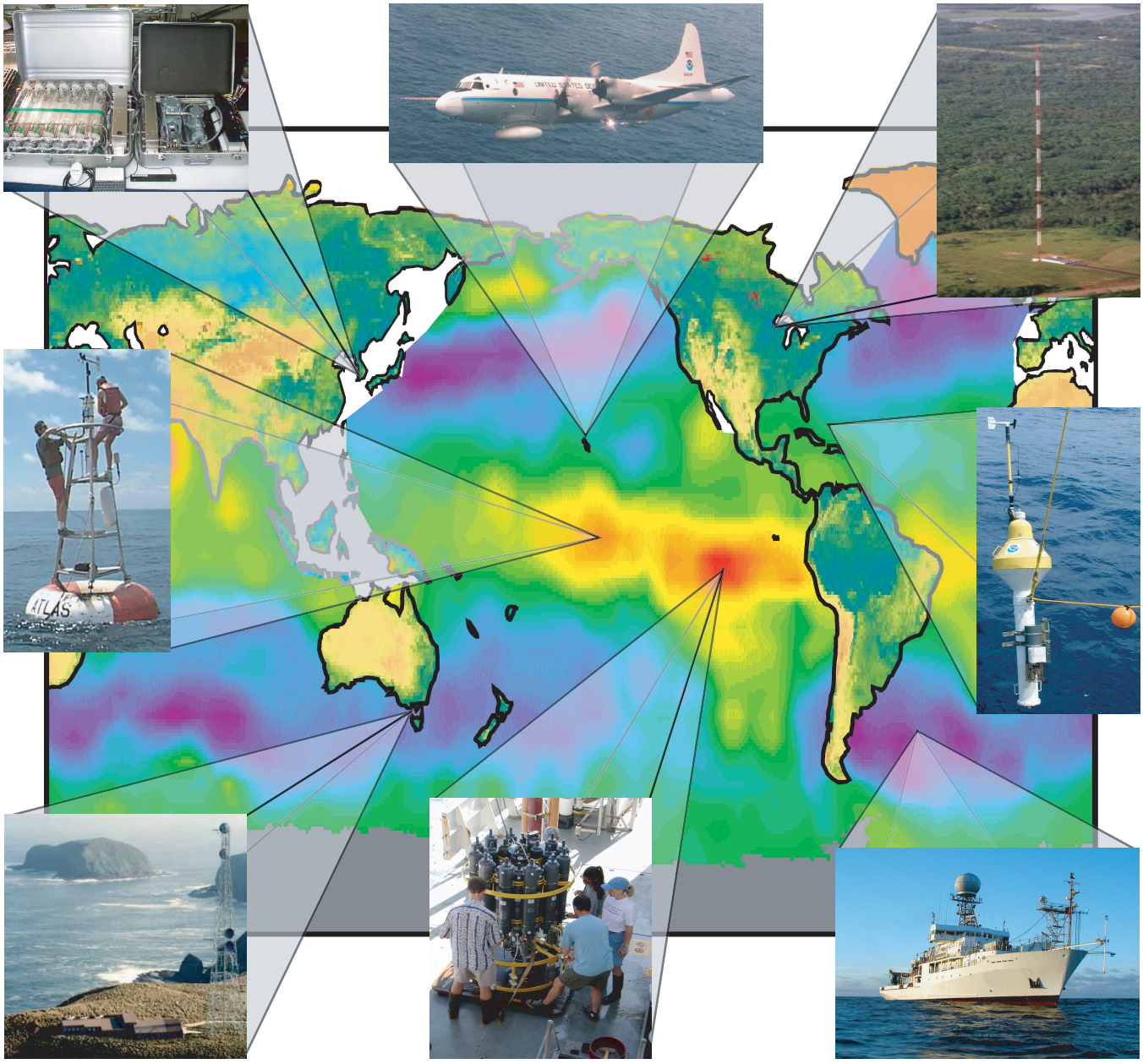
A Large-Scale CO_2 Observing Plan: In Situ Oceans and Atmosphere (LSCOP)



A Report of the In Situ Large-Scale CO_2 Observations Working Group

Front Cover: Global map of the world. The land colors show the composite NASA SeaWiFS Vegetation Index. The ocean colors show the climatological mean air-sea CO_2 fluxes for the virtual year 1995 (after Takahashi *et al.*, 2002). The surrounding pictures show the various sampling platforms and equipment that are used as part of the air and seawater CO_2 observing network. The SeaWiFS data were provided courtesy of the NASA SeaWiFS Project Office and ORBIMAGE Corporation. The CO_2 flux data were provided by Taro Takahashi of Lamont-Doherty Earth Observatory of Columbia University. The photos were provided by Christopher Sabine, Richard Feely, Britton Stephens, and Pieter Tans.

A Large-Scale CO_2 Observing Plan: In Situ Oceans and Atmosphere (LSCOP)

In Situ Large-Scale CO_2 Observations Working Group:
Bender, M., S. Doney, R.A. Feely, I. Fung, N. Gruber, D.E. Harrison, R. Keeling, J.K. Moore, J. Sarmiento, E. Sarachik, B. Stephens, T. Takahashi, P. Tans, and R. Wanninkhof

A contribution to the implementation of the
U.S. Carbon Cycle Science Plan

April 2002

NOTICE

Mention of a commercial company or product does not constitute an endorsement by NOAA/OAR. Use of information from this publication concerning proprietary products or the tests of such products for publicity or advertising purposes is not authorized.

For sale by the National Technical Information Service, 5285 Port Royal Road
Springfield, VA 22161

Contents

A Large-Scale CO_2 Observing Plan: In Situ Oceans and Atmosphere (LSCOP)

In Situ Large-Scale CO_2 Observations Working Group:
Bender, M., S. Doney, R.A. Feely, I. Fung, N. Gruber, D.E. Harrison, R. Keeling, J.K. Moore, J. Sarmiento, E. Sarachik, B. Stephens, T. Takahashi, P. Tans, and R. Wanninkhof

A Large-Scale CO_2 Observing Plan: In Situ Oceans and Atmosphere (LSCOP) was written by a core committee consisting of:

Michael Bender	Princeton University
Scott Doney	National Center for Atmospheric Research
Richard Feely	NOAA, Pacific Marine Environmental Laboratory
Inez Fung	University of California, Berkeley
Nicolas Gruber	University of California, Los Angeles
D. Edward Harrison	NOAA, Pacific Marine Environmental Laboratory
Ralph Keeling	Scripps Institution of Oceanography, University of California, San Diego
J. Keith Moore	National Center for Atmospheric Research
Jorge Sarmiento	Princeton University
Edward Sarachik	University of Washington
Britton Stephens	NOAA, Climate Monitoring and Diagnostics Laboratory
Taro Takahashi	Lamont-Doherty Earth Observatory
Pieter Tans	NOAA, Climate Monitoring and Diagnostics Laboratory
Rik Wanninkhof	NOAA, Atlantic Oceanographic and Meteorological Laboratory

Preparation of the report was sponsored by the National Oceanic and Atmospheric Administration. The core committee began its work on a draft plan at a committee meeting in February 2000. A workshop was held in November 2000 in Boulder, CO to solicit input from the scientific community and from interested Federal agency representatives. The revised draft plan was subsequently reviewed by the meeting participants and the broader scientific community. The reader is referred to Appendix A for a complete list of participants at the Boulder meeting.

The following individuals served as lead contributors for individual chapters or provided original research in support of this planning effort: Britton Stephens and Pieter Tans with contributions from Manuel Gloor, Lori Bruhwiler, and David Baker (Chapter 2); Michael Bender, Rik Wanninkhof, Nicolas Gruber, Taro Takahashi, and Wade McGillis (Chapter 3); Richard A. Feely, Piers Chapman, Francisco Chavez, Scott Doney, Rana Fine, Nicolas Gruber, Greg Johnson, Ken Johnson, Paul Quay, Paul Robbins, Christopher Sabine, Taro Takahashi, Bronte Tilbrook, Doug Wallace and Rik Wanninkhof (Chapter 4); Scott Doney, Scott Denning, Inez Fung, and Jorge Sarmiento (Chapter 5); Edward Sarachik (Chapter 6); Colm Sweeney, Taro Takahashi, Anand Gnanadesikan, Rik Wanninkhof , Richard A. Feely, Gernot Friedrich, Francisco Chavez, Nicolas Bates, Jon Olafsson, Jorge Sarmiento, Mary-Elena Carr, Charles R. McClain, and J. Keith Moore (Appendices).

Executive Summary

This report recommends a strategy for making observations of carbon dioxide (CO_2) and related properties in the atmosphere and oceans, over large spatial scales and long timescales. It also recommends process studies of air-sea gas exchange, in order to obtain more accurate estimates of CO_2 transfer between the atmosphere and oceans. Models are essential tools for understanding the distributions and fluxes of CO_2 in the atmosphere and oceans. We recommend observations and modeling efforts to enhance the skills of models used for this purpose. An ultimate product of the observations, modeling efforts, and complementary process studies will be improved projections of the trajectory of the atmospheric CO_2 increase.

The report's recommendations are summarized in Table E-1. These recommendations are prepared in the context of the U.S. Carbon Cycle Science Plan (CCSP),[1] with the goal of advancing our ability to address the two fundamental questions that the CCSP posed:

- What has happened to the carbon dioxide that has already been emitted by human activities (past anthropogenic CO_2)?
- What will be the future atmospheric CO_2 concentration trajectory resulting from both past and future emissions?

The importance of answering these questions is evident. A recent National Research Council report, *Climate Change Science,* documents the consensus scientists have reached that human emissions of greenhouse gases are increasingly affecting world climate.[2] The President's speech to the nation on global climate change[3] expressed concern about greenhouse warming at the highest levels of government and committed the United States to confront the issue. These documents recommend conducting the research necessary to understand the environmental behavior of biogenic greenhouse gases, of which carbon dioxide is the most significant. This research will lead toward the knowledge required to accurately project carbon removal rates from the atmosphere to the land biosphere and the oceans.

This report presents a plan for large-scale U.S.-sponsored observations of CO_2 in the oceans and atmosphere. This plan represents an implementation plan for the CO_2 observations component of the CCSP. We recommend observations to track the fate of fossil fuel-derived CO_2, to characterize fluxes of CO_2 from the atmosphere to the land biosphere and oceans over large scales of space and time, and to achieve process-level understanding of physical and biological controls on those fluxes now and in the future. Complementary small-scale process studies of the land and ocean biospheres are needed for a comprehensive understanding of carbon fluxes and distributions. No specific

[1] Sarmiento, J.L., and S.C. Wofsy (1999): *A U.S. Carbon Cycle Science Plan.* U.S. Global Change Research Program.

[2] National Research Council, Committee on the Science of Climate Change, *Climate Change Science: An Analysis of Some Key Questions,* National Academy Press, 2001; `http://www.nap.edu/`.

[3] Rose Garden; 11 June 2001.

Table E-1: Priorities and cost estimates for atmospheric observation program.

Element of the implementation plan	Priority	One-time Costs	Per-year Costs
Recommendations for the Next 1 to 5 Years			
Improve the quality of existing measurements and support technological development			
Continue existing network	1		\$4,000,000
Robust CO_2 analyzer	1	\$750,000	\$150,000
Quality control and methodology			
CO_2 standards propagation	1		\$50,000
Ongoing intercomparisons	1		\$225,000
CO_2 isotopic calibration scale	1	\$500,000	
$^{13}C/^{12}C$ intercomparisons	1		\$100,000
O_2/N_2 intercomparisons	1		\$100,000
Make intensive and extensive measurements of the vertical distribution of CO_2 over continents			
Intensive measurements of the North American carbon cycle	2		∼\$10,000,000 per campaign
Aircraft profiles over continents	2	\$3,000,000	\$7,000,000
Tall tower observations	2	\$2,300,000	\$800,000
Make new global measurements of CO_2 and other species			
Background CO_2 measurements	3		\$800,000
Measurements on pCO_2 platforms	3		\$15,000 per ship
Atmospheric O_2/N_2 measurements	3	\$440,000	\$240,000
$^{13}C/^{12}C$ and $^{18}O/^{16}O$ measurements	3		\$600,000
Robust CO analyzer	3	\$850,000	\$200,000
Recommendations for the Timescale of 6 to 10 Years			
Increase observations of CO_2, its isotopes, O_2/N_2, and related tracers, and their interpretation for global regional-scale CO_2 flux measurements			
100 new continental sites, 20 commercial ship tracks, and 30 mooring installations.		∼\$15,000,000	∼\$15,000,000

recommendations for such programs are offered here, because they are being planned independently.

1. Observation Objectives

We recommend that large-scale ocean and atmospheric CO_2 observations respond to the two basic questions of the CCSP by adopting the following objectives:

- To constrain natural and anthropogenic CO_2 fluxes between the land biosphere and atmosphere on the scales of continents and of coherent ecosystems within continents (on the order of 10^3 km), and between the ocean and atmosphere on the scale of ocean basins. The focus will

initially be on constraining climatologic (average) fluxes at scales of continents and ocean basins, and seasonal fluxes at the scales of coherent continental ecosystems. It will extend to studies of interannual variability as observation systems develop and models improve.

- To provide data sets that challenge models of the land biosphere and atmospheric transport, on the one hand, and models of gas exchange and ocean mixing, on the other. Current models of the land biosphere and atmospheric transport will improve when model predictions are compared with detailed data on CO_2 distributions. Similarly, ocean circulation models will improve as their predictions are compared with data on the evolving distribution of anthropogenic CO_2 and other transient tracers in the ocean.

- To improve process-level understanding of the controls on biogeochemical cycling on land and in the oceans. Variations in concentrations of CO_2, O_2, and related properties, interpreted using transport models, constrain ecosystems' productivity. We can use observations of these properties to track the evolving response to such physical forcings as weather and climate over the continents, upper ocean mixing, and nutrient supply in the oceans. The relationship between forcing and response provides process-level information and improves our understanding of responses to anthropogenic change.

- To track the fate of anthropogenic CO_2. A proper observing system will allow us to track the accumulating inventory of anthropogenic CO_2, not only in the atmosphere but also in the ocean and land biosphere as well.

- To enhance our ability to predict the evolution of the atmospheric CO_2 burden.

To date, scientists have addressed these questions with three sets of large-scale observations in the oceans and atmosphere. The first involves observations of CO_2 in the atmosphere. These observations directly record the anthropogenic CO_2 inventory in air. Comparing the rate of atmospheric CO_2 increase with rate of combustion gives the summed rate of CO_2 sequestration by the land and the oceans. Regional variations in the CO_2 concentration of air, interpreted using transport models, constrain the CO_2 uptake rate by the land biosphere and the oceans. Variations in the O_2/N_2 ratio of air and the $\delta^{13}C$ of CO_2 allow us to partition sequestration between the land biosphere and the oceans. Constraints currently apply to scales on the order of 10^4 km. As data density increases and models improve, we are gaining the ability to work at smaller scales.

The second observation set contains measurements of the partial pressure of CO_2 (pCO_2) in surface seawater. The air-sea pCO_2 difference, together with the gas exchange coefficient, gives the air-sea flux of CO_2. The global air-sea flux, annually averaged, constrains the rate at which the oceans take up anthropogenic CO_2. Spatial and seasonal variations in air-sea fluxes reflect the sum of carbon fluxes due to anthropogenic CO_2 uptake, ocean cir-

culation, biogeochemical transformations, and ocean heat fluxes. Sea surface pCO_2 data give basic information about each of these processes. Controlling processes are reflected in satellite data, which can then be used to scale up the local observations.

The third data set describes the distribution of CO_2 in the ocean interior. This property largely reflects the interaction of biological carbon fluxes, which induce depth and flow-line gradients in CO_2, and ocean circulation, which mixes water and dissipates those gradients. Superimposed on natural variations are the smaller variations in anthropogenic CO_2 concentrations. These can be teased out by using analysis techniques that rely in part on measured concentrations of other bioactive tracers (e.g., O_2). Resulting maps of the anthropogenic CO_2 distribution record both regional uptake of CO_2 at the sea surface and the effects of ocean currents in transporting and redistributing the oceanic burden.

Each of these data sets makes a unique contribution to our understanding of the ocean carbon cycle, both natural and anthropogenic. Each gives essential information about fluxes of anthropogenic CO_2, current CO_2 inventories, and the nature of processes responsible for ocean and land sequestration. Each also gives rates of air-sea or air-land CO_2 fluxes that are largely or completely independent of estimates from the other approaches at the various scales. For these reasons, we recommend that the observation system evolve as a balanced entity that continues to rely on CO_2 observations in all three realms: atmosphere, sea surface, and ocean interior. Redundant measures of carbon fluxes are also essential for confidently closing the mass balance, because calculations of anthropogenic carbon fluxes all have large uncertainties.

Models of transport and biogeochemistry are essential tools for interpreting the distribution of CO_2 and deducing carbon fluxes in the three major observation realms. We make a series of recommendations for improving skills of relevant models. One aspect of the recommendations involves collection of data that can challenge models, particularly models describing the CO_2 distribution in the continental planetary boundary layer, but ocean models as well. We also make recommendations for improvement to model structure and approaches that will lead to improved representation of basic processes and more accurate calculation of fluxes. A particular emphasis will be on including data assimilation methods in carbon cycle models. In general, our implementation plan considers that progress will be made only with close interactions between observations and modeling. Results from one will lead to improvements in the other.

Following recommendations of the U.S. Carbon Cycle Science Plan, we recommend the following observational strategy: (1) atmospheric studies focusing on North America, (2) sea surface pCO_2 studies focusing on the surrounding ocean basins (North Atlantic and North Pacific) and the Southern Ocean, and (3) ocean interior studies that center on the global scale, with the primary objective of constraining the distribution of anthropogenic CO_2 in the world's oceans.

The technology for measuring CO_2 and related properties is evolving rapidly, as are models that describe their distributions and allow us to esti-

mate source and sink strengths. We therefore recommend an initial 5-year program for atmosphere and sea surface studies. We recommend a 10-year program for ocean interior studies, which involve sampling by oceanographic research ships, a more mature technology.

2. Selected Ongoing Programs

We strongly recommend vigorous support for selected major ongoing U.S. programs to study the distribution of CO_2 and related properties in the atmosphere and oceans. These programs include flask sampling measurements of CO_2, O_2/N_2, $\delta^{13}C$ of CO_2, and related properties in air; repeat measurements of sea surface pCO_2 on oceanographic ships of opportunity; and measurements of biogeochemical properties at the sea surface and in the ocean interior at time-series study sites such as the Bermuda Atlantic Time Series site and the Hawaii Ocean Time Series site.

3. Recommended New Programs

We recommend the following new programs as high priority:

1. **Detailed measurements of atmospheric CO_2 over North America to improve understanding of the productivity of the land biosphere and our knowledge of CO_2 sequestration on the continent. Also, development of a new CO_2 analyzer for atmospheric measurements to improve the data and facilitate the measurement program.**

We recommend an intensive series of measurements of CO_2 and related properties over North America, made utilizing tall towers, vertically profiling aircraft, and aircraft sampling campaigns covering broad reaches of the continent. This work will give detailed CO_2 data, challenging models of the land biosphere and atmospheric circulation. The data, together with model improvements, will produce major advances in characterizing land ecosystem activity and the sequestration of CO_2 on the continent.

2. **Studies of the sea surface partial pressure of CO_2 (pCO_2) and air-sea fluxes in the North Atlantic, North Pacific, and Southern Ocean, to determine biogeochemical fluxes and constrain anthropogenic CO_2 uptake by these basins.**

We recommend a major expansion of sea surface pCO_2 measurements and related properties in the North Atlantic, North Pacific (including the equatorial Pacific), and the Southern Ocean. The measurements will be made primarily using volunteer observing ships, supplemented by moored samplers and other programs. The North Atlantic and North Pacific studies will yield constraints for improved estimates of the North American carbon sink, robust values of air-sea CO_2 fluxes in Northern Hemisphere oceans, and extensive new information about biogeochemical fluxes in the basins. The equatorial Pacific studies will provide measures of air-sea fluxes in a

region that accounts for a large fraction of ocean interannual variability. The Southern Ocean work will improve understanding of climatological fluxes in this region. It will also give insight into the carbon cycle of this ocean, which is an undersampled region widely regarded as susceptible to global change.

Calculating air-sea fluxes from sea surface pCO_2 data requires values for gas exchange coefficients. These coefficients are now characterized in terms of wind speed and are highly uncertain. We recommend process studies to more accurately characterize gas exchange coefficients, in terms of wind speed or other properties observed globally by satellites at high resolution.

3. **Systematic studies of CO_2 and related properties in the ocean interior, to characterize ocean mixing and map the distribution of fossil fuel CO_2.**

We recommend that 15 ocean sections, spanning all major basins, be resampled every 10 years for hydrographic and geochemical properties. The results will document the evolving inventory and distribution of fossil fuel-derived CO_2 in the ocean, constrain the distribution of surface ocean uptake, and serve as a constraint for ocean circulation models that predict the distribution of transient tracers.

These observations, along with the results of complementary process studies, and interpreted in the context of prognostic models, will lead to major advances in knowledge of the following topics:

- Fluxes and distribution of anthropogenic CO_2.
- Ocean and atmosphere mixing patterns.
- Biosphere processes that regulate CO_2 uptake on land and in the oceans.
- The expected future evolution of atmospheric CO_2.

4. **High-resolution time series studies of biogeochemical properties of the ocean using moored sensors.**

We recommend an aggressive program of developing, testing, and installing autonomous sensors of CO_2 parameters and other biogeochemical properties on moorings to make high-resolution measurements in waters of the ocean interior. The time series will inform us about the biogeochemical response to interannual and decadal timescale variability in ocean physics, giving process-level insight, and improving our understanding of the biogeochemical response to global change.

We also recommend one additional activity:

5. **Preparation of a biennial report that summarizes the status of carbon cycle studies and the known status of the carbon cycle itself.**

This report will have several functions:

- Summarizing the behavior of the global carbon cycle, with emphasis on recent results and on North America.
- Making the results of CO_2 observations and process studies available.
- Informing readers about the scope of ongoing observations, process studies, and modeling efforts.

The following tables (E-2 through E-4) summarize the recommendations from the observations chapters (Chapters 2, 3, and 4). Note that although the modeling and state of the carbon cycle assessments will require a significant level of investment, this report does not focus on delineating specifics nor the costs of those needs and they are not included in the tables. If desired, a future community group may choose to focus specifically on those needs and how much they would cost.

Table E-2: Priorities and cost estimates for surface observation program.

Element of the implementation plan	Priority	Ship time	Costs/year
Recommendations for the Next 1 to 5 Years*			
Form and improve international collaborations on unified data protocols	1		$300,000
Measure pCO_2 and related properties on volunteer observing ships			
VOS studies in the North Atlantic (4 ships)	1		$520,000
VOS studies in the Southern Ocean (existing/new 4 ships)	1/2		$600,000
VOS studies in the equatorial Pacific (2 ships)	1/2		$300,000
VOS studies in the equatorial and North Pacific (2 ships)	2		$600,000
Meridional trans-Atlantic and trans-Pacific lines (4 ships)	3		$150,000
Measurements of ancillary properties (5 ships)	1–5		$1,000,000
Improve our understanding of the physics of gas exchange			
Longer term observations	1		$750,000
Upscaling studies	2		$350,000
Process studies	3	$1,000,000	$1,500,000
Deploy moorings for time series of pCO_2 and related biogeochemical properties			
Time-series stations at HOT and BATS (including mooring)	1		$2,000,000
Equatorial Pacific time series (4 systems, excluding cost of moorings)	1		$600,000
Boreal time series in the North Atlantic and North Pacific (including mooring)	2	$1,000,000	$2,000,000
Time-series sites in the Southern Ocean (including mooring)	4	$1,000,000	$2,000,000
Design a data access system	2		$400,000
Develop improved autonomous sensors for sea surface analysis			
Develop improved autonomous sensors for sea surface analysis of pCO_2	2		$400,000
Develop for measurement of ancillary properties	3		$1,000,000
Develop formalisms for interpolating air-sea CO_2 fluxes in time and space	3		$300,000
Deploy drifters with pCO_2 sensors to map pCO_2 fields			
Southern Ocean drifters (20)	4	$1,000,000	$1,200,000
Subpolar/subtropical North Atlantic drifters (20)	4	$360,000	$1,200,000
Equatorial Pacific drifters (20)	4	$450,000	$1,200,000

*Results from years 1–5 will be used to plan for a comprehensive sea surface pCO_2 observing system 5 years hence as measurement technologies, modeling capabilities, and knowledge of ocean pCO_2 are improved.

Table E-3: Priorities and cost estimates for the interior ocean program.

Element of the implementation plan	Priority	Ship time* ($/year)	Science ($/year)
First 5-Year Period			
Meridional and Zonal Sections (Atlantic and Pacific Oceans)	1	$2,000,000	$2,100,000
Augmenting HOT, BATS, and Equatorial Pacific with autonomous sensors	1	$500,000	$1,500,000
Augmenting high-latitude time-series sites with CO_2 measurements	2	$500,000	$1,100,000
Develop/improve sensors for measurements of two CO_2 system properties	2		$500,000
Second 5-Year Period			
Meridional and Zonal Sections (Southern Oceans)	1	$1,500,000	$2,200,000
Meridional and Zonal Sections (Atlantic, Pacific, and Indian Oceans)	1	$1,500,000	$1,500,000
Augmenting Southern Ocean time-series sites with autonomous sensors	1	$500,000	$1,500,000
Instrumented profiling floats and gliders	2	$800,000	$1,500,000
Augmenting tropical and subtropical time-series sites with autonomous sensors	3	$500,000	$1,500,000

*Ship-time costs are estimated at $20,000 per day.

