Smethie Jr. 2001. Zonal circulation in the NW Atlantic and Caribbean from a meridional WOCE hydrographic section at 66oW. *J. Geophys. Res., 106,* 22,095-22,113.

Keeling, R.F., and S.R. Shertz. 1992. Seasonal to interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature, 358,* 723-727.

Keeling, R.F., S.C. Piper, and M. Heimann. 1996. Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration. *Nature, 381,* 218-221.

Khatiwala, S., M. Visbeck, and P. Schlosser. 2001. Age tracers in an ocean GCM. *Deep-Sea Res., 48,* 1423-1441.

King, B. A., E. Firing, and T. M. Joyce. 2001. Shipboard observations during WOCE. Chapter 3.1 in *Ocean Circulation and Climate,* Gerold Siedler and John Church (Eds.), Academic Press, London, pp. 99-122.

Large, W.G., G. Danabasoglu, S.C. Doney, and J.C. McWilliams. 1997. Sensitivity to surface forcing and boundary layer mixing in a global ocean model: annual-mean climatology. *J. Phys. Oceanogr., 27,* 2418-2447.

Law, C. S., and A.J. Watson. 2001. Determination of Persian Gulf Water transport and oxygen utilisation rates using SF_6 as a novel transient tracer. *Geophys. Res. Lett. 28*, 815-818.

Lee, K., F.J. Millero, and D.M. Campbell. 1996. The reliability of the thermodynamic constants for the dissociation of carbonic acid in seawater. *Mar. Chem., 55***,** 233-245.

Lee, K., F.J. Millero, and R. Wanninkhof. 1997. The carbon dioxide system in the Atlantic Ocean. *J. Geophys. Res., 102*, 15693-15707.

Lee, K., F.J. Millero, R.H. Byrne, R.A. Feely, and R. Wanninkhof. 2000. The recommended dissociation constants of carbonic acid for use in seawater. *Geophys. Res. Lett., 27*, 229-232.

Levitus, S., J.I. Antonov, T.P. Boyer, and C. Stephen. 2000. Warming of the world ocean. *Science, 287*, 2225-2229.

Levitus, S., J.I. Antonov, J. Wang, T.L. Delworth, K.W. Dixon, and A.J. Broccoli. 2001. Anthropogenic warming of earth's climate system. *Science, 292*, 267-270.

Lott, D.E. and W.J. Jenkins. 1984. An automated cryogenic charcoal trap system for helium isotope mass spectrometry. *Rev. Sci. Instr., 55*(12), 1982-1988.

Lott, D.E. and W.J. Jenkins. 1998. Advances in analysis and shipboard processing of tritium and helium samples. *Intl.WOCE Newsletter, 30*, 27-30.

Ludin, A., R. Weppernig, G. Bönisch, and P. Schlosser. 1998. Mass spectrometric measurement of helium isotopes and tritium. LDEO Tech. Rep. No. 98-6.

Lukas R. 2001. Freshening of the upper thermocline in the North Pacific subtropical gyre associated with decadal changes of rainfall. *Geophys Res Lett., 28*, 3485-3488.

Macdonald, A.M., and C. Wunsch. 1996. An estimate of global ocean circulation and heat fluxes, *Nature, 382*, 436-439.

McPhaden, M.J., and D. Zhang. 2002. Slowing of the shallow meridional overturning circulation in the Pacific Ocean. *Nature, 415*, 603-608.

Matear, R.J., and A.C. Hirst. 1999. Climate change feedback on the future oceanic CO_2 uptake. *Tellus B, 51*, 722-733.

Mensch, M., R. Bayer, J.L. Bullister, P. Schlosser, and R. Weiss, 1996. The distribution of tritium and CFCs in the Weddell Sea during the mid 1980s. *Prog. Ocean., 38*, 377-415.

Millero, F.J. 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta, 59*, 661-677.

Millero, F.J., D. G. Purkerson, P. Steinberg, E. Peltola, K. Lee, C. Edwards, J. Goen, and M.P. Roche. 1993. The carbon dioxide system in the Ross Sea during the JGOFS Southern Ocean process study. University of Miami Technical Report, 44 pp.

Millero, F.J., J.-Z. Zhang, K. Lee, and D. Campbell. 1993. Titration alkalinity of seawater. *Mar. Chem., 44*, 153-167.