Table E-4: Summary of observation plan costs.*

	One-time Costs	Annual Costs	Annual Ship Cost
1–5 Years			
Priority 1			
Atmospheric Observations	$1,250,000	$4,625,000	
Surface Ocean Observations		$6,070,000	
Ocean Interior Observations		$3,600,000	$2,500,000
Subtotals	**$1,250,000**	**$14,295,000**	**$2,500,000**
Priority 2			
Atmospheric Observations	$5,300,000	$10,000,000/campaign $7,800,000	
Surface Ocean Observations		$4,250,000	$1,000,000
Ocean Interior Observations		$1,600,000	$500,000
Subtotals	**$5,300,000**	**$13,650,000 w/o campaign**	**$1,500,000**
Priority 3+			
Atmospheric Observations	$1,290,000	$1,840,000	$15,000/ship ($pCO_2$ platforms)
Surface Ocean Observations		$8,550,000	$3,810,000
Ocean Interior Observations			
Subtotals	$1,290,000	$10,390,000	$15,000/ship
Totals	$7,840,000	$38,335,000 + $10,000,000/campaign	$4,000,000 + 15,000/ship
6–10 Years			
Priority 1			
Atmospheric Observations	$15,000,000	$15,000,000	
Surface Ocean Observations			
Ocean Interior Observations		$5,200,000	$3,000,000
Subtotals	**$15,000,000**	**$20,200,000**	**$3,000,000**
Priority 2			
Atmospheric Observations			
Surface Ocean Observations			
Ocean Interior Observations		$1,500,000	$800,000
Subtotals	**N/A**	**$1,500,000**	**$800,000**
Priority 3+			
Atmospheric Observations			
Surface Ocean Observations			
Ocean Interior Observations		$1,500,000	$500,000
Subtotals		**$1,500,000**	**$500,000**
Totals	**$15,000,000**	**$23,200,000**	**$4,300,000**

*Note that modeling costs and costs associated with the biennial report on the state of the carbon cycle are not included, as this report did not focus on delineating the specifics and costs of those needs.

Chapter One

Introduction

1.1 Overview

Through a number of exercises, national and international, disciplinary and interdisciplinary, researchers have established plans for systematic carbon cycle studies. A landmark in U.S. planning efforts was the writing of the U.S. Carbon Cycle Science Plan (CCSP), published in 1999 (Sarmiento and Wofsy, 1999).

The CCSP defined two fundamental questions about the carbon cycle: What has happened to the carbon dioxide that has already been emitted by human activities (past anthropogenic CO_2)? And, what will be the future atmospheric CO_2 concentration trajectory resulting from both past and future emissions? In connection with these questions, the CCSP offered two hypotheses, consistent with a significant body of scientific evidence: First, a large terrestrial sink for anthropogenic CO_2 exists in the Northern Hemisphere. And second, the oceanic CO_2 inventory will continue to rise in response to increasing atmospheric partial pressure of CO_2 (pCO_2), but at a slower rate, owing to changes in ocean circulation, biology, and chemistry.

To address these questions and test these hypotheses, the CCSP formulated five long-term (5- to 10-year) goals and five short-term (5-year) goals. The first two long-term goals involve long-term observations: developing an observational infrastructure, and documenting the partitioning of CO_2 sources and sinks among oceanic and terrestrial regions. The remaining three long-term goals are aimed at greater process-level understanding and predictive capability. These latter two capabilities can be advanced only if process-level models can be tested against extensive, critical observations. The first two short-term goals rely primarily on observations: quantifying and understanding the Northern Hemisphere terrestrial carbon sink, and quantifying and understanding the uptake of anthropogenic CO_2 in the oceans. Accordingly, the CCSP targets North America and Eurasia as key continental areas. It identifies the North Atlantic and North Pacific as top priority ocean basins for air-sea flux studies. The Southern Ocean is also identified as a critical region in the long-term plan, because this region may be especially affected by climate change.

Inherent in the CCSP is the idea that an integrated approach involving a comprehensive and simultaneously executed observing strategy is essential to constrain the contemporary carbon cycle and to make meaningful forecasts (Appendices E and F). In November 1999, the NOAA Office of Global Programs commissioned the writing of an implementation plan for oceanic and atmospheric CO_2 observations, as a contribution toward implementing the U.S. Carbon Cycle Science Plan. This document presents that plan.

As envisioned in the commissioning letter, the plan presented here is not comprehensive. It deals with large-scale measurements of CO_2 and related

properties in the ocean and atmosphere. "Related properties" are a limited set of gases and solutes diagnostic of CO_2 sources and fluxes. This plan requires mechanistic insight from local process studies of the land and ocean biospheres to achieve its goals. It also requires satellite data defining a wide range of physical and biogeochemical properties in space and time. The land biosphere, ocean biosphere, and satellite studies are all subjects of continuing independent planning. This document complements those plans but does not attempt to duplicate them.

1.2 Background

Combustion of fossil fuels, and the attendant CO_2 increase, are likely to have a significant impact on Earth's climate. At the global scale of interest here, the main issue is the radiative forcing of CO_2 (and of other greenhouse gases), and the implications of this forcing for the global climate system. Related issues are the effects of atmospheric CO_2 on the biosphere, and the impacts of climate change on human endeavors.

Determining the fate of fossil fuel-derived CO_2, with its consequences for the rate at which the atmospheric CO_2inventory rises, is central to understanding and predicting the environmental effects of combustion. Processes relevant to the carbon cycle span the range of scales from molecular to global. They also include a wide range of biological, oceanographic, and atmospheric phenomena, as well as interactions between humans and the environment. Studies of the carbon cycle must adequately address the entire range of issues. The strategy for doing so requires studies at four different scales. The first is the scale of fundamental processes. In biology, this scale is at the molecular, cellular, or plant level. In ocean and atmospheric physics, it includes studies of turbulence and boundary layers. The second scale is that of the local ecosystem. Examples of such studies include those of the Long-Term Ecosystem Research (LTER) sites, free air CO_2 enrichment experiments (FACE), and the time-series and process studies of the Joint Global Ocean Flux Study (JGOFS).

The third scale is that of coherent ecosystems, spanning distances on the order of 10^3 km. This scale is accessed by studies of biogeochemical properties of the sea surface and of atmospheric gradients over the continents. The fourth scale encompasses spatial areas from continents and ocean basins to the globe. In research at these large scales, one attempts to assess changing CO_2 inventories and fluxes from observations of CO_2 in the ocean and atmosphere.

Acquiring a process-level understanding of large-scale fluxes is a critical goal of carbon cycle studies, and a requirement for prediction. Achieving this understanding begins with observations. It must also include modeling, which allows the quantitative representation of processes and thus scaling the implications of process studies. Carbon cycle models of the land biosphere represent the fundamental processes of photosynthesis and autotrophic and heterotrophic respiration. These models are formulated in the context of climate models, and can be used to calculate carbon fluxes at large scales.

Carbon cycle models of the ocean biosphere represent the food chain. They are formulated in the context of ocean and atmospheric physics models, which include implications for the transport of bioactive elements. Scaling and achieving process-level understanding both rely critically on satellite data, which allow us to closely track many biosphere properties, as well as the physical systems with which the biosphere interacts, over wide scales of time and space.

Atmospheric observations of the CO_2 distribution were pioneered by C.D. Keeling in 1957, and were continued by him and others at laboratories around the world. Atmospheric measurements of CO_2 constrain the net change in the atmospheric inventory. Sources and sinks of CO_2 to the atmosphere include input from combustion, exchange with the land biosphere, and exchange with the oceans. Deducing land-air and land-sea fluxes from CO_2 distributions is most straightforward at the global scale, where the CO_2 increase is equal to fossil fuel addition minus uptake by the ocean and land biosphere. Attempts are progressing to establish regional mass balances at the scale of a hemisphere and a continent/ocean basin (Fan *et al.*, 1998; Kaminski *et al.*, 1999; Rayner and Law, 1999; Bousquet *et al.*, 2000), but are still marked by large uncertainties. Complementary atmospheric measurements, notably the $\delta^{13}C$ of CO_2 and the O_2/N_2 ratio of air, allow one to partition CO_2 uptake into land and ocean sinks at the global or hemispheric scales. Atmospheric measurements constrain seasonal net production of the land and ocean biospheres on an annual timescale. They also constrain annual global and regional sequestration of fossil fuel CO_2.

Observations of the distribution of CO_2 and related properties in the ocean interior permit one to track the increasing inventory of fossil fuel CO_2. Beginning in 1972, the Geochemical Ocean Section Study (GEOSECS) made the first set of accurate and geographically comprehensive measurements that could be used in this way (Bainbridge, 1981; Broecker *et al.*, 1982; Weiss *et al.*, 1983). The global survey of the World Ocean Circulation Experiment (WOCE)/JGOFS accumulated a large and important data set in the 1990s. These and related studies made fundamental contributions to our understanding of patterns and rates of ocean circulation. They also contributed to a comprehensive picture of the oceanic distribution of bioactive chemicals and rates of biological transformations.

The fossil fuel CO_2 content of ocean interior waters is superimposed on the large background concentration of CO_2 in seawater. Chen and Millero (1979) and Brewer (1978) first proposed methods to separate the two CO_2 pools and calculate fossil fuel inventories. Gruber (1998) and Sabine *et al.* (1999) have recently modified the earlier approaches to compute the distribution of fossil fuel CO_2 in the Atlantic and Indian Oceans, respectively. It is thus possible to accurately discern inventory changes directly over periods of about 10–20 years. The $\delta^{13}C$ of total dissolved inorganic carbon (TCO_2) in seawater is influenced by the distinctive signature of fossil fuel carbon, giving a complementary tracer of the oceanic distribution of fossil fuel CO_2 (Quay *et al.*, 1992).

Ocean CO_2 uptake results from the difference in the partial pressure of CO_2 between the atmosphere and surface seawater. One can calculate the

rate of CO_2 invasion from the partial pressure difference and the gas exchange rate, which has generally been parameterized as a function of wind speed. In principle, calculating ocean CO_2 uptake is therefore straightforward. Unfortunately, sea surface pCO_2 is highly variable in time and space, and estimates of the gas exchange coefficient are uncertain. Thus the problem is daunting. Takahashi *et al.* (1999) have assembled a database of over 700,000 individual sea surface pCO_2 determinations that give basin- and global-scale estimates of climatological air-sea fluxes. Data coverage is uneven in time and space, however. Uncertainties remain large, particularly for constraining the global net flux. Temporal and spatial variability are so large that only now, for some areas of the ocean, can we go beyond creating a climatology, and examine interannual variability in air-sea fluxes. In principle, however, it is possible to constrain sea surface pCO_2 on seasonal timescales, and to study interannual variability on regional scales.

These three approaches to constraining the balance of fossil fuel CO_2 (involving atmospheric, sea surface, and ocean interior CO_2 measurements) give redundant information. For example, atmospheric measurements of CO_2, ocean interior measurements of TCO_2, and sea surface CO_2 measurements each allow one to calculate the rate of oceanic CO_2 sequestration. This redundancy is an absolutely critical attribute of ongoing CO_2 observations, because uncertainty associated with each approach is large. In addition, of course, observations based on CO_2 complement observations from a wide range of other approaches based, for example, on land carbon inventories and process studies of land and ocean biospheres.

Each observational approach also gives unique information about CO_2 fluxes, both fossil and natural. Atmospheric measurements give definitive information about the fossil fuel burden of the atmosphere. They integrate most rapidly over large spatial scales, thereby giving the best index of large-scale seasonal fluxes and interannual variability. Atmospheric measurements also provide unique information about continent-scale rates of CO_2 uptake by the land biosphere. Sea surface pCO_2 measurements, together with essential and problematic estimates of gas exchange coefficients, constrain the regional and temporal distribution of ocean uptake. Ocean interior concentrations of anthropogenic CO_2 reflect the regions where fossil fuel CO_2 is entering the oceans and its subsequent transport.

Finally, the three approaches give process-level information about the biosphere and its response to the evolution of Earth's climate. Seasonal variations in the CO_2 concentration, isotopic composition of CO_2, and O_2/N_2 ratio of air reflect mean rates and interannual variability of photosynthesis and respiration on land and in the oceans. Long-term data sets record the changing response of the biosphere to varying climate. Notable examples include net release of CO_2 by the land biosphere during most El Niño events (e.g., Keeling *et al.*, 1995), and increasing net seasonal production on land recorded by the increasing amplitude of the annual CO_2 cycle in the Northern Hemisphere (Myneni *et al.*, 1997). Sea surface pCO_2 data give a measure of net community production in the upper ocean. The link derives from the removal of TCO_2 during net production, which drives down the partial pressure of CO_2 in seawater. Sea surface pCO_2 thus quantitatively constrains

net production, after one corrects for the injection of subsurface waters, which are rich in CO_2 and supply essential nutrients, as well as for air-sea exchange. Finally, ocean interior studies give the distribution of TCO_2, nutrients, and O_2 utilization deriving from metabolism of organic matter produced in the surface ocean. The concentrations of these constituents in the dark ocean may vary with time (e.g., Pahlow and Riebesell, 2000), particularly in the thermocline, which is ventilated on a timescale of decades. Such variations might be due to changing rates of net production, changes in the composition of organic debris that sinks and is oxidized, or variations in rates of ocean circulation and ventilation.

In summary, observations of CO_2 inventories and fluxes in the three realms combine to constitute a comprehensive CO_2 observing system for the Earth. In Chapters 2 through 5, we recommend a plan for specific aspects of this system.

1.3 Planning Activities

A committee of 14 scientists involved in observing and modeling the distribution of CO_2 in the atmosphere and ocean was established to write this implementation plan for carbon observations, in the context of the CCSP. We first met at Princeton University in February 2000, to discuss the nature of the research and the plan itself.

At that time, the group took several key decisions. First, we decided to recommend continuation of all three approaches now used to determine transfers and inventories of anthropogenic CO_2: atmospheric observations, ocean interior observations, and determinations of pCO_2 in surface water that allow the calculation of air-sea fluxes. We believe that the large uncertainties associated with each approach make redundancy essential. We also felt that all three approaches must be continued because each gives essential process-level information.

Second, we decided to base our recommended observing systems largely on objective criteria derived from modeling studies, to the extent that this is possible given inherent limitations of this approach. Gloor *et al.* (2000) first used objective design to help identify the distribution of atmospheric CO_2 sampling sites that would give the most accurate estimate of annually averaged regional carbon fluxes. In this report, we examine the potential benefits of additional sampling, to plan an enhanced air sampling network. We also extensively analyzed results of sea surface CO_2 measurements to formulate a strategy for this component.

Third, we analyzed how the accuracy of calculated ocean interior CO_2 inventories depends on sampling density, and used these results to formulate a measurement strategy. Network design studies were carried out by P. Tans and B. Stephens for atmospheric measurements, T. Takahashi, P. Murphy, C. Sweeney, H. Gnanadesikan, and J.L. Sarmiento for sea surface pCO_2 studies, and C. Sabine, S. Doney, and R. Feely for ocean interior studies. Their work involved original research that made an important contribution to this report.

Fourth, we endorsed the Northern Hemisphere focus of the CCSP, with two modifications. We extended the North Pacific to include the equatorial Pacific, which is responsible for much of the interannual variability in the growth rate of the atmospheric CO_2 inventory. We also assigned the Southern Ocean a high priority for short-term as well as long-term studies. Strong arguments suggest that the Southern Ocean will very likely be especially affected by climate change. This critical but remote region is, paradoxically, quite accessible for sea surface pCO_2 observations, because a number of ships traverse its waters periodically to resupply Antarctic bases.

Fifth, we decided that the implementation plan for CO_2 observations should include a biennial assessment on the state of the carbon cycle. This report will summarize the status of carbon cycling (e.g., atmospheric CO_2 growth rate, ocean uptake rate) and its evolving dependence on climate. It will also summarize the status of studies of the carbon cycle, with emphasis on observations and relevant modeling.

Lastly, the committee recognized that most components of a truly global carbon observing system cannot be implemented in a single step. The planning, therefore, focused on the idea of an initial 5-year period in which key observational programs (some at regional/basin scale) are initiated. During this time, other infrastructure, development, and planning issues will be addressed (e.g., testing and evaluation of autonomous measurement systems, collection of data required to confidently design aspects of the observing system). The knowledge gained during the first 5 years would then be applied in a second 5-year phase in the expansion to a fully global system. Planning of CO_2 observations in the ocean interior is an exception: we are currently able to formulate a long-term plan for this work, and recommend such a plan here.

Following the Princeton meeting, members of the committee prepared and edited draft chapters outlining the atmospheric CO_2 measurements, sea surface pCO_2 measurements, and ocean interior measurements that would comprise the observation program. We then organized a meeting in Boulder, Colorado, in November 2000, to review these draft chapters.

About 45 scientists from university research laboratories, government laboratories, and federal funding agencies attended the Boulder meeting. The meeting began with a plenary session presenting, critiquing, and discussing each chapter of the implementation plan. It included a discussion of the role of modeling. This session was followed by breakout meetings dealing with the topics of individual chapters and related issues, interwoven with plenaries at which results of breakout sessions were discussed.

The consensus at the Boulder meeting confirmed that the CO_2 observing program should include atmospheric measurements, sea surface pCO_2 studies, and an ocean interior program. There were extensive discussions of the roles of modeling, remote sensing, and autonomous observations in the CO_2 observing system. There was also discussion of a broad range of details that are necessary for a successful plan. The meeting benefited tremendously from the very broad spectrum and depth of participants' expertise.

1.4 Structure of the Report

The document that follows contains three core chapters. They outline strategies for observing the distribution of CO_2 and its evolution in the atmosphere, the sea surface, and the ocean interior. A chapter on modeling CO_2 observations follows. The report does not outline a detailed strategy for modeling studies, but it does discuss the profound ways that models and data interact, and it outlines modeling advances required to improve our understanding of carbon fluxes. A brief chapter describing an annual report on the state of the carbon cycle comes next, and a short summary chapter closes the document.

Chapter Two

Atmospheric Observations

2.1 Overview

C.D. Keeling of the Scripps Institution of Oceanography was the first to make regular measurements of atmospheric CO_2 concentrations in 1958, at Mauna Loa (Fig. 2-1), Antarctica, and La Jolla (Keeling, 1960). Among other things, these measurements revealed a steady increase in atmospheric CO_2 approximately equal to half the rate of CO_2 emissions from human activities (Keeling *et al.*, 1989a). This removal of anthropogenic CO_2 from the atmosphere and its causes have significant consequences for future CO_2 and climate trends, and remain a very active area of research today. The Scripps CO_2 measurements continue through a global network of about 10 sites, and they have been complemented by the efforts of other U.S. and international laboratories. Most notably, the Cooperative Air Sampling Network of NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL), which began in the late 1960s (Komhyr *et al.*, 1985), now includes over 60 sites around the globe (Fig. 2-2).

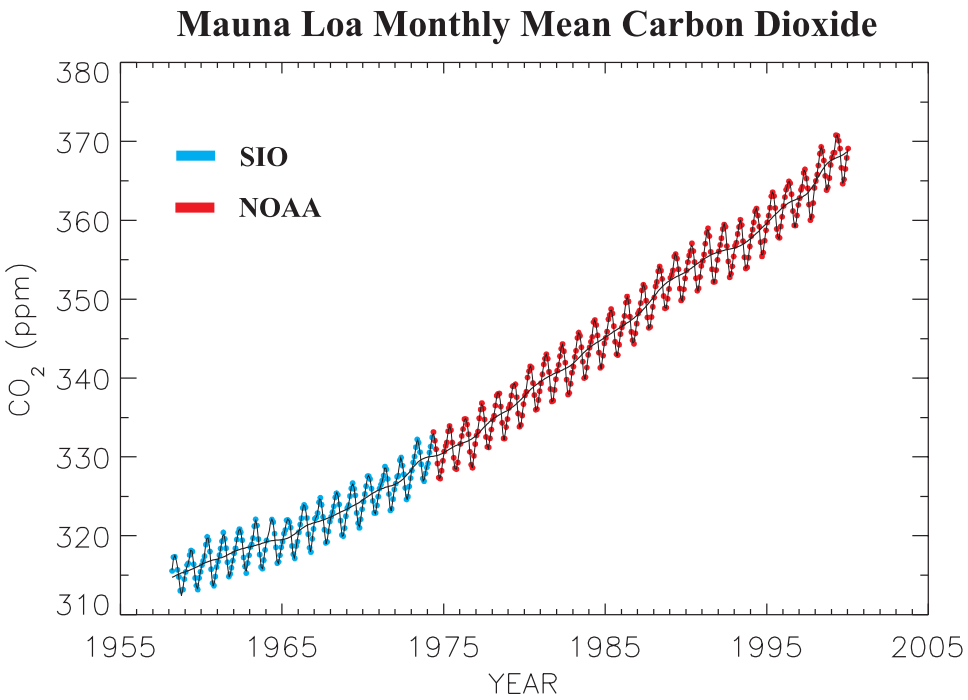


Figure 2-1: Atmospheric carbon dioxide monthly mean mixing ratios. Data prior to May 1974 are from the Scripps Institution of Oceanography, data since May 1974 are from the National Oceanic and Atmospheric Administration. A long-term trend curve is fitted to the monthly mean values.

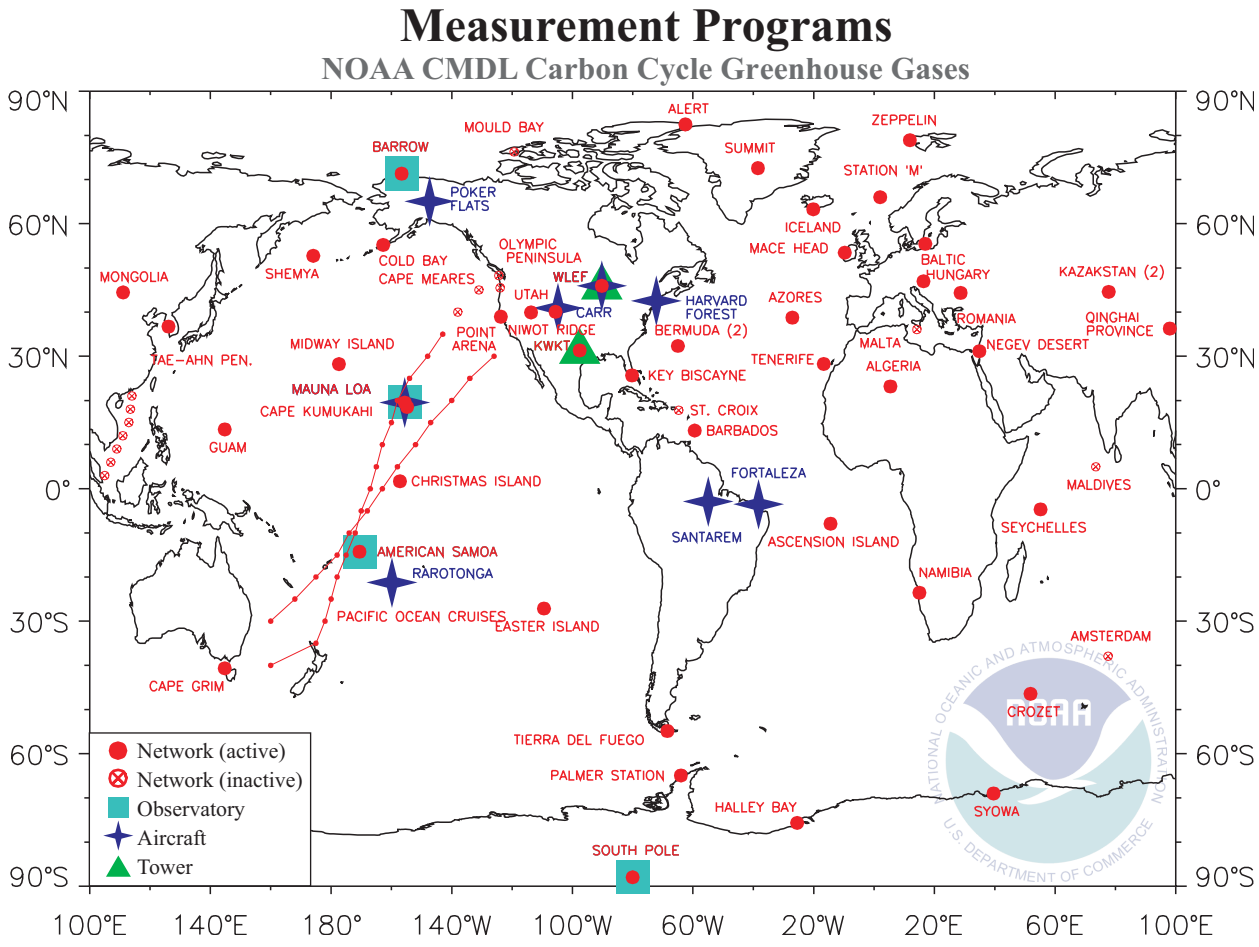


Figure 2-2: The NOAA CMDL Carbon Cycle Greenhouse Gases group operates four measurement programs. In situ measurements are made at the CMDL baseline observatories: Barrow, Alaska; Mauna Loa, Hawaii; Tutuila, American Samoa; and South Pole, Antarctica. The cooperative air-sampling network includes samples from fixed sites and commercial ships. Measurements from tall towers and aircraft began in 1992. Presently atmospheric carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexaflouride, and the stable isotopes of carbon dioxide and methane are measured.

By comparing CO_2 concentrations in the Northern and Southern Hemispheres, it appears that much of the anthropogenic CO_2 uptake must be occurring in northern mid-latitudes (Keeling *et al.*, 1989b) and that this uptake is likely a result of terrestrial processes (Tans *et al.*, 1990). Additional measurements of $^{13}C/^{12}C$ ratios in CO_2 (Keeling *et al.*, 1989a; Ciais *et al.*, 1995) and of O_2/N_2 ratios (Keeling and Shertz, 1992; Bender *et al.*, 1996) provide valuable constraints on the land-ocean partitioning of CO_2 uptake and the causes of seasonal to interannual variations in the CO_2 growth rate (Fig. 2-1) (Battle *et al.*, 2000).

Despite the significant advances to date, we must go still further in quantifying spatial and temporal variations in air-sea and air-land CO_2 fluxes, and identifying their controlling biogeochemical processes. This process-level understanding will be critical to resolving the relationships between atmospheric CO_2 and climate change, and to predicting future atmospheric CO_2

levels and climate. Atmospheric observations of CO_2, $^{13}C/^{12}C$ ratios in CO_2, and O_2/N_2 ratios will clearly continue to play a vital role in determining and predicting the fate of human-emitted CO_2. Measurements of additional atmospheric species should also be included in any attempt to understand the global carbon cycle. For example, $^{18}O/^{16}O$ ratios in CO_2 constrain gross rates of terrestrial exchange, and concentrations of CH_4 and N_2O are radiatively important and linked to terrestrial processes that also affect CO_2. Measurements of industrial tracers (e.g., CO, SF_6, $^{14}C/^{12}C$ ratios in CO_2), terrestrial tracers (e.g., ^{222}Rn), and oceanic tracers (e.g., Ar/N_2, O_2/N_2) will also be important in investigating atmospheric transport and validating fluxes calculated from inverse models. The recommendations in this report directly concern implementation of the oceanic and atmospheric components of the recently formulated U.S. Carbon Cycle Science Plan (CCSP, 1999). The CCSP and other documents provide additional background information on natural and anthropogenic effects on atmospheric CO_2 and their relationships to other atmospheric species (IPCC, 1996; CCSP, 1999; IPCC, 2001).

This chapter outlines and justifies specific research recommendations for the next decade that will ultimately result in a comprehensive atmospheric observing system for the global carbon cycle. To make this task tractable, we have divided our recommendations into two time horizons: 1 to 5 years, and 6 to 10 years. Because research directions in the second period depend on what we expect to learn in the first, we have focused our discussion and specific recommendations on the timescale of 1 to 5 years. For the timescale of 6 to 10 years, we make more general recommendations that will be adaptable according to the knowledge gained and technical and computational advances made in the interim.

The complexity of atmospheric mixing and CO_2 source and sink processes necessitates the use of sophisticated numerical models in interpreting observations and making predictions based on them. However, it is clear that existing atmospheric transport models (ATMs) are insufficient for this task (Gloor *et al.*, 2000). While the amount of background data is a fundamental limitation in these calculations, the models themselves are too coarse to use much of the information contained in existing measurements, and models also have large uncertainties in their representations of vertical transport. The modeling results we present in support of our recommendations below should not be misinterpreted as an endorsement of current models or inverse methods. Our approach with respect to existing and future models has several facets: (1) we anticipate significant modeling improvements in resolution, boundary-layer parameterization, and coupling to underlying process models in the next decade; (2) we conduct network design studies using existing ATMs to make our best estimate of what observations will be most useful in constraining regional CO_2 fluxes in conjunction with future models; and (3) we recommend specific observations that will challenge and support improvement in existing models.

2.1.1 The atmospheric observing system one decade from today

Our primary goal for the coming decade of atmospheric carbon cycle measurements is to build the U.S. contribution to sustained global observations that can accurately measure net CO_2 sources and sinks, natural and human, from large regions. Climate variations (IPCC, 1996), terrestrial ecosystem responses (Myneni *et al.*, 1997), and ocean CO_2 flux patterns (Takahashi *et al.*, 1997) are each reasonably coherent on a 1,000 km scale. For this reason, regional flux determinations will help achieve a quantitative understanding of processes controlling CO_2 fluxes between the atmosphere, oceans, and land biosphere. This knowledge is an important prerequisite for sound predictions of the carbon cycle's future behavior in response to natural and human perturbations. Regional-scale flux estimates will also help to bridge the current gap between local process-oriented studies and global constraints. Taking land use as an example, widespread regrowth of forests in the eastern half of the United States, as well as woody encroachment on grassland ecosystems in the southwest, should leave a measurable signature on atmospheric CO_2. Our future observing system should have the following characteristics:

- Regional spatial resolution, down to 10^6 km^2 on the continents and 10^7 km^2 over the oceans, with an accuracy of 0.1 Gt C/yr. This resolution will enable meaningful quantification of processes regulating surface carbon exchange. An ability to see the effects on atmospheric CO_2 of specific processes and mechanisms on these spatial scales will allow a marked increase of confidence in our understanding and predictive capability.

- Integration of satellite observations. The in situ measurements should be able to stand on their own, but will be merged with satellite CO_2 data if and when these become available, providing crucial accuracy to the latter. Space-based observations of the CO_2 mole fraction in the atmospheric column are expected to have nearly complete spatial coverage, but lower chemical resolution and accuracy.

- Assimilation of all available data. Data assimilation models must be an integral part of the observing system. The models should assimilate weather and CO_2 observations, and remotely sensed indicators of primary productivity. They should be high resolution in time and space, dynamically consistent, and include carbon processes.

2.1.2 Goals for the next 5 years

As a necessary step toward developing this observing system, we have set more immediate goals for the next 5 years. These goals are to measure the annual CO_2 flux between the temperate North American biosphere and the atmosphere to an accuracy of 0.2 Gt C/yr, while resolving the rest of the globe's continental regions to 0.5 Gt C/yr, and determining air-sea fluxes for major ocean regions to 0.1–0.2 Gt C/yr. A number of approaches show promise for achieving these goals in the near future:

- Calculation of CO_2 fluxes between surface regions and the atmosphere by direct inversion of atmospheric CO_2 data using ATMs, complemented by $^{13}C/^{12}C$ and O_2/N_2 observations (e.g., Gloor *et al.*, 2000; Fan *et al.*, 1998; Tans *et al.*, 1990; Keeling *et al.*, 1989b; see discussion below).

- Sea surface pCO_2 measurements synthesized with an ocean model and converted to fluxes using a gas-exchange parameterization (e.g., Takahashi *et al.*, 1997; see Chapter 3 of this report).

- Forward predictions or inverse calculations using biogeochemical ocean general circulation models (BOGCMs), constrained by observations of oceanic carbon, nutrients, oxygen, ^{13}C, and atmospheric O_2/N_2 (e.g., Murnane *et al.*, 1999; Gruber *et al.*, 1998; Quay *et al.*, 1992; Stephens *et al.*, 1998; see Chapter 4).

- Satellite observations of NDVI, land-use histories, tower eddy flux measurements, and forest and soil carbon inventories synthesized with terrestrial ecosystem models (TEMs) that link air-land CO_2 fluxes to terrestrial processes (e.g., Myneni *et al.*, 1997; Wofsy *et al.*, 1993; Schimel *et al.*, 2000; this research area is not a focus of report).

In the context of these broad approaches, atmospheric observations can contribute significantly to CO_2 flux estimates by providing the essential data required by inverse calculations, and by providing data to validate and improve ATMs, BOGCMs, and TEMs. With improvements to ATM boundary layer parameterizations, the existing network of atmospheric CO_2 monitoring stations (Fig. 2-2) will be sufficient to constrain surface fluxes on the scale of broad (20°–30°) latitudinal zones. In addition, atmospheric measurements of O_2/N_2 and $^{13}C/^{12}C$ will provide information on the terrestrial versus oceanic partitioning of these fluxes. Refining these atmospheric constraints to specific continental-scale areas, and in particular discriminating between fluxes from different regions at the same latitude, will require improved data quality, improved ATMs, and significant increases in data coverage.

Temperate North America is an important region for study of the terrestrial carbon cycle, because it is a potentially large sink for anthropogenic CO_2 (Fan *et al.*, 1998). Detailed knowledge of its ecosystems, soils, hydrology, past and present land use, and climate trends exist, allowing more robust modeling and analysis than in other regions. North America is also the natural region of focus for U.S.-led research. Furthermore, as the United States is currently the largest national CO_2 emitter, the region could provide a testing ground for the development of methods to measure the magnitude of fossil CO_2 emissions. We expect that initially focusing on one continental-scale region will greatly improve our chances for short-term success, and for learning how to extend similar coverage most efficiently to the entire globe.

In the next section and Addendum 2-1, we review the current status of atmospheric observations related to the carbon cycle. In the following section, we discuss the current limitations to atmospheric inverse calculations, and in Addendum 2-2 we use several ATMs to quantitatively estimate the

specific atmospheric observations, model improvements, and additional constraints required to achieve our stated 5-year goals. These analyses indicate the need for several advances: (1) additional background CO_2 measurements in specific locations primarily over the continents, (2) improvements to other global and regional constraints on the carbon cycle, (3) improved maintenance by individual laboratories of their calibration scale as well as ongoing tight comparisons of measurements between laboratories, and (4) improvements in the ATMs themselves. The potential biases and required measurement accuracy also point to the need for developing robust continuous CO_2 analyzers that allow calibrated measurements in the field. These analyzers would complement flask samples and could be used to take advantage of existing commercial ship and aircraft platforms. Finally, at the end of this chapter, we outline specific recommendations for enhanced atmospheric observations. While the scope of this chapter is restricted to the establishment of a sustained atmospheric observing system, we have indicated links to other activities needed to improve our understanding of the carbon cycle.

2.2 Background

2.2.1 Current status of atmospheric observations

Detecting regional- to continental-scale sources and sinks requires that the individual CO_2 concentration measurements have a certain level of consistency. As we show below by comparison to expected flux signals, this level is $\leq$0.1 ppm, in agreement with the internationally recognized goal set by the World Meteorological Organization (WMO) in 1981 (WMO, 1981). The accuracy of today's measurements is generally not better than $\pm$0.2 ppm, despite the fact that short-term precision or repeatability is often substantially better at about 0.05 ppm. Two measurement components are important to attaining accuracy. The first is the maintenance of a reference scale linked to primary quantities, along with the active maintenance of traceability to that scale by every laboratory. Second, the systematic biases associated with sampling and measurement methodology must be eliminated, by means of a very significant ongoing effort. The maintenance of traceability has been tested during the last decade by several "round robin" comparisons, in which sets of circulating high-pressure gas mixtures have been measured by more than 20 laboratories. The average standard deviation has been 0.15 ppm or greater (Globalview-CO_2, 2000), already short of the WMO goal. Measurement biases due to sampling, materials, gas-handling, instruments, and measurement protocols are added independently to the uncertainty of the calibration gases used. We present a discussion of such biases in Addendum 2-1.

Natural and anthropogenic CO_2 fluxes are inextricably linked to fluxes of other gases and tracers, such as O_2, CO, CH_4, N_2O, SF_6, and $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in CO_2. These linkages provide valuable opportunities to investigate CO_2 fluxes through related measurements. For example, measurements of $^{13}C/^{12}C$ ratios can distinguish contributions to CO_2 variations and fluxes from oceanic versus terrestrial (e.g., Ciais *et al.*, 1995; Battle *et al.*,

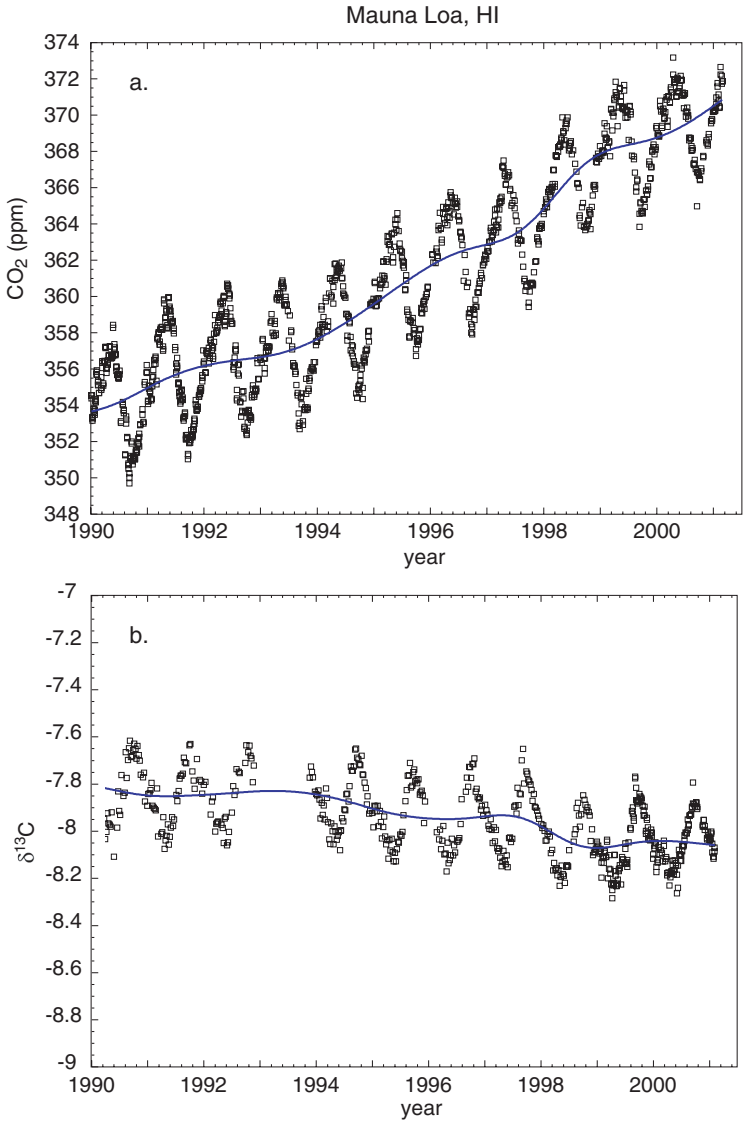


Figure 2-3: CO_2 and $^{13}C/^{12}C$ ratios measured by CMDL in air sampled at Mauna Loa. The decrease in CO_2 growth rate in 1997 combined with the corresponding decrease in the rate of $^{13}C/^{12}C$ decline is indicative of greater uptake by the land biosphere (Battle *et al.*, 2000).

2000), and C-3 versus C-4 photosynthetic processes (Farquhar *et al.*, 1989) (Fig. 2-3). This is made possible by the preferential uptake of ^{12}C relative to ^{13}C during C-3 photosynthesis, and the relatively smaller discriminations during C-4 photosynthesis and oceanic exchange. Isotopic measurements are difficult and even more prone to the type of systematic biases discussed for CO_2 concentration measurements in Addendum 2-1. Ongoing interlaboratory comparisons indicate that current agreement is typically no better than 0.02 permil, and occasionally worse than 0.05 permil. These offsets are still quite large relative to the recognized international goal of 0.01 permil (Allison *et al.*, 1995). Improvements to these measurements will lead directly to improvements in the value of the $^{13}C/^{12}C$ constraints on carbon cycling.

Recent measurements of atmospheric O_2 concentrations (expressed as O_2/N_2 ratios) have also led to new insights into the carbon cycle that were not possible through measurements of CO_2 alone. Most significantly, the detection of interannual trends in O_2 (Fig. 2-4) has allowed the separate calculation of global oceanic and terrestrial sinks for anthropogenic carbon (e.g., Keeling and Shertz, 1992; Bender *et al.*, 1996; Keeling *et al.*, 1996b). This constraint is made possible by the tight link between CO_2 and O_2 during terrestrial photosynthesis and respiration, and the lack of any O_2 release associated with the oceanic uptake of anthropogenic CO_2. In addition, measurements of seasonal cycles in atmospheric O_2 have provided hemispheric estimates of oceanic biological productivity (Keeling and Shertz, 1992; Bender *et al.*, 1996) and air-sea gas exchange (Keeling *et al.*, 1998). Observed latitudinal variations in atmospheric O_2 constrain the southward transport of O_2 and CO_2 in the oceans (Keeling *et al.*, 1996b), and have been used to test the performance of global ocean carbon cycle models (Stephens *et al.*, 1998). Because of the high level of relative precision, measurements of O_2/N_2 are even more susceptible to systematic errors than are measurements of CO_2 and ^{13}C. Interlaboratory comparisons for O_2/N_2 are currently not sufficient. Furthermore, additional work on the effects of various gas-handling methods can improve the measurements considerably.

CO_2 observations from 18 laboratories, at 65 fixed surface sites, three towers, three regular vertical profiles from aircraft, and two repeated ship transects are included in the current release of the Globalview database (Globalview-CO_2, 2000). A substantial number of existing observations have still not been included, in some cases because the records are very short, but more often because the laboratory responsible for the data does not participate in the effort to make data widely available in a global context. Measurements of $^{13}C/^{12}C$ and O_2/N_2 ratios are also made by multiple laboratories on somewhat smaller networks, but it has not yet been possible to combine measurements of these quantities from different groups into consistent data sets.

Atmospheric observations have led to some important discoveries in recent years. Figure 2-5 shows the surface interhemispheric CO_2 gradient due to fossil fuel burning alone, as modeled by 12 different transport models (Transcom 2 project, Law *et al.*, 1996). The average observed gradient from 1980 to 1990 is plotted as a thick black line. The discrepancies suggest a large net CO_2 sink at temperate latitudes in the Northern Hemisphere, a tropical source, and a sink at temperate southern latitudes. Combined with oceanic sink estimates based on CO_2 partial-pressure differences across the air-sea interface, this general picture has led to the hypothesis of a large terrestrial sink in the Northern Hemisphere (Tans *et al.*, 1990). The hypothesis has been supported by measurements of atmospheric oxygen (Keeling *et al.*, 1996b) and the $^{13}C/^{12}C$ ratio of CO_2 (Ciais *et al.*, 1995). The amplitude of the annual cycle of CO_2 has also increased significantly over the last few decades (Keeling *et al.*, 1996a). This change has been attributed to an earlier start of the growing season.

Currently, attempts are being made to interpret the observed east-west concentration difference between the North Atlantic and North Pacific basins

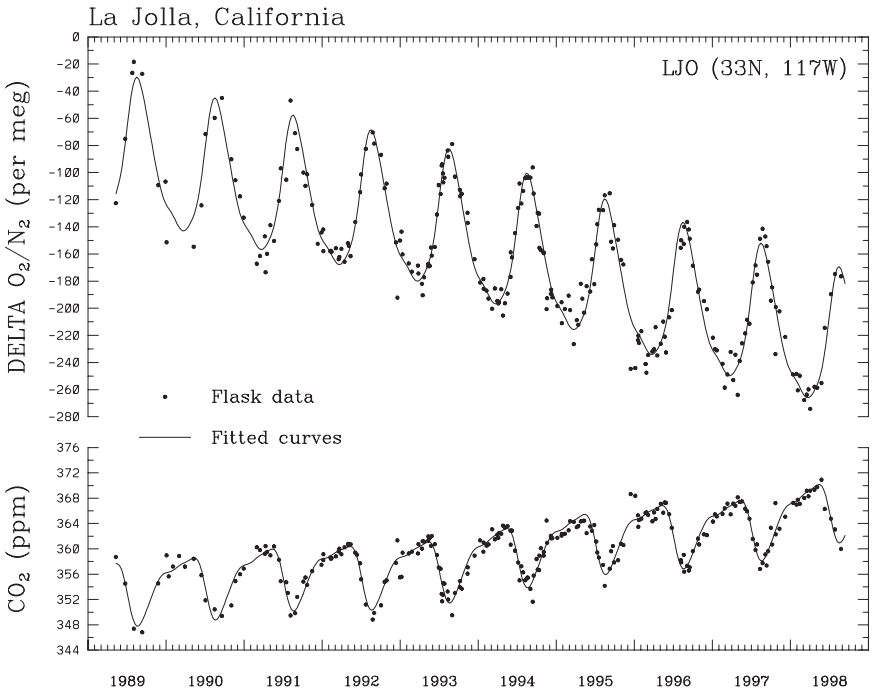


Figure 2-4: CO_2 and O_2/N_2 ratios measured by the Scripps O_2 Laboratory in air sampled at La Jolla. The vertical scales have been adjusted to be equivalent on a mole to mole basis. The greater rate of O_2/N_2 decline than CO_2 increase indicates that a significant amount of the industrial CO_2 emissions are being taken up by the oceans without a corresponding release of O_2 (Keeling *et al.*, 1996b).

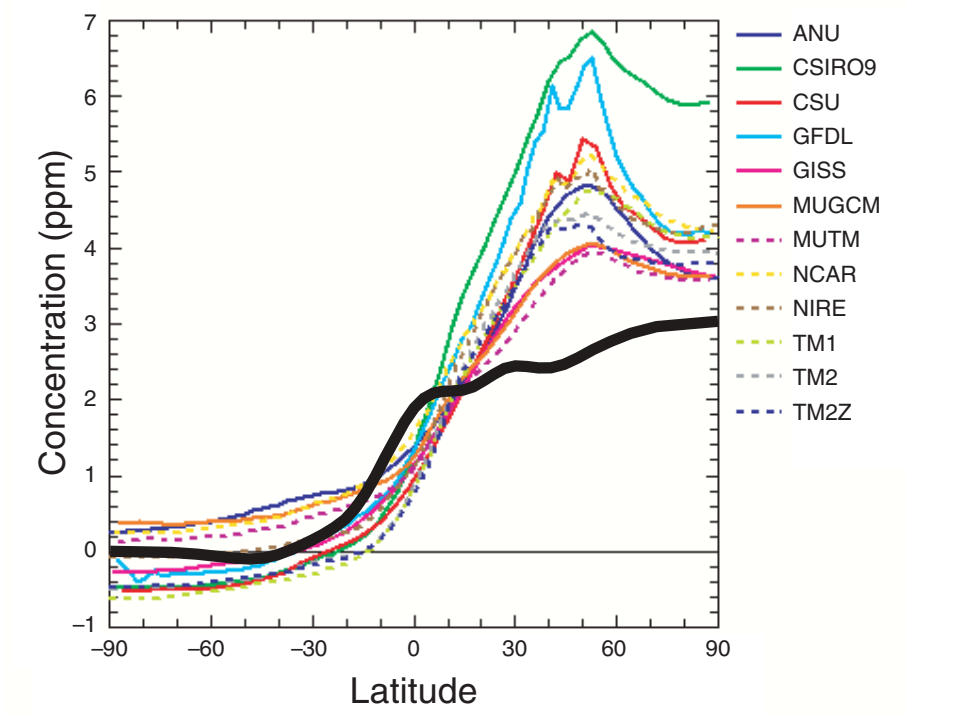


Figure 2-5: North-south zonal mean surface CO_2 concentration gradient resulting from fossil-fuel emissions, as modeled by 12 different atmospheric transport models (from Law *et al.*, 1996). The observed gradient from the CMDL network is shown as the thick black line.

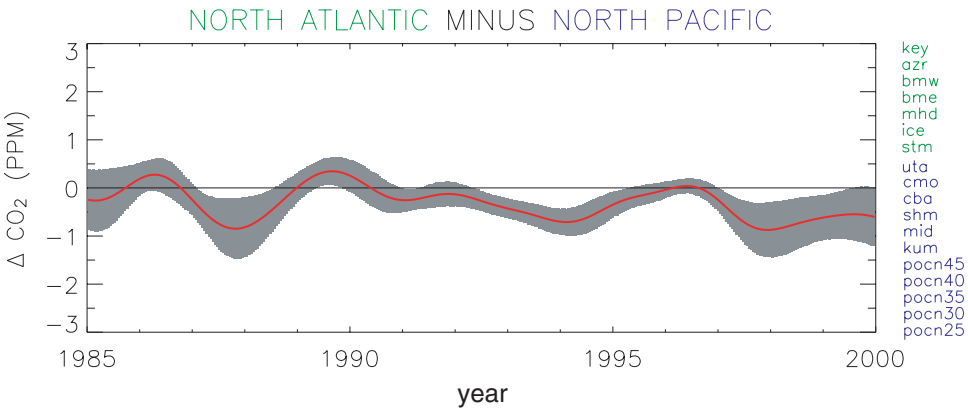


Figure 2-6: Annual-average atmospheric CO_2 concentration difference between the North Atlantic and the North Pacific basins, as observed at the CMDL network stations listed. The shaded band is an uncertainty estimate based on results using various subsets of these stations.

in terms of terrestrial and oceanic sources and sinks at these latitudes (Fig. 2-6). As discussed below, partitioning fluxes into various regions at similar latitudes will require better understanding of seasonal and diurnal mixing over the continents, in addition to the use of all available data. Sustained observations on very tall towers can be valuable in this respect. Measurements from towers in North Carolina and Wisconsin (Fig. 2-7a) (Bakwin *et al.*, 1998) show that the amplitude of the annual cycle over land is larger than, and that its phase leads, the annual cycle over the oceans. The continental boundary layer concentration also exhibits a strong and varying diurnal cycle superimposed on synoptic-scale variations (Fig. 2-7b) (Bakwin *et al.*, 1998).

2.2.2 Current limitations to inversions

A few simple calculations illustrate the strength of atmospheric CO_2 signals associated with various surface fluxes. Table 2-1 shows the magnitude of the rate of CO_2 change in the entire vertical column of air for several sources and sinks of interest. With a nominal measurement precision of 0.1 ppm, it is clear from Table 2-1 that emissions from Los Angeles should be very easy to measure. A 1 Gt C/yr sink distributed over the United States should also be detectable. If we assume a 5-day residence time for air over the United States, and that half the total column is mixed with surface air during this time, we estimate a signal in the lower atmosphere of $-0.08 \times 5 \times 2 = -0.8$ ppm for this postulated sink. This change in CO_2 mole fraction is comparable to the signals predicted by atmospheric transport models (ATMs) (Fig. 2-8a). This general relationship between flux and atmospheric surface signals of around 1 ppm /(Gt C/yr) for a continental-scale region, combined with the expected magnitudes of regional- to continental-scale fluxes, leads to our goal for interlaboratory agreement and measurement precision of 0.1 ppm or better.