Molinari, R.L., R.A. Fine, W.D. Wilson, R.G. Curry, J. Abell, and M.S. McCartney. 1998. The arrival of recently formed Labrador Sea Water in the Deep Western Boundary Current at 26.5ºN. *Geophys.Res.Letts., 25*, 2249-2252.

Musgrave, D.L., J. Chou, *et al*. 1988. Application of a model of upper-ocean physics for studying seasonal cycles of oxygen. *J. Geophys. Res., 93*, 15,679-15,700.

Nanias, J. 1972. Large-scale and long-term fluctuations in some atmospheric and oceanic variables. Nobel Symposium 20, D.D. Dyrsen and D.D. Jagner (Eds.). Almqvist and Wiksell, Stockholm, pp. 27-48.

Orsi, A.H., G.C. Johnson, and J.L. Bullister. 1999. Circulation, mixing, and production of Antarctic Bottom Water. *Prog. Oceanogr., 43*, 55-109.

Peng, T.-H. R. Wanninkhof, J.L. Bullister, R.A. Feely, and T. Takahashi. 1999. Quantification of decadal anthropogenic CO_2 uptake in the ocean based on dissolved inorganic carbon measurements. *Nature, 396*, 560-563.

Plattner, K., F. Joos, and T.F. Stocker. 2002. Revision of the global carbon budget due to changing air-sea oxygen fluxes. *Global Biogeochem. Cycles*, submitted.

Polzin, K., E. Kunze, J. Hummon, and E. Firing. 2002. The finescale response of lowered ADCP velocity profiles, *J. Atmosph. and Oceanic Technol., 19*, 205-224.

Prentice, C. *et al*. 2001. The carbon cycle and atmospheric carbon dioxide, in *Climate Change 2001: The Scientific Basis*. Contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, J. Houghton *et al*. (Eds.). Cambridge University Press, New York, NY, USA.

Prinn, R.G., R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R.H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Sturrock, P.M. Midgley, and A. McCulloch. 2000. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res., 105*, 17,751-17,792.

Quay, P.D., B. Tilbrook, and C.S. Wong. 1992. Oceanic uptake of fossil fuel CO_2: Carbon-13 evidence. *Science, 256*, 74-79.

Rhein, M., L. Stramma, and U. Send. 1995. The Atlantic Deep Western Boundary Current: water masses and transports near the equator. *J. Geophys. Res., 100*, 2441-2457.

Riser S. and D. Swift. 2002. Long-term salinity measurements from profiling floats. *J. Atmos. Ocean. Technol.*, submitted.

Roether, W., B. Klein and K. Bulsiewicz. 2001. Apparent loss of CFC-113 in the upper ocean. *J. Geophys. Res., 106*, 2679-2688.

Robbins, P.E., and W.J. Jenkins. 1998. Observations of temporal changes of tritium-^{3}He age in the eastern North Atlantic thermocline: Evidence for changes in ventilation? *J. Mar. Res., 56*, 1125-1162.

Robbins, P.E., J.F. Price, W.B. Owens, and W.J. Jenkins. 2000. On the Importance of lateral diffusion for the ventilation of the lower thermocline in the subtropical North Atlantic. *J. Phys. Oceanogr., 30*, 67-89.

Roemmich, D., and C. Wunsch. 1984. Apparent changes in the climate state of the deep North Atlantic Ocean. *Nature, 307*, 447-450.

Roether, W., and S.C. Doney (Eds.). 1999. Report of the WOCE-AIMS Tracer Workshop, WOCE Report No. 167/99, WOCE International Project Office, Southampton, UK, 70pp.

Sabine, C.L., R.M. Key, K.M. Johnson, F.J. Millero, A. Poisson, J.L. Sarmiento, D.W.R. Wallace, and C.D. Winn. 1999. Anthropogenic CO_2 Inventory in the Indian Ocean. *Global Biogeochem. Cycles, 13*, 179-198.

Sabine, C., R. Wanninkhof, R.M. Key, C. Goyet, and F.J. Millero. 2000. Seasonal CO_2 fluxes in the tropical and subtropical Indian Ocean. *Mar. Chem., 72*, 33-55.

Sabine, C.L., R.A. Feely, R.M. Key, J.L. Bullister, F.J. Millero, K. Lee, T.-H. Peng, B.Tilbrook, T. Ono, and C.S. Wong. 2002. Distribution of anthropogenic CO_2 in the Pacific Ocean. *Global Biogeochem. Cycles*, submitted.