Actual boundary layer signals will depend on the boundary layer thick-

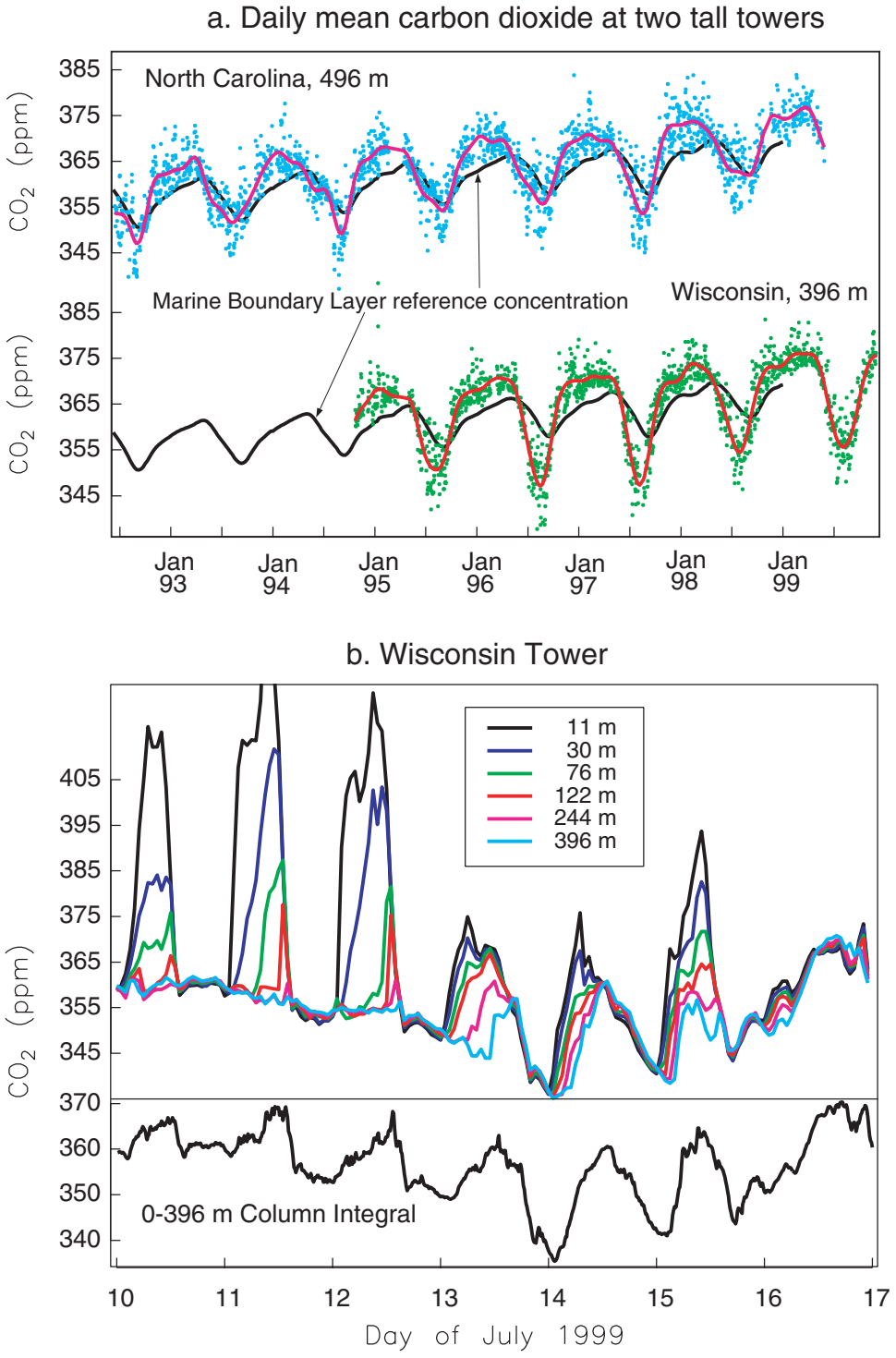


Figure 2-7: (a) Daily mean CO_2 mole fraction observed at two very tall towers. Also indicated are the simultaneous CO_2 trends observed over the oceans at the same latitudes as each tower. (b) One week of continuous CO_2 data collected from different heights on the WLEF transmitter tower in Wisconsin.

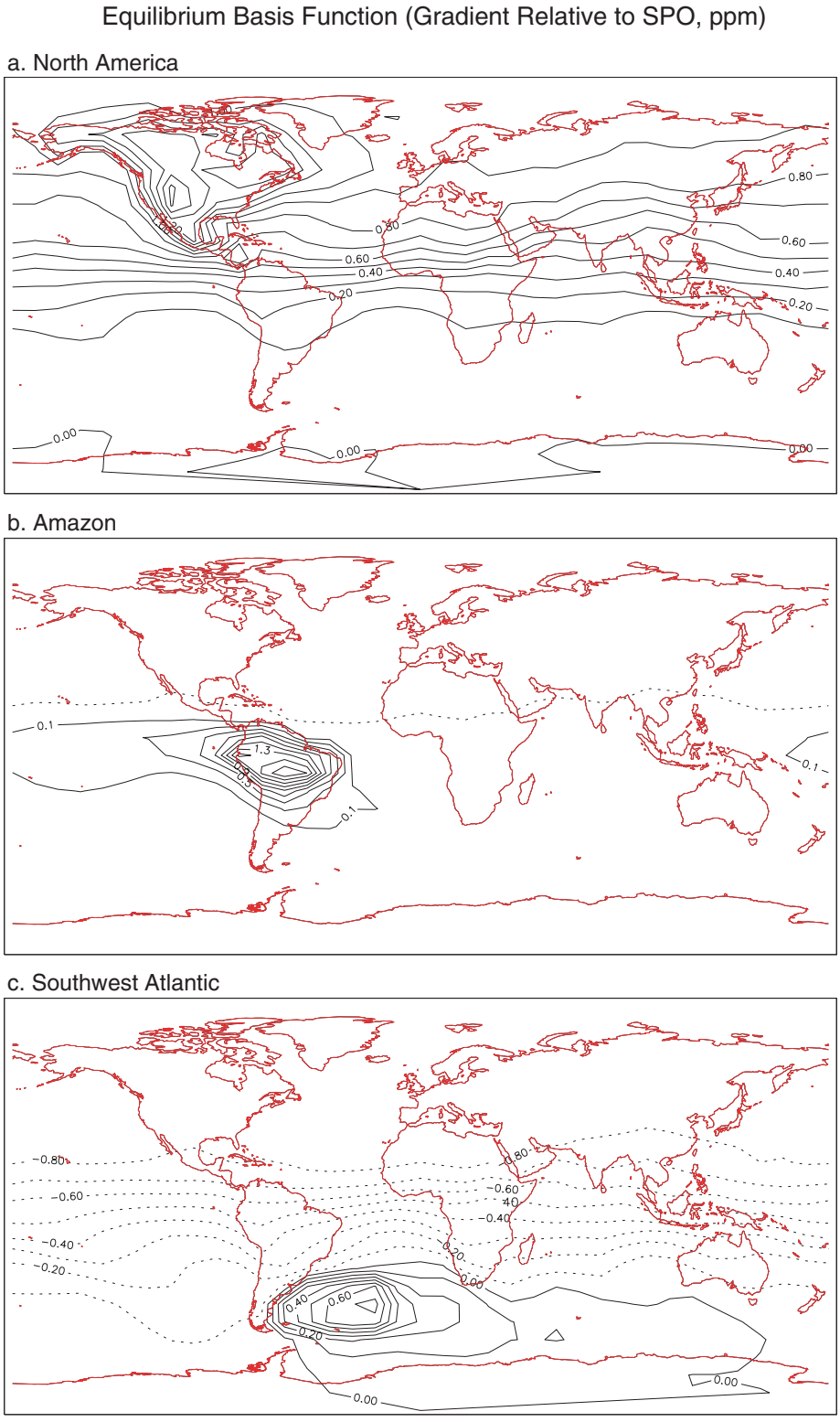


Figure 2-8: Equilibrium surface CO_2 concentrations ("footprints"), relative to the South Pole, calculated with the TM3 model for 1 Gt C/yr sources evenly distributed over (a) North America, (b) tropical South America, and (c) the western mid-latitude South Atlantic. The source in (c) corresponds to a region of significantly high chlorophyll and low pCO_2. Compare these signals to the locations of flask sites shown in Fig. 2-2.

ness, the rate of mixing with the free troposphere, and the residence time of air over the region. ATMs are thus needed to estimate the specific CO_2 concentration changes, as a function of time and place, resulting from a given surface flux. Conversely, ATMs can also be used to estimate surface fluxes from observed atmospheric CO_2 concentration changes. This approach is known as an atmospheric inverse calculation, or inversion. Sensitivity studies using ATMs show that the direct inversion of atmospheric CO_2 concentrations to obtain continental-scale fluxes is feasible. However, present uncertainties are large because of several factors: (1) limited CO_2 data relative to the dilution of signals by atmospheric mixing; (2) the coarse resolution of current inverse models, leading to the treatment of unresolved spatial and temporal variability as noise; and (3) systematic errors in ATMs. Focusing first on data sparseness, Gloor *et al.* (1999) investigated data requirements for calculating fluxes using existing models, assuming there were no errors in atmospheric transport. They found that resolving fluxes for 17 global regions to ± 0.2 Gt C/yr required a network of 150 randomly placed surface stations. This is approximately double the size of the current network.

The primary factor that leads to this high number of required stations is the mismatch in time and space between high-resolution variability in the CO_2 data and sources and the coarse resolution resolvable by existing ATMs. Figure 2-8a shows the atmospheric "footprint" of a 1 Gt C/yr source, invariant in time and uniform over North America, as calculated using the TM3 ATM (Heimann, 1995). Again, it is clear from the calculation above, together with this figure and the numbers in Table 2-1, that resolving temperate North American fluxes to a few tenths of a Gt C/yr will require measurements of annual mean spatial gradients at a precision of 0.1–0.2 ppm. Table 2-2 lists the observed short-term CO_2 variance from a subset of the CMDL network. For the remote marine boundary-layer continental high-altitude sites, the natural variability is small enough that annual mean gradients of a few tenths of a ppm can be resolved with good interstation consistency of calibrations and other quality control measures. However, because of the high variability of sources and boundary layer mixing over the continents, the annual mean precision at a continental boundary layer station is limited to around 0.4 ppm even with continuous data. The continental measurements shown in Fig. 2-7 illustrate this enhanced variability.

There is a strong need for inverse models with actual winds and accurate boundary layer representations that can use the information contained in this natural variability, rather than treating it as noise. Even at marine boundary layer sites, the inability of models to deal with natural variability is a major limitation. For example, consider two flasks from the Bermuda sampling site, one collected when air was coming directly off of temperate North America and the other when air was coming from over the North Atlantic. Current inverse approaches attempt to distinguish between temperate North American and North Atlantic CO_2 sources using only the average concentration of such flasks. There is obviously much more information contained in the difference in concentration between such flasks, and an approach that could account for synoptic variability and use this information to constrain continental-scale fluxes would be much more powerful.

Table 2-1: Rate of change in integrated vertical column abundance for specific CO_2 sources and sinks.

Source	Assumptions	ppm/day
Los Angeles Basin	12×10^6 people, 4,000 km^2, 1100 mol C/person/day	+10
Netherlands	16×10^6 people, 40,000 km^2, 500 mol C/person/day	+0.6
Germany	83×10^6 people, 350,000 km^2, 580 mol C/person/day	+0.4
Photosynthetic Uptake	Harvard Forest, July	–1.2
U.S. Carbon Sink	1 Gt C/yr, constant in time, uniform over the lower 48 states	–0.08
Southern Oceans	$\Delta pCO_2 = -30$ μatm, wind 15 m/s	–0.06
Eastern Equatorial Pacific	$\Delta pCO_2 = 100$ μatm, wind 7 m/s	+0.04

A second major source of uncertainty in inverse calculations results from the fact that, because of the high CO_2 variability over continents, most of the monitoring stations have been located in the remote marine boundary layer (Fig. 2-2). However, as the footprints in Fig. 2-8 indicate, it is very important to extend the scope of observations to monitor regional CO_2 over the continents in order to quantify fluxes from these regions and link them to specific processes. By comparing the Amazon footprint in Fig. 2-8b to the station locations in Fig. 2-2, it is clear that the existing NOAA/CMDL network observes almost none of this signal. In fact, current inverse calculations must estimate the CO_2 balance of the tropical land biosphere as a residual between fluxes that are estimated in other regions and the global budget, leading to large uncertainties. Furthermore, while some continental footprints do extend out over the oceans, in general these remote signals partly overlap those from other continental-scale regions. For example, a mean difference between the Azores and Barbados could result from either a North American or Eurasian temperate source. Figure 2-9 shows the difference between source footprints from North American and Eurasian boreal sources, as calculated by one ATM (Gloor *et al.*, 1999). The unique elements of these signals are confined almost entirely over the continents. Not surprisingly, the Gloor *et al.* (1999) study found that the number of required stations increased dramatically if they were limited to marine boundary layer locations.

A third source of uncertainty in inverse calculations is systematic error in transport models. Fluxes determined from present inversions are highly model-dependent. Gloor *et al.* (1999) found that inferred SF_6 fluxes varied by a factor of two among 10 different ATMs all inverting the same simulated data on the Globalview network. The magnitude of the North American sink appears to be quite model-dependent (Fan *et al.*, 1998; Rayner *et al.*, 1999; Bousquet *et al.*, 1999), though these differences in magnitude are also influenced by choices in data selection, assumed flux patterns, and presubtracted responses to seasonal biospheric fluxes.

The greatest inconsistency among ATMs is their treatment of vertical

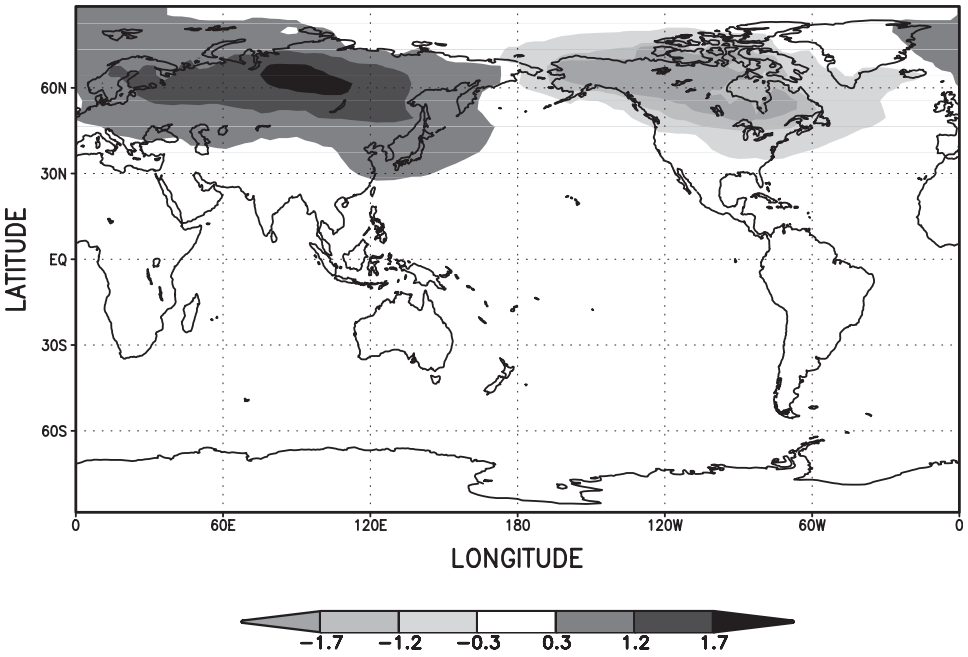


Figure 2-9: Difference between flux footprints, in ppm (Gt C/yr), from Eurasian boreal and North American boreal regions (from Gloor *et al.*, 1999).

mixing through the planetary boundary layer (PBL). This is particularly significant because covariations between mixing and surface fluxes, known as rectifier effects, can produce significant mean CO_2 gradients. For example, during summer when mixing through the PBL is vigorous, the CO_2 deficit due to net biospheric uptake is mitigated by dilution. In contrast, during winter when the PBL is shallow, the CO_2 increase due to net biospheric efflux is enhanced, thus resulting in higher annual-mean CO_2 concentration at the surface and over the continents. The TransCom study showed that rectifier effects produced north-south gradients in 11 ATMs ranging from –1.4 to + 3 ppm, as large or larger than gradients expected from net surface fluxes (Rayner and Law, 1995). Rectifier effects are likely to be just as important to investigating zonal variations in concentrations and fluxes, because of the potential for temporal and vertical variations in atmospheric transport between continents and oceans. Such transport uncertainties must be resolved before inverse calculations can be confidently carried out.

Yet another difficulty associated with the present form of inverse models is the need to prescribe the spatial and temporal patterns of fluxes within each region. Any mismatches between the chosen patterns and the real ones, and particularly interannual variations in the flux patterns, will result in significant model biases. A potential solution to this problem would be to use coupled models that could invert for parameters controlling the underlying processes, rather than for fixed scaling factors.

All of the limitations discussed above become even more significant when trying to invert atmospheric observations to calculate surface fluxes on regional ($\sim 10^6$ km^2) instead of continental scales. Figure 2-10 shows the footprint from a 10^6 km^2 region in the southwestern United States, simulated

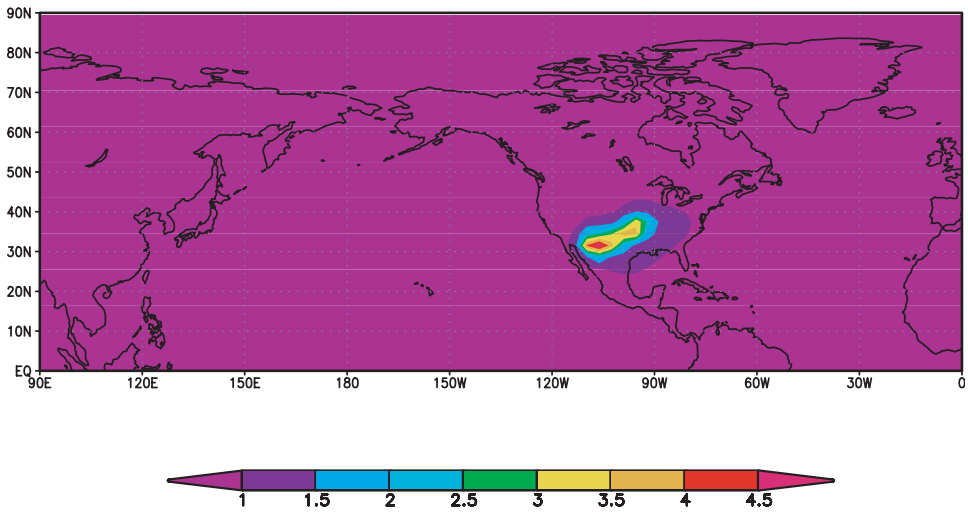


Figure 2-10: Flux footprint, in ppm (Gt C/yr), for a 10^6 km^2 chaparral region in the U.S. Southwest (Gloor *et al.*, 1999).

by an ATM (Gloor *et al.*, 1999). A flux from this region of 0.2 Gt C/yr is predicted to produce measurable annual mean gradients on the order of 0.8 ppm, but on a much smaller spatial scale than those shown for continental-scale regions in Figs. 2-8 and 2-9. Detection of such gradients is also made difficult by the high continental CO_2 variability, which limits annual mean concentration determinations at continental sites to no better than 0.3 ppm (Table 2-2). It appears from Fig. 2-10 and Table 2-2 that a minimum requirement for observing regional fluxes over temperate North America is boundary layer measurements at about 20 sites, and a modeling framework that allows interpreting actual data and synoptic conditions, rather than using monthly or annual means.

Current ATMs, though not perfect, can provide a basis for estimating the most favorable location and nature of our future measurements. The sensitivity tests presented in Addendum 2-2 indicate that reducing the error over temperate North America to 0.2 Gt C/yr is achievable, but will likely require a combination of approaches. Specifically, additional measurements of background CO_2 over South America, Africa, Siberia, the Southern Ocean, and temperate North America, and additional measurements of atmospheric O_2/N_2, $^{13}C/^{12}C$ ratios in atmospheric CO_2, and ocean surface pCO_2 will all advance future atmospheric inverse calculations. If ATMs and inverse methodology can be improved to account for a significant fraction of the high-frequency variability now dealt with as noise, especially at continental sites, this task will be much easier. In that case, the observing system will also be much more fruitful in providing links to process observations, which will improve our understanding of the carbon cycle and predictive capability. An essential element of model improvements is that they be challenged with measurements specifically targeted to test the models' assumptions and performance. These include both intensive measurement campaigns and long-term observations, especially in the vertical dimension.

Table 2-2: Variance in CO_2 observations at selected CMDL sites.

Station Location	Sample frequency	Standard deviation of residuals from smoothed, seasonal curve (ppm)	Estimated standard error of annual mean
South Pole	1/wk	0.1	0.01
Cape Grim	1/wk	0.2	0.03
Samoa	1/wk	0.4	0.06
Cape Kumukahi	1/wk	0.7	0.10
Point Barrow	1/wk	1.1	0.15
Bermuda	1/wk	1.3	0.18
WLEF 400 m	1/day*	3.0	0.26
WITN 500 m	1/day*	4.0	0.35
Baltic Sea	2/wk	4.0	0.40
Mauna Loa	1/wk	0.5	0.07
Niwot Ridge	1/wk	1.0	0.14
Carr 3,000 m	1/wk	1.3	0.18
Carr 6,000 m	1/wk	0.7	0.10
Gobi Desert	1/wk	1.6	0.22

*Assuming two independent measurements per week for conversion to annual mean.

2.3 Recommendations

The overall research objective is to use atmospheric measurements on a space and timescale detailed enough to quantify the effect of all processes, natural and human, that have a major effect on the carbon cycle. This objective corresponds to the first long-term goal of the U.S. Carbon Cycle Science Plan (CCSP, 1999), namely, developing an observational infrastructure and documenting the partitioning among major CO_2 sources and sinks. We make specific recommendations concerning research activities on a timescale of 1 to 5 years, and more general recommendations for the timescale of 6 to 10 years hence.

As discussed above, the existing observational network has contributed greatly to current understanding of the carbon cycle and will provide a critical foundation for expanded measurements in the future. Thus, our first priority is to continue support for these measurements. It is also clear that improving atmospheric constraints on CO_2 fluxes, from the current resolution of broad latitudinal zones to the regional scales that will give process information and prognostic capability, will require significant advances in both the quantity and quality of the measurements. Therefore our second priority is developing a robust and inexpensive in situ CO_2 analyzer to improve the quality of background data by providing measurements independent of potential flask-sampling and analysis biases, and the quantity of data by allowing extensive measurements from aircraft, tall tower, and oceanographic platforms. Our third top priority is improving the quality and comparability of measurements made by various groups to the high levels required for regional- to continental-scale flux determinations.

The observational system that we recommend will have a large numerical modeling component. However, because of the existing sensitivity to

high-frequency data variability and systematic atmospheric transport model (ATM) errors discussed earlier, these models must undergo major improvements in terms of their boundary layer representations, and their ability to use assimilated meteorological data and discrete observations, before they can be used to take advantage of the recommended measurements. A more comprehensive modeling goal is to develop carbon cycle models that incorporate known carbon cycle processes, that are capable of incorporating remote-sensing data, that are fully dynamically consistent, and that have resolution high enough to make the confrontation with CO_2 data compelling. These developmental efforts are already underway in several modeling groups.

While we make no specific modeling recommendations in this chapter (see Chapter 5), potential model-data interactions weigh heavily in our choice of recommended measurements. Our second priority level focuses on making intensive and extensive measurements of the vertical and continental distribution of CO_2 that will confront and drive model improvements. The intensive observations will also allow direct flux estimates and column-integrated CO_2 measurements, which can provide valuable process and network-design information independent of improvements to existing ATMs. In our third priority level, we recommend increased measurements of CO_2 and other species in important regions. These last measurements will also be valuable and necessary to achieving our goals, and in some cases their cost-effectiveness may suggest that they be implemented before items higher on the list. We describe the recommendations below, and list them collectively in Table 2-3.

2.3.1 Recommendations for the next 1 to 5 years

Priority Level 1: Improve the quality of existing measurements and support technological development.

1.a. Continue the existing network. The continuation of existing atmospheric measurement programs for CO_2, its isotopic ratios, O_2/N_2, and supporting data, and their interpretation needs to be assured. For CO_2, this includes the airborne profiles recently begun over South America and other regions, as well as modest participation in the Siberian tall tower and aircraft projects currently being implemented by European groups. For O_2/N_2, this recommendation includes tropical stations and shipboard sampling recently and currently being implemented. The data produced from existing atmospheric measurement programs have proved essential to our understanding of the carbon cycle and its development in recent times. Gradually increasing support to counter inflation is necessary to sustain these observations over many years. Also, a modest increase in support is appropriate to achieve the full workup of data as close as possible to its time of collection.

Cost estimate: Currently $4,000,000 per year (ongoing).

CCSP: Program Element 3.

1.b. Develop and implement a new CO_2 analyzer that is robust, precise, and autonomously operated. The goal is to attain measurement consistency between sites and among laboratories to a level of 0.1 ppm, and to allow extensive measurements on aircraft, tall tower, and oceanographic

Table 2-3: Priorities and cost estimates for atmospheric observation program.

Element of the implementation plan	Priority	One-time Costs	Per-year Costs
Recommendations for the Next 1 to 5 Years			
Improve the quality of existing measurements and support technological development			
Continue existing network	1		\$4,000,000
Robust CO_2 analyzer	1	\$750,000	\$150,000
Quality control and methodology			
CO_2 standards propagation	1		\$50,000
Ongoing intercomparisons	1		\$225,000
CO_2 isotopic calibration scale	1	\$500,000	
$^{13}C/^{12}C$ intercomparisons	1		\$100,000
O_2/N_2 intercomparisons	1		\$100,000
Make intensive and extensive measurements of the vertical distribution of CO_2 over continents			
Intensive measurements of the North American carbon cycle	2		∼\$10,000,000 per campaign
Aircraft profiles over continents	2	\$3,000,000	\$7,000,000
Tall tower observations	2	\$2,300,000	\$800,000
Make new global measurements of CO_2 and other species			
Background CO_2 measurements	3		\$800,000
Measurements on pCO_2 platforms	3		\$15,000 per ship
Atmospheric O_2/N_2 measurements	3	\$440,000	\$240,000
$^{13}C/^{12}C$ and $^{18}O/^{16}O$ measurements	3		\$600,000
Robust CO analyzer	3	\$850,000	\$200,000
Recommendations for the Timescale of 6 to 10 Years			
Increase observations of CO_2, its isotopes, O_2/N_2, and related tracers, and their interpretation for global regional-scale CO_2 flux measurements			
100 new continental sites, 20 commercial ship tracks, and 30 mooring installations.		∼\$15,000,000	∼\$15,000,000

platforms (see recommendations for level *2*). An essential feature of quality control is redundancy. The introduction of in situ analyzers in parallel with the traditional flask-sampling effort would catch many potential systematic errors. Flask samples can then also be collected during times of known clean air conditions, improving our ability to relate them to coarse resolution models. The temporal resolution of the data would improve enormously, providing the opportunity to turn a part of the "noise" into signal through use of the appropriate models. Less labor would be required at both the sampling location and the analysis laboratory, thereby decreasing the cost of the entire long-term observing program. This analyzer should be operable by anyone with moderate technical skills, and should be capable of running autonomously for approximately 1 year. The latter requires

that the instrument can be calibrated with very small amounts of reference gas. This instrument should be developed by or with close involvement of carbon cycle scientists, but ultimately must be produced in volume by an independent company.

Cost estimate: One-time development, $350,000; initial production of 10 instruments, $400,000; operation and data processing, $150,000 per year.

CCSP: Program Elements 2 and 3.

1.c. Improve quality control and measurement methodology. For logistical, cost, and political reasons, increasing data coverage to support flux estimates can and should be achieved through a truly international effort. Also, because of the quality control value of independent measurements, background measurement efforts in the United States should continue to be shared by multiple government and academic institutions. History shows that the potential for calibration differences and other systematic biases is significant. Gas-handling techniques have to be systematically investigated. The propagation of the WMO Mole Fraction Scale for CO_2 should be improved, and similar common calibration scales should be developed for other species. Ongoing comparisons for CO_2, ^{13}C, and O_2/N_2, between many different laboratories and between different techniques using the same calibration scale, should be instituted as the only acceptable way of making long-term measurements.

Cost estimate: For improved CO_2 standards propagation, $50,000 per year; for 15 ongoing comparisons (at $15,000 each), $225,000 per year; for one-time development of a calibration scale for isotopic ratios of CO_2 in air, $500,000; for $^{13}C/^{12}C$ intercomparisons, $100,000 per year; and for O_2/N_2 intercomparisons, $100,000 per year.

CCSP: Program Element 3.

Priority Level 2: Make intensive and extensive measurements of the vertical distribution of CO_2 over continents.

2.a. Conduct intensive CO_2 measurements to elucidate the North American carbon cycle through a combination of airborne, tower, and ground and ship-based measurements. The purpose of these intensive measurements is to learn how to best measure fluxes on regional scales with an ongoing program, to demonstrate this capability, and to develop the infrastructure to leave in place for a long-term North American observational system. These measurements will address the crucial question of how to scale up from local source estimates, through landscape, regional, and continental to global scales by observing the development and propagation of terrestrial, industrial, and oceanic signals across the continent. They will guide the location of long-term observations such as aircraft profiles and tall towers, and will allow the investigation of potential gaps and sampling biases in these observations such as those due to diurnal, fair-weather, continental, or low-altitude sampling. These intensive campaigns will also provide a wealth of data for testing and improving the next generation of coupled

carbon cycle models, which in turn will be able to use these data for network design purposes.

Cost estimate: Approximately $10,000,000 for a month-long campaign (of which $2,000,000 is for aircraft time and rental).

CCSP: Program Elements 2 and 6.

2.b. Repeated vertical profiles by aircraft sampling over continents. In addition to the intensive measurements, ongoing observations of continental CO_2 distributions will be required. The temporal coverage of the intensive measurements will be limited, and many important processes, such as the seasonal rectifier effect, only manifest themselves on longer timescales. Over North America, these measurements must be at a high enough resolution to provide a context for more intensive measurements and to answer the question of how many and what type of continental observations are required for our ongoing network. For these purposes, synoptic-scale coverage of around 25 sites over North America with a sampling frequency of every 2 days is appropriate. This resolution will only be possible using the analyzer recommended in ***1.b.***, but a subset of the flights should include flask samples for purposes of quality control and for measurement of additional tracers. For continental regions other than North America, a few profiling sites will greatly improve the quality of global inverse calculations. At least two aircraft sampling locations over South America, and one each over Africa, and eastern and western Russia are required to fill the largest gaps in global coverage. Aircraft profiles will also be critical for validating future satellite CO_2 systems and ground-based spectrometers, both of which have significant promise for measuring column CO_2 as well as significant potential biases. It would also be highly advantageous to include measurements of CO as a pollution tracer on these flights, if a robust analyzer becomes available (see recommendation ***3.e.***).

Cost estimate: One-time setup costs, $3,000,000 (includes flask units and laboratory instruments); operational costs, $7,000,000 per year (of which $4,000,000 is for aircraft rental).

CCSP: Program Elements 2 and 3.

2.c. Tall tower observations. Aircraft and satellite measurements may suffer from diurnal or fair-weather sampling biases. Continuously operating tall towers can provide critical data at night and in bad weather, and extensive data sets for investigating the interaction between CO_2 fluxes and boundary layer mixing. Species other than CO_2, such as CO (see recommendation ***3.e.***), should be measured for air mass characterization, which will allow an ongoing assessment of sources and sinks over hundreds of kilometers surrounding the tower. A few towers, such as the WLEF tower in Wisconsin, should be selected for a more intensive program involving flux measurements and studies addressing boundary layer mixing, with a full complement of meteorological observations. All of these high-intensity towers will be located in North America, to improve our estimates of temperate North American CO_2 exchange and to leverage numerous other investigations and resources. It is anticipated that investigators in other countries will initiate additional

tall tower programs. Vertical extrapolation methods (Potosnak *et al.*, 1999; the "virtual tall tower" concept, K. Davis) should also be pursued as a possible means of obtaining additional information on continental background concentrations.

Cost estimate: One-time setup for 12 towers, $2,300,000; operational costs, $800,000 per year.

CCSP: Program Element 3.

Priority Level 3: Make new global measurements of CO_2 and other species.

3.a. Increase classical background CO_2 measurements. It will also be advantageous and relatively inexpensive to augment the amount of marine boundary layer CO_2 data, particularly in currently undersampled regions. Several desert and remote island sites are still potentially useful. The largest gaps in the marine boundary layer network are in the Southern Ocean (Fig. 2-2). Sampling from commercial ships has the potential to significantly increase the background CO_2 data coverage in the Southern Ocean and elsewhere. Atlantic transects would be an important addition to existing Pacific transects. The advantage of using commercial ships is that they cover large distances at relatively high speed and repeat the same tracks regularly. Oceanographic research vessels have the advantage of excellent scientific support, but they generally do not repeat regular transects. Several scientific research and resupply ships do, however, operate on repeated transects. These could easily be used as platforms for atmospheric sampling. Such scientific ships of opportunity include the NOAA Ship *Ka'imimoana*, which conducts repeated transects in the equatorial Pacific in support of the TAO buoy array, and NSF ships making repeated transects between Chile and Palmer Station as well as between Christchurch and McMurdo. Continuous CO_2 measurements should be made on these ships (see recommendation ***3.b.***). Continuous CO_2 measurements should also be made at many of the already existing network sites when new instrumentation is available.

Cost estimate: $800,000 per year.

CCSP: Program Element 3.

3.b. Background CO_2 measurements on pCO_2 observing platforms. Chapter 3 of this report recommends extensive pCO_2 measurements from a number of oceanographic platforms. In many cases, the instrumentation required to measure pCO_2 will also be suitable for making high-precision background atmospheric CO_2 measurements at the same time. However, such measurements will require additional investments in calibration gases and quality control. The benefits in terms of increased data coverage will be well worth this cost.

Cost estimate: $15,000 per ship per year.

CCSP: Program Element 3.

3.c. Increased atmospheric O_2/N_2 measurements. The strongest constraint on the long-term terrestrial vs. oceanic flux partitioning comes

from measurements of trends in the background O_2 concentration, expressed as deviations in the O_2/N_2 ratio from an arbitrary reference (e.g., Keeling *et al.*, 1996b). In addition, observations of the seasonal cycle in O_2/N_2 provide information on hemispheric oceanic primary productivity and gas-exchange rates, while latitudinal variations in O_2/N_2 are sensitive to the deep overturning circulation of the oceans. There is currently an unresolved discrepancy between the observed north-south atmospheric O_2/N_2 gradient and that predicted by coupled atmosphere-ocean models (Stephens *et al.*, 1998). This discrepancy may be related to how much deep water upwells at low vs. high southern latitudes, and imparts considerable uncertainty into predicted latitudinal CO_2 transports. Additional O_2 measurements are needed in equatorial regions to constrain BOGCMs. More atmospheric O_2 observations are also needed over the Atlantic basin to improve the constraints on Atlantic productivity and the zonal representativeness of the data set. Flask sampling and/or continuous analyzers should be implemented at more background sites and on oceanographic vessels with repeating transects. Airborne measurements are feasible through adaptations to existing technologies, and promise additional insights into marine and continental boundary-layer mixing, as well as a potential means for industrial emission verification.

Cost estimate: One-time setup for three ships and five sites, $240,000; operational costs, $240,000 per year; one-time airborne instrument development, $200,000.

CCSP: Program Elements 2 and 3.

3.d. Measurements of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ fractionation signatures. Measurements of the $^{13}C/^{12}C$ ratio in atmospheric CO_2 provide valuable constraints on the terrestrial vs. oceanic partitioning of the anthropogenic carbon sink, particularly on latitudinal spatial scales and interannual timescales (e.g., Ciais *et al.*, 1995). Additional atmospheric ^{13}C measurements can help elucidate and track the relative contributions of C-3 and C-4 photosynthesis and their isotopic discrimination, which would improve estimates of partitioning between oceanic and terrestrial sources. The oxygen isotopic signatures of CO_2 are influenced differently by photosynthesis and respiration, and thus provide unique information on gross CO_2 exchange rates (e.g., Peylin *et al.*, 1999). The power of ^{13}C and ^{18}O constraints is currently limited by uncertainties regarding the degree of fractionation by various processes and their variability. These isotopic measurements should be done in specific ecosystems and can be integrated with tower studies at several sites.

Cost estimate: $600,000 per year.

CCSP: Program Element 3.

3.e. Develop a robust CO analyzer. Measurements of atmospheric CO can be very useful in interpreting the influence of industrial emissions on measured CO_2 concentrations. Gas chromatography and other technologies exist that could be adapted into an analyzer that could be included on the routine aircraft and tall tower measurements recommended under priority

level ***2*** at a marginal cost. A further benefit of a gas chromatography technique would be additional measurements of CH_4 and H_2.

Cost estimate: One-time development, $350,000; initial production of 10 instruments, $500,000; operation and data processing, $200,000 per year.

CCSP: Program Elements 2 and 3.

2.3.2 Recommendations for the timescale of 6 to 10 years

A number of advances in modeling, technology, and measurement programs are necessary before we can seriously plan the best way to measure regional-scale CO_2 fluxes from the atmosphere. For example, the best combination of methods for determining CO_2 concentrations over a continent will be a tradeoff between the costs of acquiring relatively low-variability data, such as tall tower boundary-layer concentrations or airborne column integrals, and the inverse models' need for such data. If the numerical representation of boundary layer mixing processes advances sufficiently, then either shorter towers or flights with more horizontal and less vertical coverage may be advantageous. Further, if the vertical extrapolation techniques now being considered, such as the "virtual tall tower" concept (K. Davis), prove useful, the instrumenting of existing flux towers may be an alternative to initiating new tall tower or aircraft-profiling sites. The development of satellite or ground-based spectrometric CO_2 sensors will also affect these decisions, and obtaining vertical profiles to test and validate these measurements may take on enhanced priority.

Based on regional-scale flux signatures, such as that shown in Fig. 2-10, we can make several educated guesses as to the resources required by the atmospheric observing system described earlier in this chapter. Thus, we recommend the following.

Increase observations of CO_2, its isotopes, O_2/N_2, and related tracers, and their interpretation for global-wide regional-scale CO_2 flux measurements.

Building on the knowledge gained through the intensive and extensive measurements recommended in priority B, the necessary observations should be implemented to achieve ongoing regional-scale flux resolution over North America and to expand this coverage to the globe. Over North America, a scaling-back from the network put in place in years 1 to 5 may be possible. The chosen network design will likely include about 25 measurement sites (tall tower, airborne, or other) over temperate North America, similar coverage over other continental regions, and atmospheric CO_2 measurements (using the new analyzer recommended in ***1.b***) on commercial ships and mooring networks in every ocean basin. Additionally, a coordinated effort will be required to ensure critical tasks: the synthesis of all available atmospheric and related biogeochemical data; the calculation of regional fluxes and their relationship to regional climate variations and human disturbances; the prediction of future trends in atmospheric CO_2; the assessment of adaptation

and mitigation options; and especially, the planning and execution of the necessary measurements (see Chapter 6).

Preliminary cost estimate: For observations at 100 new continental sites, 20 commercial ship tracks, and 30 mooring installations, $15,000,000 one-time setup, and $15,000,000 per year.

CCSP: Program Elements 2 and 3.

2.4 Summary

As an entirely independent means of determining surface fluxes, and as top-down checks on fluxes estimated from oceanographic and terrestrial methods, atmospheric observations will continue to play a vital role in our assessments of the global carbon cycle. However, it is clear from the analyses presented here that we can now only perform these calculations with limited spatial resolution. Nonetheless, with a directed effort over the next decade, we can hope to achieve our goal of a robust regional-scale atmospheric observing system. With the set of research activities we recommend for the next 1 to 5 years—continuing our existing measurements, developing a new CO_2 analyzer, improving quality control measures, conducting intensive and extensive measurements of CO_2 over continents, and making focused additions to the observational network—we should be able to measure the overall carbon balance of temperate North America to an accuracy of 0.2 Gt C/yr, while resolving the rest of the globe's continental regions to 0.5 Gt C/yr and major ocean regions to 0.1–0.2 Gt C/yr. This level of resolution will already allow us to test many process-based models, which will be important to predicting the future behavior of the carbon cycle. In addition, by building on what we learn during this initial 5-year phase, we should be able to design and implement an observing system capable of resolving global fluxes on regional (1,000 km) scales, which will improve our understanding of the terrestrial and oceanic biogeochemical processes most important to the carbon cycle.

Addendum 2-1: Sampling and Measurement Biases

Examples of potential sampling biases are shown in Figs. 2-A1 and 2-A2. Figure 2-A1 shows continuous CO_2 measurements at the Mauna Loa Observatory, Hawaii, during July 1998. Clearly visible are low-CO_2 episodes due to upslope winds during the day, when vegetation at lower elevations on the mountain has depleted CO_2 from the air reaching the observatory. The blue dots are hours that meet the selection criteria for background air, which exclude upslope winds but preserve large-scale synoptic variations. Many of the sites in the network have similar potential local effects, but very few have in situ analyzers to help select clean air periods and diagnose potential biases. Another example of challenging local effects is seen in the sampling of air from a platform such as a large container ship. Figure 2-A2 shows a continuous CO_2 record collected by D. Kitzis, with an air intake on one side of the bridge of a ship transiting from Los Angeles to Wellington, New Zealand. There are many pollution spikes from the ship's funnel close to the bridge, but there are also clean air periods. A continuous record provides the option to select clean air episodes, as suggested in the lower panel of this figure, which presents one full day. While pair disagreement in duplicate grab samples usually indicates whether a sample may be contaminated, it is possible that, without the continuous record, a pair of polluted flasks could be equally biased and remain in the database.

At Mauna Loa and several other background sites, independent measurements are made by in situ analyzers and by the collection of air samples in flasks that are analyzed a few weeks later at the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder. The results of those analyses for March to May 1998 are compared in Fig. 2-A3a, while Fig. 2-A3b separately plots the difference of each flask value (a flask is filled in 20 s) from the corresponding hourly average measured by the continuous analyzer on Mauna Loa. This comparison cannot be precise because measurement integration

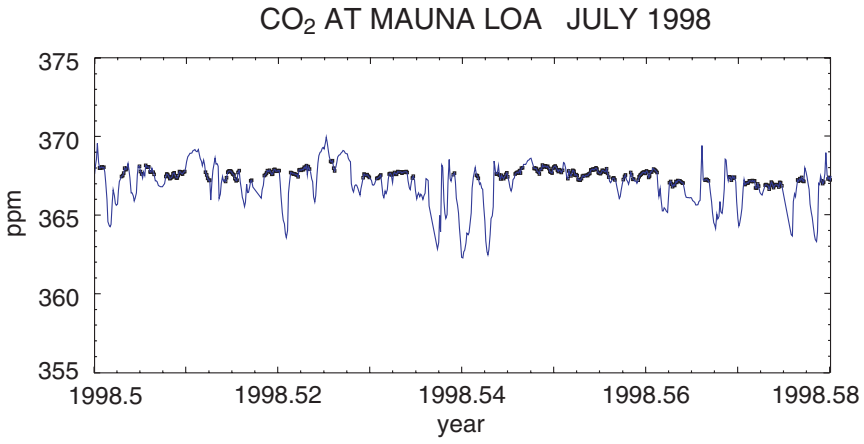


Figure 2-A1: Hourly CO_2 mole fraction observed at the Mauna Loa Observatory, Hawaii, during one month (line), and selected background data (dots).

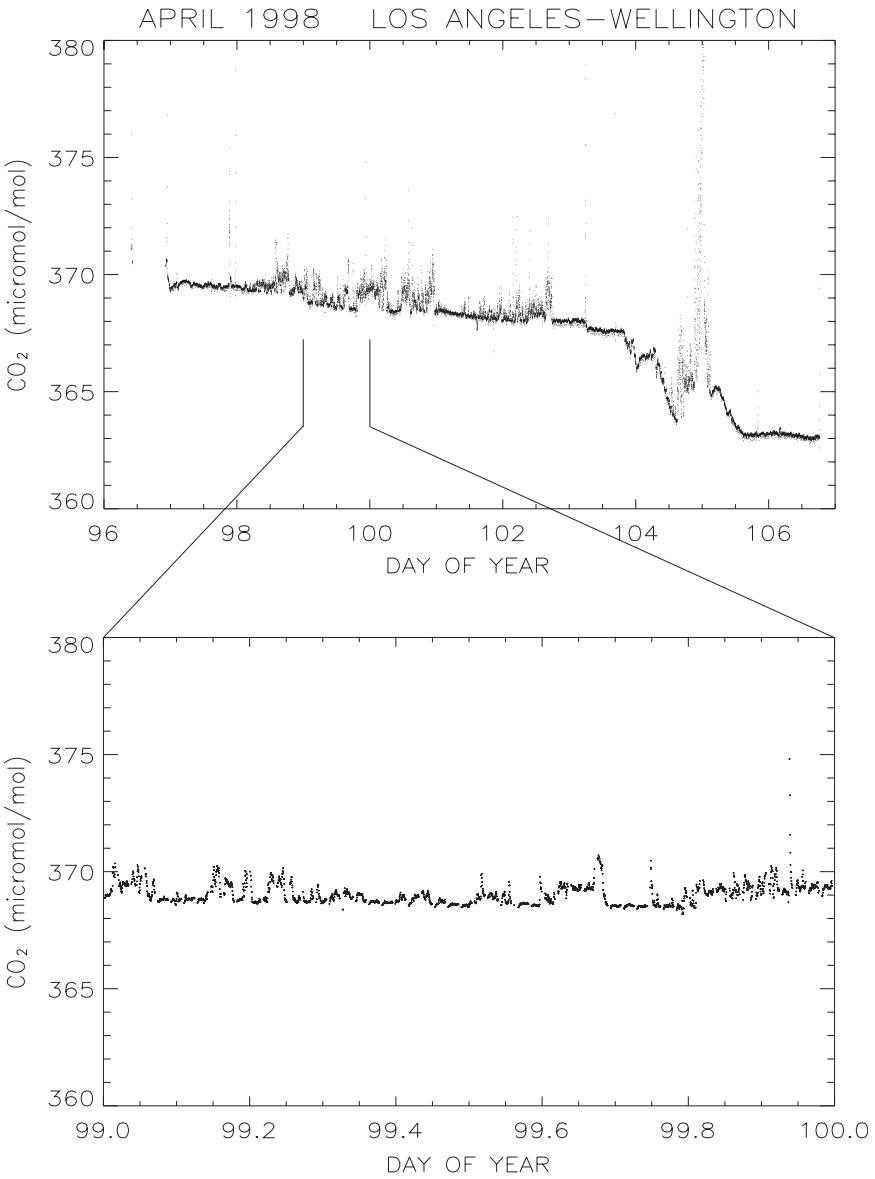


Figure 2-A2: Continuous CO_2 data acquired on a container ship transecting from Los Angeles to Wellington, New Zealand.

times do not match and the air intakes are different. However, persistent offsets of up to 0.3 ppm are indicative of accuracy. These offsets may result from a host of potential problems, such as flask storage effects, analytical errors at CMDL, and analyzer or gas-handling problems at the observatory, but not to inconsistencies between standard reference gases in this case.

A different type of comparison can be made between independent laboratories. The difference of CO_2 monthly mean values (selected for background conditions) at Mauna Loa from 1974 to 1999 between the Scripps Institution of Oceanography and CMDL is 0.20 ppm (1σ). The overall average difference is close to zero, but there are a few extended periods in which the average difference is as large as 0.3 ppm. In this case, the instruments, air

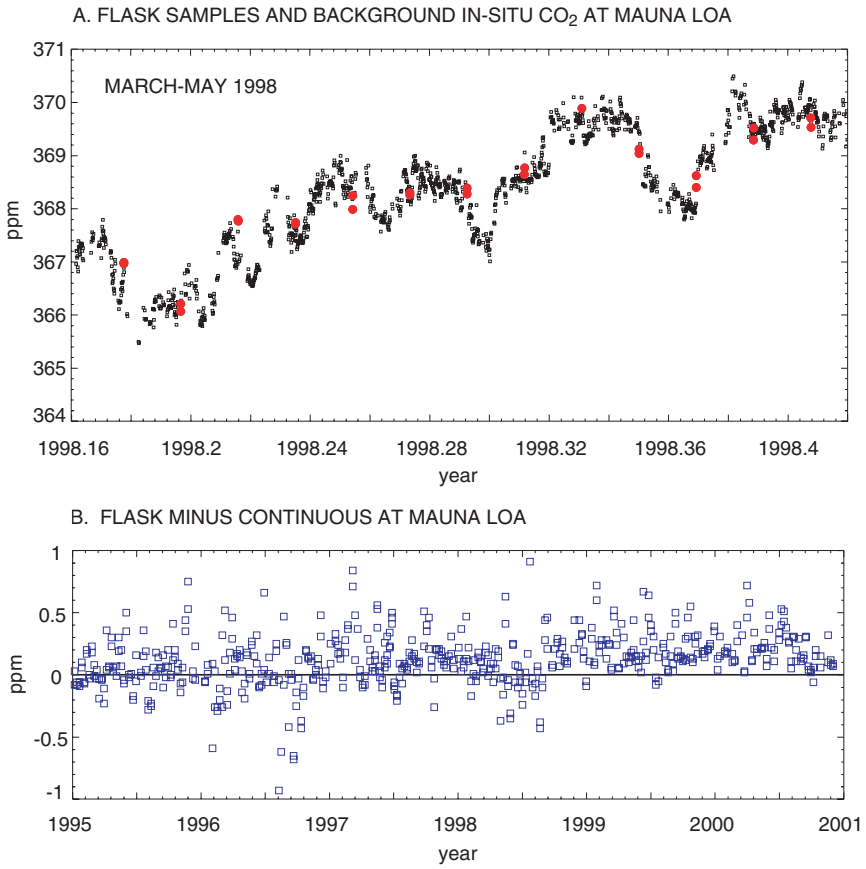


Figure 2-A3: (a) Hourly continuous CO_2 data at Mauna Loa Observatory selected for background conditions (black), and CO_2 in pairs of grab samples in flasks (red). (b) CO_2 mole fraction difference between flask samples and the corresponding hourly average at the Mauna Loa Observatory.

intake lines, data selection, measurement protocol, and reference standards are all different. Since 1992 the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Melbourne, Australia, and CMDL have been comparing measurements in which both laboratories take a sample from the same air. A flask, after filling at Cape Grim, is first analyzed at CSIRO, and then sent on to CMDL for a second analysis. Results are shown in Fig. 2-A4. The agreement is closer than in the case of the comparisons described above, because in this instance the same air is being analyzed. However, the occasional persistent offsets of up to 0.2 ppm are still too large to achieve our stated 5-year goals. As a result of the ongoing intercomparison, analysis problems have been detected and corrected in both labs. Based on our accuracy requirement of 0.1 ppm, and analyses such as those presented in Figs. 2-A3 and 2-A4, we conclude that improving the quality of existing atmospheric CO_2 measurements, through developing and implementing robust in situ analyzers and improved propagation of the calibration scale, must be a high priority in carbon cycle research.