Sarmiento, J.L., T.M.C. Hughes, R.J. Stouffer, and S. Manabe. 1998. Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature, 393*, 245-249.

Schlitzer, R. 2000. Applying the adjoint method for global biogeochemical modeling, in *Inverse Methods in Global Biogeochemical Cycles*, edited by P. Kasibhatla *et al.*, AGU Geophys. Monograph Series, American Geophysical Union, Washington D.C., 107-124.

Schlosser, P., G. Boenisch, M. Rhein, and R. Bayer. 1991. Reduction of deep water formation in the Greenland Sea during the 1980s: Evidence from tracer data. *Science, 251*, 1054-1056.

Schlosser, P., J.L. Bullister, R. Fine, W.J. Jenkins, R. Key, J. Lupton, W. Roether, and W. M. Smethie, Jr. 2001. Transformation and Ages of Water Masses. In *Ocean Circulation and Climate, Observing and Modeling the Global Ocean*, G. Siedler, J. Church and J. Gould (Eds.), Academic Press, London, pp. 431-452.

Sloyan, B.M., and S.R. Rintoul. 2001. The Southern Ocean limb of the global deep overturning circulation. *J. Phys. Oceanogr., 31*, 143-173.

Smethie, W.M., Jr. 1993. Tracing the thermohaline circulation in the North Atlantic using chlorofluorocarbons. *Prog. Oceanogr., 31*, 51-99.

Smethie, W. M., Jr. 1998. CFC Measurements Along the 53º and 66ºW ACCE Sections. The 1998 Conference of The World Ocean Circulation Experiment: Ocean Circulation and Climate, Halifax, Canada, 24-29 May 1998, p. 216, abstract volume.

Smethie, W. M., Jr. 1999a. Meridional distribution of CFCs in the western subtropical Atlantic Ocean. *International WOCE Newsletter, No. 37*: 15-17.

Smethie, W.M., Jr. 1999b. Meridional distribution of CFCs in the western subtropical Atlantic Ocean. Report of the WOCE North Atlantic Workshop Institut fur Meereskunde, Universitat Kiel, Germany, 23-27 August 1999, WOCE Report No. 169/2000, p107.

Smethie, W.M., R.A. Fine, A. Putzka, and E.P. Jones. 2000. Tracing the flow of North Atlantic Deep Water using chlorofluorocarbons. *J. Geophys. Res., 105*, 14,297-14,234.

Smethie, W.M., and R.A Fine. 2001. Rates of North Atlantic Deep Water formation calculated from chloroflorocarbon inventories. *Deep Sea Res. I, 48*, 189-215.

Spitzer, W.S., and W.J. Jenkins. 1989. Rates of vertical mixing, gas exchange and new production: estimates from seasonal gas cycles in the upper ocean near Bermuda. *J. Mar. Res., 47*, 169-196.

Stammer, D., K. Ueyoshi, W.G. Large, S. Josey, and C. Wunsch. 2002. Global sea surface flux estimates obtained through ocean data assimilation. *Bull. Amer. Meteor. Soc*., submitted.

Suga, T., K. Ayato, and H. Kimio. 2000. North Pacific Tropical Water: its climatology and temporal changes associated with the climate regime shift in the 1970s. *Prog. Oceanogr., 47*, 223-246.

Takahashi, T., R.A. Feely, R.F. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi. 1996. Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference. *Proc. Nat. Acad. Sci., Roger Revelle Symposium Volume, 94*, 8292-8299, 1996.

Talley, L.D. 1996. North Atlantic circulation and variability reviewed for the CNLS conference. *Physica D., 98*, 625-646.

Tans, P.P., J.A. Berry, and R.F. Keeling. 1993. Oceanic $^{12}C/^{13}C$ observations: a new window on ocean CO_2 uptake. *Global Biogeochem. Cycles, 7*, 353-368, 1993.

Tokar, J.M., and T.D. Dickey. 2000. Chemical Sensor Technology - Current and Future Applications. In *Chemical Sensors in Oceanography*, M.S. Varney, Gordon and Breach (Eds.), Amsterdam, 303-329.

Visbeck, M. 2002. Deep velocity profiling using lowered Acoustic Doppler Current Profiler: Bottom track and inverse solutions. *J. Atmosph. Oceanic Technol*., in press.

Vollmer, M. K., and R.F. Weiss. 2002. Simultaneous determination of sulfur hexafluoride and three chlorofluorocarbons in water and air. *Mar. Chem*., in press.