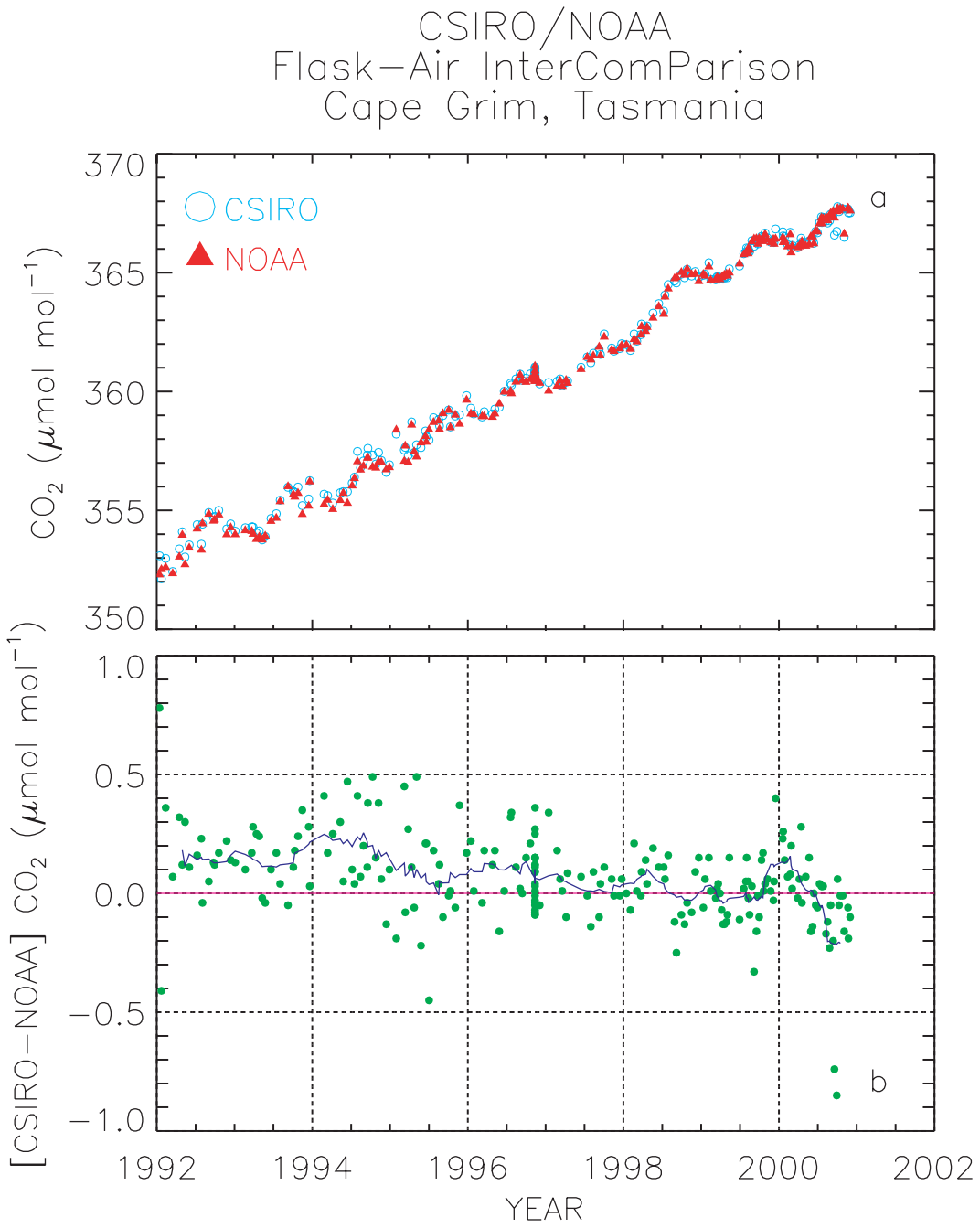


Figure 2-A4: Comparison of CO_2 mole fraction measurements in the same air samples by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and CMDL.

Addendum 2-2: Error Assessments for Enhanced Networks

There are a number of ways to assess uncertainty in inverse flux calculations. One approach starts with a forward ATM run, which is then sampled at specific station locations and times, with an assumed amount of added noise. Depending on the question to be addressed, this added noise can be used to account for the mismatch in time and space between the model predictions and the measured concentrations, or for only the actual measurement error. By inverting these pseudodata with the same ATM, one can derive an estimate of the flux error associated with specific regions and sampling networks. Errors calculated in this way do not reflect the influence of potential systematic biases in the ATM or measurements, and may not reflect the influence of mismatches between the spatial patterns of the true and inverted fluxes (Gloor *et al.*, 1999). Nevertheless, they do contain important information on the contributions of additional measurements in specific locations. We use the annual 17-region synthesis inversion model of Gloor *et al.* (2000), the monthly 14-region assimilation model of Bruhwiler *et al.* (2000), and the monthly 17-region synthesis inversion model of Baker (2000). Table 2-A1 shows the errors these models predict for selected continental-scale regions using surface stations from the existing Globalview network (Globalview-CO_2, 2000). The three inverse models differ considerably in their methodology and temporal/spatial resolution. However, the most significant differences in the sensitivity tests presented here are in the assumed error associated with matching the data and model predictions.

The Gloor *et al.* (2000) study used a relatively conservative noise model, including a subjective assessment of the error associated with current models' inability to represent the high-resolution spatial and temporal variability in the fluxes and atmospheric transport, and the exact location of a station within a model grid cell. The noise models used in the other two studies simply accounted for the error associated with averaging naturally variable data to get monthly means (see footnote to Table 2-A1). The first of these approaches represents a more realistic assessment of what current models can do, whereas the latter indicates the potential of numerical models with moderately improved resolution and accuracy. As discussed below, the development of models that interpreted discrete data rather than monthly or annual means would lead to even further error reductions. Allowing for the relatively higher noise model used by Gloor *et al.* (2000), the three models are generally consistent. As Table 2-A1 shows, the existing network and inverse models can constrain temperate North America to no better than around ±1 Gt C/yr. Allowing for systematic biases in model transport or data would increase this number. As expected, even larger errors are associated with other less constrained regions such as South America and Africa.

Using the spatial information in the Gloor *et al.* (2000) results as a guide, we first ask how much these errors might be reduced by the addition of a tractable number of sampling locations. We divide the addition of these sites into four cases:

Table 2-A1: Annual mean estimation errors for selected regions using surface sites from the Globalview network (in Gt C/yr).

	Gloor *et al.* (2000)[1]	**Bruhwiler *et al.* (2000)**[2]	**Baker (2000)**[3]
Temperate North America	1.1		0.5
North America		0.3	
Temperate Eurasia	2.0		0.4
Eurasia		0.2	
South America	14.0	0.9	2.2
Africa	8.9	1.0	1.0
North Pacific	0.6	0.2	0.2
North Atlantic	0.7	0.3	0.2
Equatorial Pacific	0.8	0.3	0.1
Southern Ocean >55°S	0.4		0.2
Southern Ocean >15°S		0.5	

[1]Using a noise model with approximately 0.7 and 2 ppm random variability on *annual mean* oceanic and continental observations, respectively. From covariance matrix, no prior constraints.

[2]Using a noise model with 0.5 and 2.5 ppm random variability on *monthly* oceanic and continental observations, respectively. Direct comparison of prescribed and retrieved fluxes.

[3]Using a noise model with approximately 0.8 and 1.5 ppm random variability on *monthly* oceanic and continental observations, respectively. From covariance matrix, prior constraints set to ±200 Gt C/yr.

Case 1: Existing tower and airborne sites, including tall towers in Wisconsin and Texas and airborne flask profiles over Colorado, Massachusetts, Hawaii, Alaska, and Rarotonga.

Case 2: Case 1 plus continental sites over South America, Africa, and Eastern and Western Russia, and a commercial ship track from Buenos Aires to Melbourne.

Case 3: Case 2 plus four additional sites over temperate North America.

Case 4: Case 2 plus 10 additional sites over temperate North America.

For the added continental sites, we assume biweekly measurements in the second level of the model, because surface data are likely to be too locally influenced to be useful. Also, mid-boundary-layer concentrations should be measurable by several approaches. The locations of the additional international sites are close to optimized locations found by Gloor *et al.* (2000), and the locations of the additional U.S. sites coincide with existing Ameriflux measurement programs. For the ship track, we assume monthly surface values every 20 degrees of longitude.

Table 2-A2 shows the expected reduction in error for North and South America, Africa, and the North Atlantic and Southern Oceans for these cases. Including the existing tower and airborne site data yields moderate improvements for all the continental regions. Adding the new continental sites and the Southern Ocean ship track greatly improves the South American and African estimates. The addition of proximal sites in Cases 3 and 4

Table 2-A2: Estimation errors for various cumulative network enhancements.

	Gloor *et al.* (2000) (high error estimate)					Bruhwiler *et al.* (2000) (low error estimate)				
Region	**TNA**	**SA**	**AF**	**NAO**	**SO**	**NA**	**SA**	**AF**	**NAO**	**SO**
Surface Globalview	1.1	14.0	8.9	0.7	0.4	0.3	0.9	1.0	0.3	0.4
+ existing data aloft	0.9	13.4	8.7	0.7	0.4	0.2	0.7	0.6	0.2	0.4
+ continents + ship	0.8	0.5	1.0	0.6	0.5	0.2	0.3	0.5	0.2	0.2
+ four U.S. sites	0.7	0.5	1.0	0.6	0.5	0.1	0.3	0.5	0.2	0.2
+ six more U.S. sites	0.6	0.5	1.0	0.6	0.5	0.1	0.3	0.4	0.2	0.2

TNA = temperate North America, SA = South America, AF = Africa, NAO = North Atlantic, SO = Southern Ocean, NA = North America

continues to improve the temperate North American estimates. The Bruhwiler *et al.* (2000) model, with a relatively lower noise model, suggests that the network represented by Case 2 is theoretically capable of providing our desired constraints. However, these sensitivity tests do not allow for systematic biases in modeled transport or measured concentrations, either or both of which could be significant. The higher observational errors assumed by Gloor *et al.* (2000) provide a more realistic estimate of our potential flux constraints using existing models, and indicate that further data enhancements beyond Case 4 may still be necessary.

Alternatively, by taking a very different approach to the inversion of atmospheric data, it may be possible to invert using actual measurements rather than either annual or monthly means. This approach would require high-resolution meteorological models that could define influence functions individually for every measurement in the data set. The inversion would then be performed on these influence functions rather than on the annual or monthly mean response functions as is currently done (M. Gloor, personal communication; S. Denning, personal communication). If such an approach were successful, then the uncertainty now associated with averaging records with high variability (see Table 2-2) would diminish.

While we don't have a model to test this explicitly, we can get some idea of the potential improvements by setting the assumed error over the continents to a similar low value as over the oceans, an admittedly optimistic scenario. Applying this potential improvement in the Bruhwiler *et al.* (2000) model reduces error by a factor of four for the temperate North American flux estimates (not shown in tables). An important additional benefit of using actual data rather than means would be the improved detection of carbon flux anomalies in the region surrounding the observation site. The flux anomalies could be matched with climate variations, thus improving the understanding of relevant processes. While this large error reduction is promising, model improvements will take some time and may never reach the level of noise reduction we assume above. Their short-term success may depend on how much of the high-frequency variability (see Fig. 2-7b) is due to synoptic transport, which we can presently model, and how much is due to local-flux and boundary-layer interactions, which we cannot presently model.

Continental-scale atmospheric inversions can also benefit from additional

a priori constraints on various regions. For example, atmospheric O_2/N_2 and ^{13}C measurements provide constraints on the annual mean global partitioning of terrestrial versus oceanic CO_2 sources (Battle *et al.*, 2000; Manning, 2001). With moderate enhancements to the O_2/N_2 and ^{13}C observational networks, and improvements in understanding their budgets, we might be able to constrain the global annual mean partitioning of CO_2 uptake between land biosphere and oceans to within 0.5 Gt C or better. By comparison, the error on this partitioning using the Bruhwiler *et al.* (2000) model, as shown in Tables 2-A1 and 2-A2, is 1.3 Gt C/yr for the enhanced Case 4. Thus, applying an a priori constraint based on O_2/N_2 and ^{13}C data can further improve the continental-scale estimates (Rayner *et al.*, 1999).

Oceanic measurements of pCO_2 and other quantities constrain air-sea CO_2 fluxes for specific ocean basins. It may be possible to constrain the annual mean CO_2 flux for continental-scale ocean regions to within 0.1–0.2 Gt C by significantly extending oceanic pCO_2 coverage and improving estimates of gas exchange rates (see Chapter 3 of this report). Including these air-sea flux constraints in an inversion will lead to improved estimates of terrestrial fluxes. Using the Gloor *et al.* (2000) model, we find that knowing fluxes for ocean regions to within 0.2 Gt C/yr reduces the estimation error on temperate North America by 0.3 Gt C/yr using the surface Globalview sites, and by 0.1 Gt C/yr for Case 4 above. Finally, these inverse models can be used to assess the sensitivity of our flux determinations to systematic interlaboratory biases (e.g., Fig. 2-A4). Because laboratories tend to focus measurements in their own regions of the world, such biases could lead to significant errors in flux estimates. Artificially offsetting the measurements over North America by 0.5 ppm resulted in a 0.7 Gt C/yr error over temperate North America for our enhanced Case 4 when using the Bruhwiler *et al.* (2000) inversion model. The Gloor *et al.* (2000) model shows a similar sensitivity, with an artificial increase of 0.2 ppm over North America, resulting in a 0.2 Gt C/yr error over temperate North America. Thus both models support our approximate estimate for a continental-scale flux-response ratio of 1 ppm/(Gt C/yr). However, if only marine boundary layer stations are used, the signals for a given flux are much smaller. These sensitivities highlight the need for tight interlaboratory comparisons and frequent maintenance of the traceability of reference gas standards.

Chapter Three

Integrated Studies of the Surface Ocean and Air-Sea Interface

3.1 Overview

A comprehensive observing system of sea surface pCO_2 distributions and air-sea CO_2 fluxes will greatly enhance our understanding of the carbon cycle and its anthropogenic perturbations. In this chapter, we recommend a series of studies to dramatically extend our knowledge of the distribution of pCO_2 values at the sea surface, and of the fluxes of CO_2 between ocean and atmosphere. We recommend process studies of gas exchange to improve the characterization of air-sea CO_2 fluxes. We also recommend large-scale measurement of upper ocean properties that reflect and constrain biogeochemical transports and fluxes. This work will improve our knowledge of the nature and rates of biogeochemical processes. It will also improve our ability to characterize the surface pCO_2 field by advancing our ability to quantify these rates. The timescale of interest is seasonal to interannual, and the primary spatial scales of interest are sub-basin to basin.

The upper ocean studies recommended here complement studies recommended in the chapters on atmospheric observations (Chapter 2) and ocean interior measurements (Chapter 4). These other chapters advocate powerful approaches to constraining atmospheric and oceanic CO_2 inventories on large space scales and multiyear timescales. The measurements proposed here will offer insights about air-sea CO_2 fluxes on subregional and seasonal scales, as well as at larger scales of space and time. Knowledge of air-sea CO_2 fluxes as constrained by sea surface pCO_2 measurements will also give powerful information for modeling, leading to more accurate CO_2 uptake estimates by the land biosphere at continental scales. Systematic observations of seasonal changes in sea surface pCO_2 and ancillary properties (e.g., O_2, nutrients, TCO_2, isotopes, dissolved organic matter) yield information about instantaneous and integrated rates of biological carbon transformations in the mixed layer. Measurements of mixed layer $\delta^{13}C$ of dissolved CO_2, in particular, are important for estimates of terrestrial CO_2 uptake and net oceanic production (Francey *et al.*, 1995; Keeling *et al.*, 1995; Ciais *et al.*, 1995; Battle *et al.*, 2000). Sea surface pCO_2 measurements will contribute to be a basic long-term goal: making independent observations from the atmosphere, surface ocean, and ocean interior that yield consistent CO_2 flux measurements, without having to invoke "missing" sources and sinks. Studies recommended here will thus contribute to many priority objectives of the U.S. Carbon Cycle Science Plan (CCSP).

This chapter advocates the following long-term strategy and goals for characterizing the time-dependent distribution of pCO_2 in the surface ocean, gas transfer velocities and air-sea fluxes, and the biogeochemical processes determining the large-scale pCO_2 distribution:

- Making extensive measurements of the distribution of sea surface pCO_2 and related biogeochemical properties, to map the variations of these properties in time and space.
- Interpreting these data (1) to achieve a deeper understanding of upper ocean biogeochemical processes, and (2) to quantify their impact on sea surface pCO_2 distributions. This work will involve integrating observations made with satellite-borne sensors, results of biogeochemical process studies, and models of ocean physics and biogeochemistry.
- Carrying out process studies to improve parameterizations of gas transfer velocities in terms of environmental forcing, giving more accurate values of air-sea CO_2 fluxes determined from sea surface pCO_2 values.
- Integrating results from the observation systems (including satellites), associated databases, gas exchange parameterizations, and models of upper ocean biogeochemistry and physics to calculate surface water pCO_2 and air-sea CO_2 fluxes at seasonal timescales and regional spatial scales, in near real time. This last exercise serves as a framework to upscale results to the global scale in the future.

The plan proposed here focuses on measurements in the open ocean, and may not incorporate all important components of the oceanic carbon sink. The coastal oceans are an unknown, but possibly significant, sink for carbon. The land-ocean pathway through rivers delivers about 0.6 Pg C/yr to the ocean. This pathway will receive attention in the RIOMAR program (`http://www.tulane.edu/~riomar/workshop.htm`). This plan does not discuss in detail satellite observations, which offer unparalleled synoptic coverage of parameters that influence surface CO_2 levels and gas transfer rates. These parameters include wind speed, sea surface temperature, and ocean color (from which values for chlorophyll and primary productivity can be derived). Satellite fields of these data will contribute fundamental information to sea surface studies. An outline of these capabilities is provided in Appendix F. NASA carbon planning activities (`http://www.earth.nasa.gov/visions/researchstrat/research_strategy.htm`) address coastal observations and satellite observations.

To lay the foundation for fulfilling the objectives above, we present a plan for a 5-year program with two broad goals. The first goal is to determine climatological air-sea CO_2 fluxes on seasonal timescales and achieve greater biogeochemical understanding of factors controlling pCO_2 in priority ocean basins. The second is to improve measurement technologies, advance modeling skills, and extend our knowledge of ocean pCO_2 and flux variations. In this way we will also acquire the information to plan for a comprehensive sea surface pCO_2 observing system 5 years hence. These objectives are now becoming tractable thanks to recent advances in measurement techniques, and because remote sensing offers synoptic coverage of key properties.

An obvious way to characterize air-sea CO_2 fluxes is by direct measurement. In fact, achieving this ability has been a major recent advance in carbon cycling studies (Fairall, 2000). However, such measurements are too

demanding for global or regional coverage. Rather, air-sea CO_2 fluxes must be constrained using two terms. The first is the pCO_2 difference between air and surface seawater, ΔpCO_2. The second is the gas transfer velocity, which converts the pCO_2 gradient to flux. Constraining these terms at the basin scale is problematic. Sea surface pCO_2 is highly variable in time and space. Gas transfer velocities need to be parameterized in terms of some widely characterized property of the sea surface, such as satellite estimates of wind speed or wave slope. Such parameterizations are currently not well constrained. They must be significantly improved to accurately calculate air-sea gas fluxes. We separate the discussion and recommendations on sea surface pCO_2 studies from those on determining gas transfer velocity.

This report proposes a 5-year ramp-up program with the following general objectives:

1. Design and implement an observing system for sea surface pCO_2 observations to improve climatological estimates of air-sea CO_2 fluxes for regions where added data will significantly improve continental and oceanic constraints. Studies should cover the global ocean, with a focus on the North Atlantic, equatorial Pacific, North Pacific, and Southern oceans.

2. Gain the required experience with various platforms and sensors, and improve our analytical capabilities, including standardization and instrument development, so that we can begin a comprehensive program to constrain basin-scale interannual variability to ±0.1–0.2 Pg C/year, 5 years hence.

3. Make observations aimed at achieving process-level understanding of (a) space scales and timescales of sea surface pCO_2 variability, which define the frequency of observations required for accurately constraining interannual variability on a basin scale, and (b) physical and biological processes influencing pCO_2 variations between observations. This work will involve measuring ancillary biogeochemical properties as well as pCO_2 itself, and will require close coordination with process studies of ocean biology and physics.

4. Improve our understanding of gas exchange parameterizations and scaling, so that we can accurately calculate CO_2 fluxes from air-sea pCO_2 differences.

5. Establish data and modeling systems so that results are accessible to all interested users.

3.2 Background

Fluxes of CO_2 across the air-sea interface are commonly determined from the bulk formula:

$$FCO_2 = ks(pCO_{2a} - pCO_{2w}) = ks\Delta pCO_2 \tag{3.1}$$

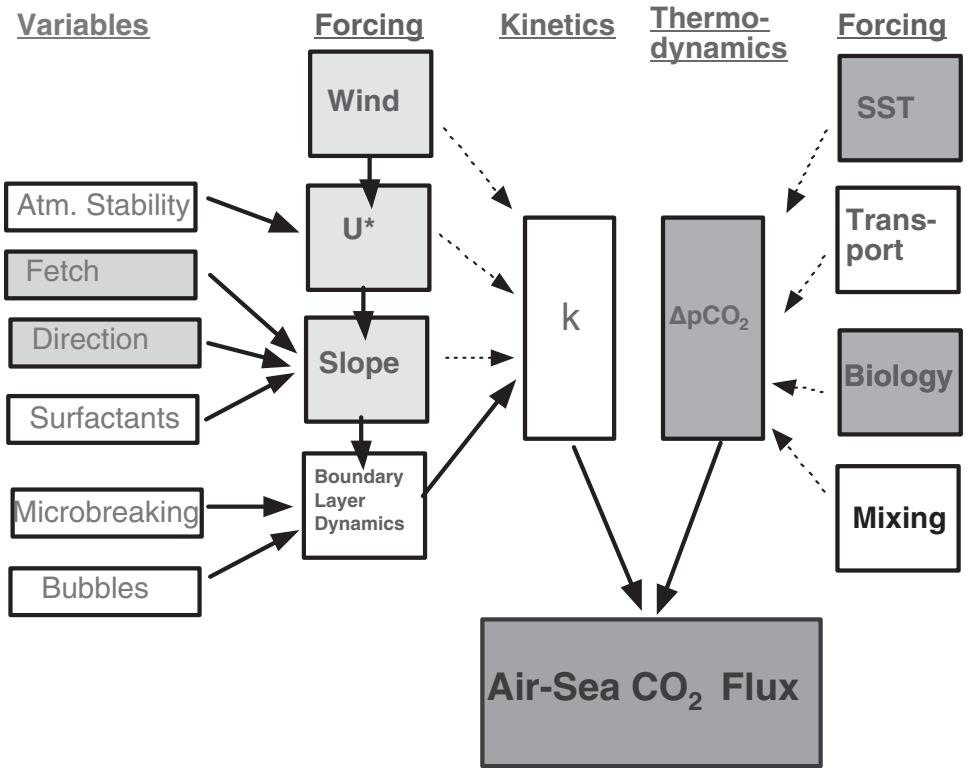


Figure 3-1: Factors influencing air-sea CO_2 fluxes, broken down into those that influence k and those that influence ΔpCO_2 (SST, sea surface temperature).

where FCO_2 is the flux (mol m^2/yr), k is the gas transfer velocity (m/yr), s is the solubility (mol/m^3/atm), and pCO_{2a} and pCO_{2w} are the partial pressures of CO_2 (atm) in air and water, respectively.

The product of the gas transfer velocity and the solubility (ks) is sometimes referred to as the gas exchange coefficient. The ΔpCO_2 is the thermodynamic driving force, while the gas transfer velocity is the kinetic term. Both terms must be quantified to constrain the air-sea flux. Figure 3-1 illustrates the processes that influence each term. As the figure indicates, a complex set of variables controls the fluxes at small scale. To quantify regional fluxes, the controlling properties must be understood and parameterized.

This chapter deals independently with our current knowledge of the sea surface pCO_2 field and gas exchange parameterizations, and approaches for studying these properties. We start by summarizing information about the climatological sea surface pCO_2 field and basin/global scale fluxes. A discussion about characterizing gas transfer velocities follows. We then discuss issues associated with making a more detailed characterization of the sea surface pCO_2 field, including the relevance of biogeochemical processes. The section ends with a discussion of network design, based on analysis of existing sea surface pCO_2 data.

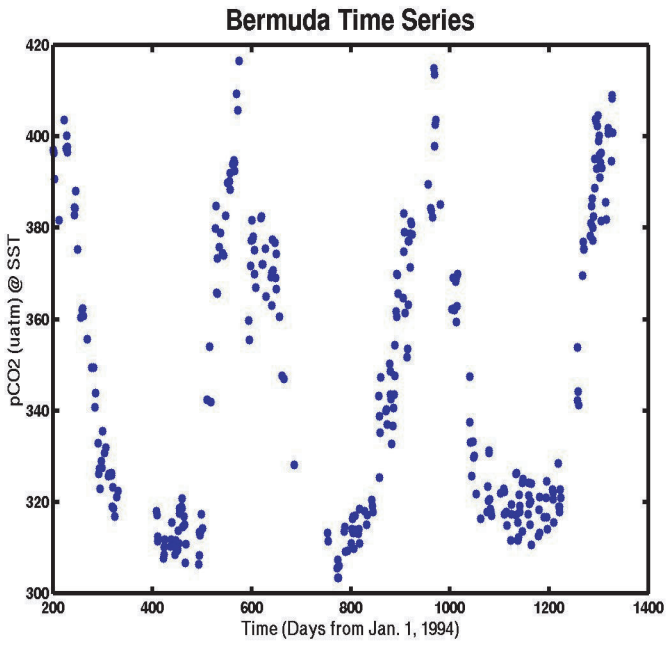


Figure 3-2: Temporal variation of surface water pCO_2 observed in the vicinity of the BATS site (31°N, 64°W), observed from mid-1994 through early 1998 by N. Bates (BBRS; Bates, 2001).

3.2.1 Studies of sea surface pCO_2 and climatology of air-sea fluxes

A major effort has gone into mapping the distribution of pCO_2 at the sea surface and determining air-sea CO_2 fluxes using gas exchange rates obtained from wind speed. The data are sufficiently extensive that we can now estimate monthly climatological air-sea CO_2 fluxes by ocean basin, if sometimes with a large uncertainty.

The partial pressure of CO_2 (pCO_2) in surface ocean waters was first measured over the global ocean with sufficient precision (± 3 μatm) in 1957–1960, as part of the International Geophysical Year (Takahashi, 1961; Keeling, 1968). This work successfully documented the large-scale pattern of sea surface pCO_2 variations: (1) warm equatorial waters are a strong source for atmospheric CO_2; (2) cold subpolar and polar waters are often a strong sink for CO_2; and (3) temperate oceans are nearly in equilibrium with atmospheric CO_2.

During the following 40 years, over a million pCO_2 measurements have been made in surface ocean waters of the global ocean. These measurements include data on waters sampled underway along ship tracks as well as several important time series. Long time series at Bermuda (Bates, 2001) (Fig. 3-2), Station "P" (Wong and Chan, 1991) (Fig. 3-3), and Iceland and the French KERFLUX Station in the Kerguelen Islands (Louanchi *et al.*, 2001) constrain seasonal rates of net production, as well as seasonal to interannual changes in pCO_2. The Japanese Meteorological Agency has maintained a

program of repeated measurements along 137°E in the eastern North Pacific between the equator and 38°N, during January–February of each year since 1984. Detailed sea surface pCO_2 fields are being measured in the equatorial Pacific using both a volunteer observing ship (VOS) and moorings. These data reflect the degassing rate of this important region, as well as interannual variability of air-sea fluxes resulting from El Niño. Table 3-1 provides a summary of several major surface observational programs.

These efforts notwithstanding, the oceans remain seriously undersampled in time and space (Fig. 3-4). Except for the time-series sampling described above, information on interannual variability in sea surface pCO_2 is sparse. Extratropical manifestations of ENSO (El Niño/Southern Oscillation) are uncharacterized. Large-scale climate reorganizations such as the Pacific Decadal Oscillation (PDO) or the North Atlantic Oscillation (NAO) could affect air-sea fluxes of CO_2 by changing wind regimes, sea surface temperatures (SSTs), biological productivity, and ecosystem structure. There are almost no data for some large reaches of the ocean, such as most of the South Pacific. The current monthly climatology of pCO_2 was produced by T. Takahashi and colleagues from a synthesis of the available data (Takahashi *et al.*, 1997, 1999, and 2001). Sea surface pCO_2 values are expressed as monthly climatological values on a $4° \times 5°$ grid for the global ocean. These researchers' approach illuminates three continuing challenges to our efforts.

The first involves creating a climatology for a transient signal. The ΔpCO_2 values have to be calculated for a single virtual year from data collected over several decades. The sea surface pCO_2 during recent decades rose at the atmospheric rate in a subtropical region (Bermuda Atlantic Time Series, BATS), but did not increase with time in boreal and polar regions (Station P and Iceland). The regional pCO_2 observations were normalized according to these observed trends, thereby projecting data collected over several decades to a single virtual year. Second, the data cover periods of different oceanic states, notably including both El Niño and La Niña. Equatorial Pacific data collected during El Niño years were excluded. Still unresolved are questions about the extratropical response to El Niño, the influence of the NAO on sea surface pCO_2 fields, and the contribution of El Niño itself to surface wind fields. Third, the ocean remains seriously undersampled in time and space even after collapsing all the data onto a single year. Takahashi and collaborators dealt with inadequate spatial and temporal sampling by placing data into $4° \times 5°$ grid fields and used sea surface current fields from a transport model and data for nearby areas to estimate pCO_2 values for unsampled points on the grid. Basin and global scale fluxes of CO_2 between the atmosphere and oceans (Fig. 3-5) are summarized in Table 3-2; the uncertainty caused by interannual variations and use of different wind-speed products is expressed in Table 3-3. Errors in ΔpCO_2 that lead to an uncertainty of ± 0.1 Pg C/yr in air-sea carbon fluxes are summarized by basin in Table 3-4.

Table 3-1: Summary of ongoing observations of sea surface biogeochemical properties.

Ship	Type	Group	Line	Frequency	Funding Source	Status	Notes
Ron Brown	research	Wanninkhof/Feely	random	1 Eq. Pac. cruise/yr	NOAA/OGP	year 2 of 3 funding	pCO_2, chl, [DIC & O_2]
Ka'imimoana	research	Feely/Wanninkhof	Eq. Pac. (East of 160°E)	2 × year	NOAA/OGP	year 2 of 3 funding	pCO_2
Voyager of the Sea	cruise ship VOS	Wanninkhof	Miami-Caribbean	1 × week	NOAA/OAR	starting up 2001	pCO_2, chl, ADCP
Skaugran	cargo ship VOS	Nojiri	Japan-West Coast America	1 × month	Japan Science Agency	1995–2000	pCO_2, chl, nutrients, Alk, DIC & O_2
Alligator Hope	cargo ship VOS	Nojiri	Japan-West Coast America	1 × month	Japan Science Agency	2000 onward	pCO_2, chl, nutrients, Alk, DIC & O_2
Supply ship	cargo/research	Lefèvre/Watson	UK-Falklands	1 year	UK	1996 onward	pCO_2, chl
Supply ship	cargo/research	Metzl	S. Indian	2 × year	France	1996 onward	pCO_2 chl
Palmer	research	Takahashi/Sweeney	New Zealand/Antarctica	4 × year	NOAA/OGP	1998–2000	pCO_2
Palmer	research	Takahashi/Sweeney	New Zealand/Antarctica	4 × year	NSF	2001 onward	pCO_2
Gould	research	Takahashi/Sweeney	Chile-Antarctica	8 × year	NSF	2001 onward	pCO_2
Tulley	research	Wong/Degrandpre	Vancouver-Sta. P	4 × year	Canada	2000 onward	pCO_2, chl, Alk, DIC, & O_2
Polarstern	research		N. Atlantic-Antarctic	1 × year	German		pCO_2
Falstaff	cargo ship VOS	Körtzinger	Germany/Canada	1 × month	funded	2001 for 3 years	pCO_2
Nuka Arctica	cargo ship VOS	Johannessen	Denmark/Greenland	1 × month	funded	2001 for 3 years	pCO_2
City of London	cargo ship VOS	Lefèvre	UK-Caribbean	1 × month	funded	2001 for 3 years	pCO_2
Hesperides	research	Rios	Spain-Antarctica	2 × year	funded	2001 for 3 years	pCO_2
Polar Star	Coast Guard	Wanninkhof/Feely	W. Coast Antarctica	2 × year	planned	2001 for 1 yr	pCO_2
Oleander	cargo ship VOS	Bates		24 × year	planned		pCO_2/ADCP/XBT
American Star	cargo ship VOS	Dickson/Robbins	W. Coast-Australia	1 × month	planned		air measurements (Tans/Bender)
Moorings							
Bermuda Test bed		Dickey, Degrandpre, Chavez, YSI				Current	pCO_2, NO_3, chl, radiation
Sta. P		Degrandpre, Wong				Planned	pCO_2
Eq Pac, 150°W, 170°W		Chavez, Friederich			NOAA/OGP	since 1996	pCO_2, NO_3, chl
Labrador Sea		Wallace, DeGrandpre			EU	5/00–5/01	pCO_2
Leo-15 (NJ)		DeGrandpre			NSF-OCE	1998–present	pCO_2
Buzzards Bay (MA)		McGillis, DeGrandpre			NSF	1999–present	pCO_2
Historical							
Baldrige	research	Wanninkhof/Feely	random		NOAA/OGP	1990–1996	pCO_2
Discoverer	research	Gammon/Feely	Pacific	1 × year	NOAA/OGP	1985–1995	pCO_2
APL	cargo VOS	Takahashi	N. Pacific	4–6 × year	DOE	1988–1992	pCO_2, ^{14}C, ^{13}C
TFL	cargo VOS	Takahashi	N. Atlantic	4–6 × year	DOE	1988–1992	pCO_2, ^{14}C, ^{13}C
Exxon Tanker	Oil tanker VOS	Garvey/Takahashi	Atlantic & Indian	4 × year	Exxon	1980	
	VOS	Wong	Pacific	4–6 × year		1986–90	pCO_2, nutrient
Knorr	research	Weiss	random			1978–1997	pCO_2, CH_4, N_2O
Melville	research	Weiss	random			1978–1997	pCO_2, CH_4, N_2O
Wecoma	research	Weiss	Hawaii Tahiti Shuttle	6 × year		1980	pCO_2, CH_4, N_2O

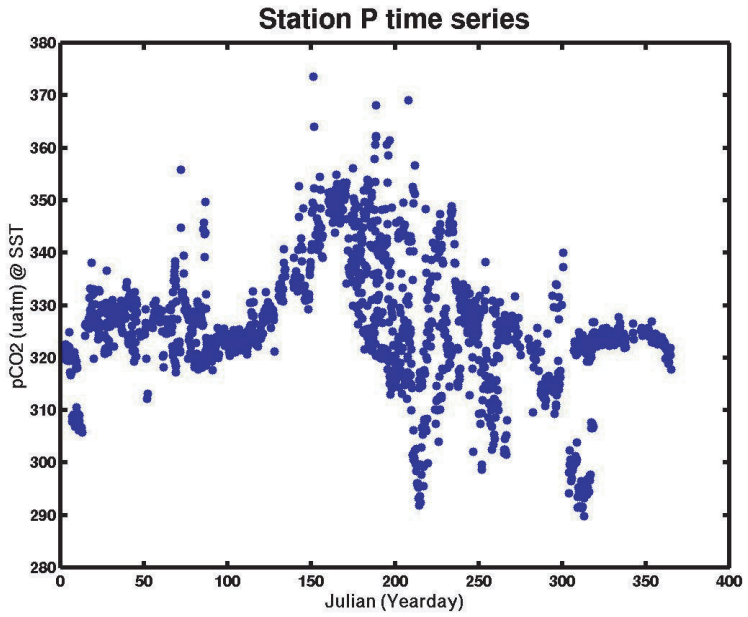


Figure 3-3: Seasonal variation of surface water pCO_2 and sea surface temperature (SST) observed at Station "P" (50°N, 145°W) in 1972–1975 (Wong and Chan, 1991). Note that SST changes are more or less sinusoidal, with a seasonal amplitude of 8°C, while surface water pCO_2 does not exhibit a simple sinusoidal pattern, changing only by 50 μatm, rather than the 130 μatm that might be expected from a 8°C change.

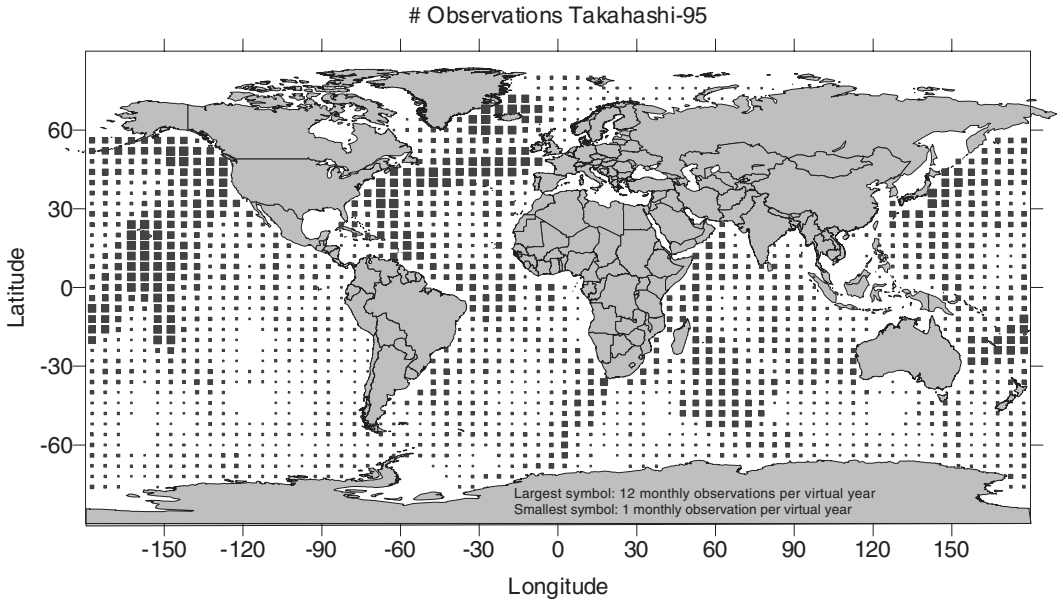


Figure 3-4: Schematic of number of monthly observations taken in each $4° \times 5°$ grid box. The largest square denotes 12 months of coverage in a virtual year.

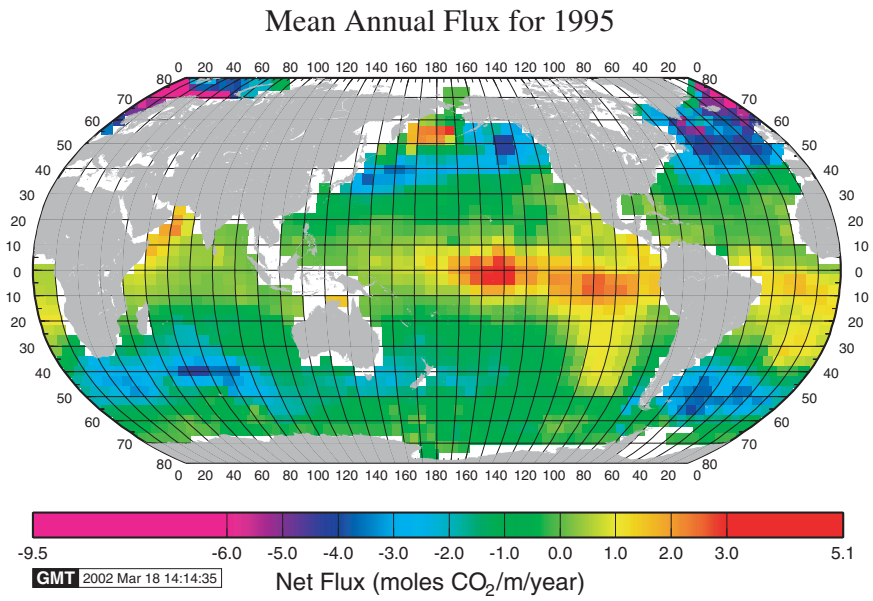


Figure 3-5: Net air-sea CO_2 flux over the globe, (wind speed)^2—from Wanninkhof (1992).

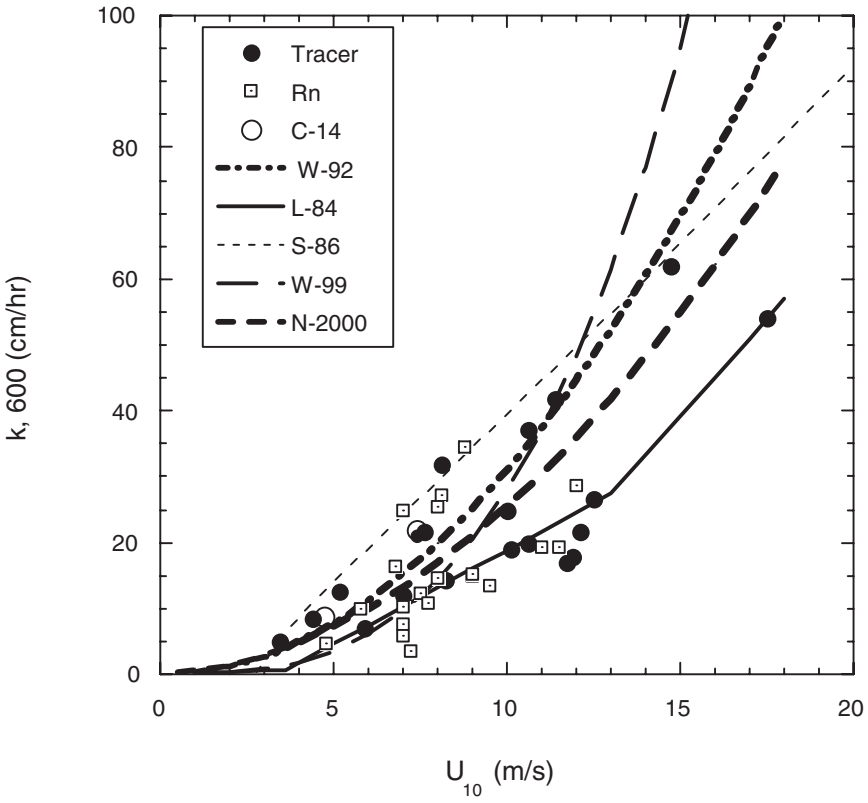


Figure 3-6: Summary of gas exchange results in the ocean and empirical relationships derived in part from this data. All data have been normalized to Sc = 600. Tracer: dual-tracer results; Rn: ^{222}Rn results; C-14: global estimate based on bomb-radiocarbon. The empirical relationships are those of Liss and Merlivat (1983) (L-83), Wanninkhof "steady winds" (1992) (W-92), Smethie *et al.* (1986) (S-86), Wanninkhof and McGillis "steady winds" (1999) (W-99), and Nightingale *et al.* (2000) (N-2000).

Table 3-2: Comparison of regional fluxes*.

Lat. Band	ΔpCO_2 Data	Gas Transfer Coefficient	Pacific Ocean	Atlantic Ocean	Indian Ocean	Southern Ocean	World Ocean
N of 50°N	T-01	W-92	+0.01	−0.40	—	—	−0.39
	T-99	W-92	−0.02	−0.48	—	—	−0.49
	T-01	W&M-99	+0.03	−0.55	—	—	−0.52
14°N–50°N	T-01	W-92	−0.64	−0.34	+0.07	—	−0.92
	T-99	W-92	−0.62	−0.32	+0.06	—	−0.87
	T-01	W&M-99	−0.94	−0.48	+0.10	—	−1.31
14°N–14°S	T-01	W-92	+0.74	+0.15	+0.18		+1.07
	T-99	W-92	+0.73	+0.18	+0.15	—	+1.06
	T-01	W&M-99	+0.67	+0.14	+0.20	—	+1.00
14°S–50°S	T-01	W-92	−0.51	−0.33	−0.67	—	−1.51
	T-99	W-92	−0.48	−0.27	−0.79	—	−1.54
	T-01	W&M-99	−0.68	−0.51	−0.97	—	−2.16
S of 50°S	T-01	W-92	—	—	—	−0.47	−0.47
	T-99	W-92	—	—	—	−0.59	−0.59
	T-01	W&M-99	—	—	—	−0.74	−0.74
Oceanic Regions	T-01	W-92	−0.40	−0.92	−0.43	−0.47	−2.22
	T-99	W-92	−0.39	−0.88	−0.58	−0.59	−2.44
	T-01	W&M-99	−0.92	−1.39	−0.67	−0.74	−3.72
Regional Flux (%)	T-01	W-92	18	41	19	21	100
	T-99	W-92	16	36	24	24	100
	T-01	W&M-99	25	37	18	20	100
Area	(10^6 km^2)	—	151.6	72.7	53.2	31.7	309.1
	(%)	—	49.0	23.5	17.2	10.2	100

*Based on the Takahashi climatology (Takahashi *et al.*, 1999) and a recent update (Takahashi, 2001). Two different parameterizations of gas exchange and wind speed are used—Wanninkhof (1992) (W-92), and Wanninkhof and McGillis (1999) (W&M-99)—illustrating the effect of the different parameterizations. In this analysis, the NCEP 41-year averaged wind-speed product is used. However, if NCEP winds for 1995 are utilized, the global uptakes of –2.22, –2.44, and –3.72 in the last column of "oceanic regions" change to –1.95, –2.06, and –2.97 Pg/yr, illustrating the sensitivity to wind speed. Moreover, if the 6-hour NCEP winds are used rather than monthly winds, the –2.96 Pg/yr (W&M-99) drops to –2.34 Pg/yr (Wanninkhof *et al.*, 2001—from Feely *et al.*, 2001).

3.2.2 Parameterizing Gas Transfer Velocities for Calculating Air-Sea Fluxes

Determining ΔpCO_2 and k on appropriate time and space scales

As noted above, direct CO_2 flux measurements, based on observations of very small CO_2 gradients in the air immediately above the ocean surface, can only be performed on dedicated oceanographic process cruises. Moreover, k and ΔpCO_2 are affected by different factors on different timescales (Fig. 3-1). Large-scale CO_2 fluxes are therefore determined from experimental measurements of ΔpCO_2, together with parameterized values of k (Fig. 3-1).

Calculating the mean air-sea fluxes by simply averaging k and ΔpCO_2 on arbitrary time and space scales, and computing their product, gives incorrect values. The error arises because of the cross-correlation between the parameters, and also because of the nonlinearity of the gas exchange–wind-speed relationship. The average flux can be expressed as:

$$F_{av} = (ks\Delta \mathrm{pCO}_2)_{av} = (ks)_{av}\Delta \mathrm{pCO}_2)_{av} + ((ks)'\Delta \mathrm{pCO}_2')_{av} \qquad (3.2)$$

where "av" is the averaged quantity over a specified timescale.

The term $(ks)_{av}$ is not simply related to the mean wind because of the nonlinear dependence of k and u. The cross-correlation term $((ks)'\ \mathrm{pCO}_2')_{av}$ accounts for the correlation between the two quantities. The magnitude of the cross-correlation term is poorly constrained. For instance, at high winds the cross-correlation is caused by increasing gas transfer velocities and mixed layer deepening. These changes can lead to entrainment of either high or low pCO_2 waters into the mixed layer depending on season, euphotic zone depth, and mixed layer depth. Nonlinearity in the gas transfer velocity can lead to biases on the order of 30% if monthly averages are used rather than hourly quantities. Regional fluxes must therefore be derived from a robust extrapolation scheme that takes temporal and spatial variability of k and $\Delta \mathrm{pCO}_2$ into account. Global satellite observations of wind and surface roughness from scatterometer and altimeters will lead to improved determinations of gas transfer velocity. Remotely sensed sea surface temperature (SST) and ocean color will also lead to a better understanding of patterns of sea surface pCO_2 variability.

Measurements of k

To obtain accurate regional fluxes, we must be able to relate the gas transfer velocity to environmental forcing and obtain regional estimates of k on the timescale of the variability in forcing (hours). This involves improving techniques to measure k. We also need a better understanding of the controls on k. Possible artifacts and biases must be assessed, and results must be validated/verified by independent approaches. Achieving these advances will require dedicated field efforts and measurements on platforms of opportunity.

Until recently, the gas transfer velocity was determined exclusively from indirect measurements based on mass balance techniques in the surface mixed layer. The techniques utilized natural or deliberate tracers that yielded gas transfer velocities averaged over periods of days to weeks (Lapitan *et al.*, 1999; Nightingale *et al.*, 2000). The successful improvement of direct flux techniques now makes it possible to measure the flux and determine k from collocated $\Delta \mathrm{pCO}_2$ measurements, on the timescale of variability of forcing (of order 1 hour). Algorithms relating gas exchange to wind speed are developed either from compilations of field data (Nightingale *et al.*, 2000), controlled studies at a single field or laboratory site (Watson *et al.*, 1991), or a combination of field and laboratory data (Liss and Merlivat, 1986). Several recent gas exchange models are constrained by budgets of radiocarbon in the ocean (Wanninkhof, 1992; Wanninkhof and McGillis, 1999). Radiocarbon is also used as a constraint or validation of global ocean biogeochemistry models so that such parameterizations facilitate consistent observation and model-based results. Data from past field experiments are insufficient for

Table 3-3: The effects of wind speeds and of the wind-speed dependence of the CO_2 gas transfer coefficient on the net sea-air CO_2 flux using the climatological sea-air pCO_2 difference obtained in this work*.

		Pg C/yr					
Lat. Band	**Gas Transfer Wind Data**	**Pacific Ocean**	**Atlantic Ocean**	**Indian Ocean**	**Southern Ocean**	**Global Ocean**	**Errors in Flux**
N of 50°N	W-92/41-yr	+0.01	−0.40	—	—	−0.39	+28%, −23%
	W-92/1995	+0.03	−0.18	—	—	−0.14	
	W&M-99/41-yr	+0.03	−0.55	—	—	−0.52	+44%, −35%
	W&M-99/1995	+0.07	−0.17	—	—	−0.10	
14°N–50°N	W-92/41-yr	−0.64	−0.34	+0.07	—	−0.92	+25%, −23%
	W-92/1995	−0.29	−0.28	+0.03	—	−0.54	
	W&M-99/41-yr	−0.94	−0.48	+0.10	—	−1.31	+43%, −32%
	W&M-99/1995	−0.29	−0.38	+0.02	—	−0.64	
14°N–14°S	W-92/41-yr	+0.74	+0.15	+0.18	—	+1.07	+29%, −24%
	W-92/1995	+0.61	+0.07	+0.15	—	+0.83	
	W&M-99/41-yr	+0.67	+0.14	+0.20	—	+1.00	+43%, −31%
	W&M-99/1995	+0.62	+0.05	+0.12	—	+0.79	
14°S–50°S	W-92/41-yr	−0.51	−0.33	−0.67	—	−1.51	+22%, −20%
	W-92/1995	−0.57	−0.31	−0.50	—	−1.38	
	W&M-99/41-yr	−0.68	−0.51	−0.97	—	−2.16	+37%, −30%
	W&M-99/1995	−0.88	−0.51	−0.63	—	−2.02	
S of 50°S	W-92/41-yr	—	—	—	−0.47	−0.47	+26%, −21%
	W-92/1995	—	—	—	−0.58	−0.58	
	W&M-99/41-yr	—	—	—	−0.74	−0.74	+41%, −32%
	W&M-99/1995	—	—	—	−1.02	−1.02	
Oceanic Regions	W-92/41-yr	−0.40	−0.92	−0.43	−0.47	−2.22	+22%, −19%
	W-92/1995	−0.21	−0.69	−0.33	−0.58	−1.81	
	W&M-99/41-yr	−0.92	−1.39	−0.67	−0.74	−3.72	+40%, −32%
	W&M-99/1995	−0.48	−1.01	−0.48	−1.02	−3.00	
Regional Flux (%)	W-92/41-yr	18	41	19	21	100	
	W-92/1995	12	38	18	32	100	
	W&M-99/41-yr	25	37	18	20	100	
	W&M-99/1995	16	34	16	34	100	

*The flux values have been computed using the (wind speed)^2 dependence of the CO_2 gas transfer coefficient by Wanninkhof (1992) (W-92) and the (wind speed)^3 dependence of this coefficient by Wanninkhof and McGillis (1999) (W&M-99), respectively, for each of the two sets of wind data: the NCEP/NCAR 41-year and 1995 mean monthly wind speeds. Errors in flux (expressed as percentage of the flux) in the far right column represent the flux changes resulting from plus or minus one standard deviation (about ± 2 m sec^{-1} on the global average) from the annual mean wind speed in each pixel area. The positive errors in the flux represent when the mean monthly wind speed over each pixel area was increased by one standard deviation; the negative errors represent when the mean wind speed was reduced by one standard deviation (Takahashi *et al.*, 2001).

deriving authoritative parameterizations of gas transfer velocities. Part of the problem is that measurements and forcing scales are not aligned.