Walker, S.J., R.F. Weiss, and P.K. Salameh. 2000. Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113 and carbon tetrachloride. *J. Geophys. Res., 105*, 14,285-14,296.

Wallace, D.W.R., P. Schlosser, M. Krysell, and G. Bonisch. 1992. Halocarbon ratio and tritium/^{3}He dating of water masses in the Nansen Basin, Arctic Ocean. *Deep-Sea Res., 39*, S435-S458.

Wallace, D.W.R., P. Beining, and A. Putzka. 1994. Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, 19°S. *J. Geophys. Res., 99(C4)*, 7803-7819.

Wanninkhof, R., and K. Thoning. 1993. Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods. *Mar. Chem., 44* (2-4), 189-205.

Wanninkhof, R., and R.A. Feely. 1998. fCO_2 dynamics in the Atlantic, Pacific, and South Indian Ocean. *Mar. Chem., 60*, 15-31.

Wanninkhof, R., S.C. Doney, T.-H. Peng, J.L. Bullister, K. Lee, and R.A. Feely. 1999. Comparison of methods to determine the anthropogenic CO_2 invasion into the Atlantic Ocean. *Tellus, 51B*, 511-530.

Warner, M.J., J.L. Bullister, D.P. Wisegarver, R.H. Gammon, and R.F. Weiss. 1996. Basin-wide distributions of chlorofluorocarbons F-11 and F-12 in the North Pacific: 1985-1989. *J. Geophys. Res., 101*, 20,525-20,542.

Watanabe, Y.W., T. Ono, A Shimamoto, T. Sugimoto, M. Wakita, and S. Watanabe. 2001. Probability of a reduction in the formation rate of the subsurface water in the North Pacific during the 1980s and 1990s. *Geophys. Res. Letts., 28*, 289-3292.

Weiss, R.F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem., 2*, 203-215.

Weiss, R.F., and B.A. Price. 1980. Nitrous oxide solubility in water and seawater. *Mar. Chem., 8*, 347-359.

Weiss, R.F. 1981a. Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *J. Chromatog. Sci., 19*, 611-616.

Weiss, R.F. 1981b. The temporal and spatial distribution of tropospheric nitrous oxide. *J. Geophys. Res., 86*, 7185-7195.

Weiss, R.F., J.L. Bullister, R.H. Gammon, and M.J. Warner. 1985. Atmospheric chlorofluoromethanes in the deep equatorial Atlantic. *Nature, 314*, 608-610.

Weiss, R.F., E.C. Carmack, and V.M. Koropalov. 1991. Deep water renewal and biological production in Lake Baikal. *Nature, 349*, 665-669.

Weiss, R.F., F.A. Van Woy, and P.K. Salameh. 1992. Surface Water and Atmospheric Carbon Dioxide and Nitrous Oxide Observations by Shipboard Automated Gas Chromatography: Results From Expeditions Between 1977 and 1990. *Scripps Institution of Oceanography, Reference Series*, 92-11, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, ORNL/CDIAC-59, NDP-044, 144 pp.

Weiss, R.F., M.J. Warner, P.K. Salameh, F.A. Van Woy, and K.G. Harrison. 1993. South Atlantic Ventilation Experiment: SIO Chlorofluorocarbon Measurements. *Scripps Institution of Oceanography, Reference Series*, 93-49, 466 pp.

Wijffels, S. E., E. Firing, and H. Bryden. 1995. Direct observations of the Ekman balance at 11ºN in the Pacific. *J. Geophys. Res., 100*, 18,421-18,435.

Wijffels, S.E. 2001. Ocean transport of fresh water. In Ocean Circulation and Climate: Observing and Modelling the Global Ocean, G. Siedler, J.Church, and J. Gould (Eds). Academic Press, London, 715 pp.

Wofsy, S.C., and R.C. Harriss. 2002. The North American Carbon Program. A report of the NACP Committee of the U.S. Carbon Cycle Steering Group, U.S. Global Change Research Program. Washington, D.C. 20024. 56 pp.

Wong, A.P.S., N.L. Bindoff, and J.A. Church. 1999. Large-scale freshening of the intermediate waters in the Pacific and Indian Oceans. *Nature, 400*, 440-443.

Wong, A.P.S., G.C. Johnson, and W.B. Owens. 2002. Delayed-mode calibration of autonomous CTD profiling float salinity data by theta-S climatology. *J. Atmos. Oceanic Technol.*, submitted.