Broecker *et al.* (1986) expressed a number of concerns about attempts to measure gas exchange rates in oceanic conditions. Fairall *et al.* (2000) demonstrated important technical improvements that now allow such measurements. Advances in direct flux measurement techniques, and airside gradient and covariance measurements, have decreased the temporal scale to hours and spatial scale to below 1 kilometer. Successful examples include the ocean-atmosphere direct covariance method for CO_2 (McGillis *et al.*, 2001a; McGillis *et al.*, 2001b) and the gradient method for DMS (dimethylsulfide) (Dacey *et al.*, 1999; McGillis *et al.*, 2001b). The ability to measure k

Table 3-4: Mean annual sea-air pCO_2 difference, annual flux, and sea-air pCO_2 required for 0.1 Pg C flux*.

Ocean Region	Average ΔpCO_2 (μatm)	Ocean Area (10^6 km^2)	ΔpCO_2 per 0.1 Pg C (per yr uptake)	Annual Flux (Pg C/yr)
Northern North Atlantic	−47.4	7.45	11	−0.39
Temperate North Atlantic	−9.3	23.95	6	−0.27
Equatorial Atlantic	+19.9	15.43	14	+0.13
Temperate South Atlantic	−3.1	26.08	4	−0.24
Polar South Atlantic	−26.4	7.10	11	−0.22
Northern North Pacific	−8.8	4.45	20	−0.02
Temperate North Pacific	−10.0	43.04	3	−0.47
Equatorial Pacific	+29.67	50.19	4	+0.64
Temperate South Pacific	−7.4	53.05	3	−0.36
Polar South Pacific	−9.0	17.44	4	−0.20
Temperate North Indian	+35.9	2.12	132	+0.03
Equatorial Indian	+14.0	21.05	14	+0.10
Temperate South Indian	−20.0	30.49	4	−0.57
Polar South Indian	−10.1	7.16	10	−0.10
Global Oceans		308.99		−1.94

*All values are for the reference year 1995. The wind-speed data of Esbensen and Kushnir (1981) and wind-speed dependence of the gas transfer coefficient of Wanninkhof (1992) have been used.

locally in the field now provides the tools to properly relate the gas transfer to the appropriate forcing function. However, wind parameterizations will continue to be used extensively in the near future, both because wind is an important driver of surface turbulence controlling gas transfer, and because synoptic measurements and assimilation products of wind speed are readily available. Improvements in these parameterizations, especially in our ability to apply the relationships over appropriate time and space scales, will improve flux estimates.

Future work must be geared toward characterizing the near surface turbulence that controls gas transfer. Capillary waves are closely related to turbulence, and k is strongly affected by these waves (Bock *et al.*, 1999). Moreover, capillary waves generate a large return on scatterometers that are in orbit to measure global winds on daily timescales. The initial work suggests that k is more closely related to the scatterometer return than the winds derived from the return. Parameterizing k in terms of scatterometer return promises an improvement in the algorithms used to estimate k (Wanninkhof and Bliven, 1991; Frew *et al.*, 1999).

3.2.3 Studies of Biogeochemical Fluxes at the Sea Surface: Climatology and Interannual Variability

Sea surface pCO_2 and Upper Ocean Biogeochemisty

Sea surface pCO_2 is the second term determining air-sea CO_2 fluxes. While gas transfer velocities are determined by wind speed or sea surface roughness,

sea surface pCO_2 is regulated by biogeochemical processes and fluxes in the upper ocean. In principle, we can characterize sea surface pCO_2 fields from observations alone, perhaps with the aid of simple interpolation schemes. Interpolating in the context of the physical circulation field (e.g., Takahashi *et al.*, 1999) will give improved results. We can derive still more accurate sea surface pCO_2 fields by utilizing biogeochemical models specifying carbon fluxes. The pCO_2 data themselves inform us about such models, because they reflect upper ocean biogeochemical fluxes controlling total dissolved CO_2 (TCO_2), total alkalinity (TA), and pCO_2 in the mixed layer.

A number of ancillary biogeochemical properties give complementary information about upper ocean carbon fluxes. We define "ancillary properties" as concentrations or isotopic compositions of solutes that constrain organic carbon fluxes, provided that water mixing and gas exchange rates are well constrained. Ancillary properties that constrain upper ocean net production include TCO_2 (Gruber *et al.*, 1998); TA; biological O_2 supersaturation, estimated from O_2 and Ar supersaturation (Wannikhof *et al.*, 1995; Emerson *et al.*, 1995; Luz and Barkan, 2000); nutrients (Sweeney *et al.*, 2000; Zhang *et al.*, 2001; Louanchi and Najjar, 2000); dissolved organic carbon (DOC); dissolved organic nitrogen (DON); dissolved organic phosphorous (DOP); and $\delta^{13}C$ of CO_2 (Zhang and Quay, 1997). $\delta^{15}N$ and $\delta^{18}O$ of nitrate reflect nutrient sources to the euphotic zone and nutrient utilization (Sigman *et al.*, 2000). The triple isotope composition of O_2 constrains gross photosynthetic O_2 production (Luz and Barkan, 2000). Utilizing these tracers will advance many aspects of our understanding of the quantitative influence of biogeochemical fluxes on pCO_2 of the mixed layer and air-sea CO_2 fluxes at various scales.

These properties constrain carbon fluxes only in the proper physical settings and are often not applicable. There are other high-priority biogeochemical properties whose study is being planned by other efforts. Iron, for example, is clearly a high-priority property that lies outside our mandate.

Below, we recommend systematic measurements of ancillary properties as an adjunct to the pCO_2 measurements themselves. These measurements will give information about net and gross euphotic zone production over broad reaches of the oceans. The results will allow us to build improved models of upper ocean physics/biogeochemistry, leading to more accurate interpolated sea surface pCO_2 fields. As well, net and gross production rates constrained by pCO_2 and ancillary properties will give mechanistic insights for improving prognostic models to calculate sea surface pCO_2 fields in future decades and centuries.

Among the ancillary properties, $\delta^{13}C$ of TCO_2 is of special interest. This property, when combined with atmospheric CO_2 and $\delta^{13}C$ measurements, yields estimates of anthropogenic CO_2 uptake rates by the land biosphere and the oceans (e.g., Francey *et al.*, 1995; Keeling *et al.*, 1995; Ciais *et al.*, 1995). A major limitation of this approach is insufficient sea surface $\delta^{13}C$ data. Geographical and seasonal coverage is limited. Time series data have been collected only at BATS and HOT, in subtropical gyres where seasonal variations are smaller than in eutrophic waters. Extended sea surface $\delta^{13}C$ measurements, recommended below, will reduce the uncertainty in the

air-sea $\delta^{13}C$ disequilibrium and significantly improve estimates of the CO_2 uptake rates based on atmospheric CO_2 and $^{13}CO_2$ budgets.

Studies of synoptic and seasonal variability in sea surface pCO_2

Below, we recommend two primary approaches for studying the variability of sea surface pCO_2: underway measurements on ships, and continuous measurements on moorings. Ship-based measurements give CO_2 variations over long oceanic lines. Measurements made on repeat transits also give information about seasonal variability. Data collected on ocean crossings give pCO_2 fields of waters covering different physical and biogeochemical provinces of the oceans.

Moorings give complementary information by informing us about variations in pCO_2 and other properties in response to physical forcing over five important timescales. The first is the timescale of synoptic events, which influence surface properties and biogeochemistry by driving vertical mixing. The passage of eddies, whose dynamics also influence biogeochemistry (Garcon *et al.*, 2001), occurs at a similar timescale. The second timescale of interest is seasonal. Physical forcing induces large changes in water column structure, nutrient supply, solar irradiance, and consequently biogeochemical dynamics due to the seasonal progression. In most regions, pCO_2 variations are largest at the period of a year (e.g., seasonal changes dominate the variability). The third timescale is the annual. This period is the basic unit for defining fluxes that are important with respect to anthropogenic carbon as well as transport into the ocean interior. The fourth timescale of interest is the interannual. Fifth and finally, of course, there is the decadal and longer timescale associated with global anthropogenic change. The latter two timescales are discussed next.

Ocean biogeochemistry and decadal variability

Above, we noted that two modes of temporal variability could influence biogeochemistry on decadal timescales: natural interannual variability, and long-term evolution of ecosystems driven by anthropogenic global change. There is considerable observational evidence for the former, and modeling evidence that the latter will eventually be important.

Natural interannual variability in biogeochemistry is driven by interannual and decadal changes in the coupled ocean-atmosphere system. The phenomena most relevant here are ENSO, the NAO, and the PDO. ENSO variations comprise the most intense mode of interannual variability. They have a correspondingly strong influence on ocean biogeochemistry. During ENSO years, upper ocean waters in the eastern equatorial Pacific are warmer, more stratified, and consequently lower in nutrients (Barber *et al.*, 1996; Strutton and Chavez, 2000). Biomass and primary production is correspondingly lower, and there are indications that net or new production is lower as well. Fisheries yields are suppressed.

Recent studies at HOT and BATS show that biogeochemical processes at both sites have varied in response to physical forcing associated mainly

with the Southern Oscillation Index (SOI) and the NAO, respectively. This work suggests the pervasiveness of interannual variability as well as its complexity. In the 1970s, there was a shift in the SOI, linked with greater water column stratification at HOT (Karl, 1999). Associated with this shift was a decrease in dissolved SiO_2 and reactive phosphate concentrations, an increase in chlorophyll concentrations, and an increase in productivity (Karl *et al.*, 2001). There was also a shift in the nature of primary producers, with prokaryotes replacing eukaryotes.

During the 1990s, there were two cycles of the NAO, manifested in surface water temperature variations at BATS (Bates, 2001). During cooler phases, stratification was weaker, nutrient concentrations in the upper ocean were higher, and productivity was higher than during warmer phases (Bates, 2001; Steinberg *et al.*, 2001). Steinberg *et al.* (2001) did not find compelling links between the physical forcing and other biogeochemical properties. Nevertheless, at BATS as well as HOT, interannual variability is accompanied by some changes in biogeochemistry. A provocative result of this combined work is that increased stratification at HOT and decreased stratification at BATS both lead to higher productivity.

Systematic interannual variations in climate affect much of the world's surface oceans. They induce variations in upper ocean temperature and mixing that clearly have the potential for biogeochemical consequences. In three regions studied sufficiently to date (BATS, HOT, and the equatorial Pacific), we do observe significant biogeochemical responses to this forcing. Additional long-term studies of physical forcing and biogeochemical responses can provide us with insights for quantifying biogeochemical fluxes and their effects on sea surface pCO_2. Two additional attributes make time series studies important for understanding the effects of global change on ecosystems, ecosystems' influence on sea surface pCO_2, and their effects on oceanic sequestration of anthropogenic CO_2. First, interannual variability is by far the natural mode of change that comes closest to simulating effects of anthropogenic global change, and is arguably the best modern study subject for determining effects of global change. Second, some modes of global change are likely to be amplifications of interannual variability. This may be the case for the tropical Pacific, where simulations suggest that global change will push the ocean toward mean conditions closer to one of the existing modes.

3.2.4 Constraints on network design

We examined optimal sampling strategies for sea surface pCO_2 through a network design study. The results allowed us to determine the feasibility of constraining regional air-sea fluxes at a given level of accuracy, and to configure an appropriate sampling network. Our general strategy for addressing this question was to determine the resolution of pCO_2 measurements needed for constraining regional ΔpCO_2 to yield a flux accurate to 0.1 Pg C/yr, assuming that the gas transfer velocity is perfectly known. We determined this resolution based on observations of pCO_2 measured continuously along

cruise tracks. Results are given in appendices to this document (Appendix D, Appendix E).

The results show that regional ΔpCO_2 values can be accurately characterized with a small number of sea surface pCO_2 samples, even when variability is large. For example, Sweeney *et al.* calculate that one needs to characterize ΔpCO_2 to ± 3 μatm in the temperate North Pacific to constrain the basin scale flux to ± 0.1 Pg C/year. They calculate that this ΔpCO_2 accuracy can be achieved by sampling at evenly spaced 400 km intervals nine times per year. This analysis suggests that regional fluxes could be constrained with a small number of discrete observations, but there remain several unresolved issues. A similar analysis by Sweeney *et al.* (2001, unpublished results) shows that the correlation-length scales for fluxes, in contrast to those for pCO_2, are 5-fold shorter. Limited discrete sampling would not give process level information on air-sea CO_2 fluxes or biological carbon transformations, hampering modeling and assimilation efforts. Thus, closer spacing is necessary, at least until the spatial and temporal variability can be properly characterized.

We believe that we can obtain better accuracy with an automated unit that measures pCO_2 of surface water samples continuously on ships. There is the added benefit of being able to characterize small-scale pCO_2 variability, which can then be investigated using data about concentrations and fluxes inferred from auxiliary measurements. The network design studies provide an important constraint on the resolution of continuous, parallel, zonal or meridional CO_2 lines required to calculate basin-scale fluxes. Required resolution for repeat VOS lines is $\sim$5–10°, depending on the basin and the precise objectives.

Autonomous sensors would greatly enhance our ability to observe the distribution of CO_2 and related properties in the oceans. Such instruments can be installed on a variety of platforms, such as moorings, moored profilers, floats, drifters, and gliders. They can then be used to make continuous measurements with little or no subsequent support. Currently, sensors are available or under advanced development to measure pCO_2, TCO_2, O_2, total gas pressure, nutrients, and particulate organic carbon (POC). As well, autonomous moored seawater collectors allow us to measure many of these properties, as well as trace metals and concentrations of other terms of interest. In addition, autonomous sensors measure critical biological properties that, while outside the scope of our planning, are relevant because they give critical information about biogeochemical processes in the upper ocean. These include chlorophyll and other bio-optical properties that allow us to continuously determine primary production. The combination of concentration and biogeochemical measurements on the same moorings will greatly enhance the significance of the results. Autonomous platforms and instruments are described in more detail in Appendix G.

3.3 Recommendations for Observations of Sea Surface pCO_2 and Related Properties

Surface water pCO_2 observations should have the overall goal of constraining and ultimately forecasting air-sea CO_2 fluxes on seasonal timescales. Reaching this goal requires a range of measurements from process-scale studies to autonomous measurements of pCO_2 on large scales. We thus envision a close relationship between process-oriented studies and the longer-term and larger-scale observing systems described here. The process-oriented studies must include investigations of biogeochemical and physical controls on sea surface pCO_2, and studies of the physical controls on gas transfer velocity. Biogeochemical process studies are being planned independently. However, this plan addresses the first-order need to accurately constrain gas transfer velocities using satellite-measured property fields. Remotely sensed data are an essential tool for scaling observations and process-level insights to ocean basins and the globe. They will also provide improved understanding of the controlling processes. We thus foresee a spectrum of studies, including dedicated research ships for process studies, research ships of opportunity with more extensive measurement capabilities, commercial VOS, and autonomous platforms.

Recommended programs are given priorities ranging from 1 (highest) to 3. The following recommendations define a 5-year plan and are described below roughly in order of priority. The proposed projects, priorities, and cost estimates can be found in tabular form in Table 3-5.

3.3.1 Form and improve international collaborations on unified data protocols and standardization (priority 1)

Significant efforts are underway in other nations and regions, most notably Japan, the EU, Canada, and Australia, to gather surface pCO_2 data. A summary of the EU plans can be found in Appendix H. Reciprocal arrangements should be negotiated with the foreign laboratories for a full exchange of data. Ideally, all data would be in a compatible format; but if not, foreign data should be modified for posting on the American website.

International collaborations should include the sharing of sampling and analytical protocols. Executing this objective successfully will require international workshops, assistance in setting up data reduction protocols, and perhaps provision of technical support and hardware. Estimated cost is $300,000 per year.

3.3.2 Measure pCO_2 and related properties on volunteer observing ships

The measurement of pCO_2 and related properties on VOS will provide the first-order data set for constraining air-sea fluxes of CO_2 and rates of biogeochemical processes that mediate sea surface pCO_2 values. Again, we note the particular importance of $\delta^{13}C$ of CO_2 among the ancillary properties. We recommend the following studies in the next 5 years.

Table 3-5: Priorities and cost estimates for surface observation program.

Element of the implementation plan	Priority	Ship time	Costs/year
Recommendations for the Next 1 to 5 Years*			
Form and improve international collaborations on unified data protocols	1		$300,000
Measure pCO_2 and related properties on volunteer observing ships			
VOS studies in the North Atlantic (4 ships)	1		$520,000
VOS studies in the Southern Ocean (existing/new 4 ships)	1/2		$600,000
VOS studies in the equatorial Pacific (2 ships)	1/2		$300,000
VOS studies in the equatorial and North Pacific (2 ships)	2		$600,000
Meridional trans-Atlantic and trans-Pacific lines (4 ships)	3		$150,000
Measurements of ancillary properties (5 ships)	1–5		$1,000,000
Improve our understanding of the physics of gas exchange			
Longer term observations	1		$750,000
Upscaling studies	2		$350,000
Process studies	3	$1,000,000	$1,500,000
Deploy moorings for time series of pCO_2 and related biogeochemical properties			
Time-series stations at HOT and BATS (including mooring)	1		$2,000,000
Equatorial Pacific time series (4 systems, excluding cost of moorings)	1		$600,000
Boreal time series in the North Atlantic and North Pacific (including mooring)	2	$1,000,000	$2,000,000
Time-series sites in the Southern Ocean (including mooring)	4	$1,000,000	$2,000,000
Design a data access system	2		$400,000
Develop improved autonomous sensors for sea surface analysis			
Develop improved autonomous sensors for sea surface analysis of pCO_2	2		$400,000
Develop for measurement of ancillary properties	3		$1,000,000
Develop formalisms for interpolating air-sea CO_2 fluxes in time and space	3		$300,000
Deploy drifters with pCO_2 sensors to map pCO_2 fields			
Southern Ocean drifters (20)	4	$1,000,000	$1,200,000
Subpolar/subtropical North Atlantic drifters (20)	4	$360,000	$1,200,000
Equatorial Pacific drifters (20)	4	$450,000	$1,200,000

*Results from years 1–5 will be used to plan for a comprehensive sea surface pCO_2 observing system 5 years hence as measurement technologies, modeling capabilities, and knowledge of ocean pCO_2 are improved.

Initiate VOS studies in the North Atlantic (priority 1)

We recommend that four commercial VOS that run repeat cruise tracks spanning the entire basin be instrumented to measure pCO_2 and ancillary properties. Ships should be chosen based on cruise track, likely stability on route, available scientific infrastructure (e.g., whether the ship has TSG, XBT, or ADCP operations), and access for maintenance. The primary scientific criterion for choosing cruise track should be to sample the North Atlantic waters that are now most seriously undersampled with respect to CO_2 fluxes. This criterion directs more attention to areas of large ΔpCO_2 and higher wind speeds. The work should be coordinated with a recently funded European effort (CAVASOO; see Appendix H). Estimated total cost for four ships is $520,000 per year.

Continue and initiate VOS studies in the Southern Ocean (priority 1 for continuing sampling studies, priority 2 for new sampling studies)

The Southern Ocean may be an important sink region for anthropogenic CO_2. It plays a large role in the global carbon cycle (Sarmiento *et al.*, 1998). Understanding biogeochemical dynamics here is particularly important because models consistently show the potential for anthropogenic effects to induce large changes (Sarmiento *et al.*, 1998; Matear *et al.*, 1999; Matear *et al.*, 2000). There is also a large discrepancy in the estimated magnitude of the Southern Ocean CO_2 sink based on atmospheric CO_2 distributions and fluxes calculated from the Takahashi climatology (Takahashi *et al.*, 1999; 2001). The VOS program for the Southern Ocean would involve a total of at least four ships. It should take advantage of both American ships and other nations' ships of opportunity. We particularly note the availability of scientific and resupply ships that operate regularly in the Southern Ocean. The program might also include commercial VOS running great circle routes in the Southern Ocean, or cruise ships, if either of these offer reliable and desirable cruise tracks. Here as elsewhere, we should encourage and assist in other national efforts, and plans should be made for data sharing. For example, the Australians have almost a decade's worth of data south of Australia but currently this program is under considerable financial stress. Total estimated cost for the four ships is $600,000 annually.

Continue VOS studies in the equatorial Pacific (priority 1)

The equatorial Pacific is an important region that accounts for a large part of the interannual variability in air-sea pCO_2 fluxes. Ongoing underway measurements of sea surface pCO_2 should continue in the equatorial Pacific using one or two scientific ships of opportunity operating in that region. Total estimated cost for the two ships is $300,000 per year.

Initiate VOS studies in the North Pacific (priority 2)

Four commercial VOS operating along repeat tracks in the North Pacific should likewise be instrumented for continuous measurements of sea surface pCO_2 and ancillary properties. Selection criteria for these ships should be similar to those for ships used in the North Atlantic. Total estimated cost is $600,000 per year.

Initiate meridional transects on ships of opportunity in the Atlantic and Pacific (priority 2)

Since the largest CO_2 gradients in air and water are observed in the north-south direction, and since there are large uncertainties in fluxes deduced from atmospheric inversion studies for South America and Africa, some meridional lines should be occupied. These lines should include atmospheric sampling of CO_2 and related isotopes and tracers. Lower cost will be realized by placing instruments on established VOS/XBT lines that have infrastructure already set up. Total cost is $150,000 per year for two ships.

Measure temperature, salinity, and ancillary biogeochemical properties (priorities 1–3, depending on property and cost)

Temperature and salinity need to be measured wherever pCO_2 is measured. Vertical profiles of T and S should be measured along lines where data on mixed layer thickness and water column stratification is particularly important to understand upper ocean chemistry and biogeochemical fluxes. Cost of thermosalinograph installation is approximately $40,000. XBTs can be obtained for $35 each. Whenever possible, VOS selection should be based on infrastructure already in place.

Ancillary biogeochemical measurements are of interest along all cruise tracks, and especially so in two cases. The first is where they provide information about seasonal biological processes that induce large seasonal variations in sea surface pCO_2. The second is where data on the distribution of chemical and biological properties can give important information about anthropogenic carbon fluxes as well as biogeochemical processes and their rates.

$\delta^{13}C$ of CO_2 in the mixed layer is considered priority 1, because it is a critical term when using $\delta^{13}C$ of atmospheric CO_2 to partition CO_2 uptake between the land biosphere and ocean. Other ancillary properties are provisionally assigned a priority that is one level lower than that of the CO_2 measurements in their respective ocean basins. Again, decisions need to be made in individual cases based on cost and scientific justification. Total estimated cost for ancillary properties (which do not include T and S) is $1 million annually.

3.3.3 Develop understanding of the physics of gas exchange, to improve our ability to parameterize gas transfer velocities using data collected from satellites; develop and test gas exchange parameterizations with eddy accumulation experiments (priorities 1–3)

The general approach for the CO_2 observation plan is to perform process-level studies of long duration (more than 1 year) to compare detailed measurements of the sea surface CO_2 flux field with air-sea fluxes using parameterized gas exchange velocities. These parameterizations will be based on wind speed and the surface wave field, inferred largely from buoy arrays and satellite retrievals of these properties. In this manner, the process and time-series studies can be scaled up from mesoscale to larger regions.

Our recommendations focus on scaling up process-level information to the larger scale, with the necessary validations at each step of the assimilation process. Doing so involves several development steps:

- *Collocate gas transfer velocity measurements with ocean-surface pCO_2 measurements.* Air-sea CO_2 flux estimates are only as good as the product of measurements of ocean surface pCO_2 and k. Conversely, information on spatial and temporal variability of surface pCO_2 is needed to compute accurate transfer velocities from direct CO_2 flux measurements.

- *Validate fluxes.* Simultaneously measure fluxes using independent approaches, because direct flux measurements are susceptible to biases. Specifically, implement direct air-sea flux measurements of CO_2 and other gases, and employ proxies such as mass balance approaches of radon and deliberate tracers. On larger scales, this includes independent constraints to determine whether regional air-sea gas fluxes are consistent with atmospheric measurements of O_2/N_2, $^{13}C/^{12}C$, and ^{13}C disequilibrium measurements between water and air.

- *Improve the accuracy of gas transfer velocities.* Target measurements to improve accuracy of calculated fluxes and understanding of controls. Time-series stations and stable platforms are particularly effective for carrying out long-term observations to improve quantification of air-sea CO_2 fluxes.

- *Improve algorithms for parameterizing gas transfer velocities.* Perform studies to improve parameterizations by adding measurements of air-sea CO_2 fluxes and controlling physical processes of the sea surface to those research cruises involved in ocean surface pCO_2 surveys. Conduct cruises to different regions to study spatial and seasonal variability.

- *Develop tools for spatial extrapolation.* We must utilize satellite products for remote sensing of gas transfer velocity, and possibly properties used to derive pCO_2, to be assimilated in models. Remotely sensed

products and surface ocean pCO_2 climatology should be made openly and readily available.

These goals must be implemented through three approaches: process studies to quantify fluxes and factors controlling the fluxes, longer term observations to determine flux variability, and studies to quantify the upscaling of local fluxes. *The distinction between process studies of gas exchange and longer duration studies is in the platform of choice and number of support measurements.* The longer-term observations would take place on fixed ocean platforms or dedicated ships, such as *SeaOrbiter*, which are stable and have well-characterized flow distortion profiles. The process studies are ship-based campaigns. They will be more exploratory and will include water column measurements to understand the processes controlling pCO_2.

The recommended gas exchange studies follow.

Carry out longer-term observations of gas exchange (priority 1)

Direct flux measurements must be performed to determine whether we can derive unique parameterizations for the gas transfer velocity, and to assess the impacts of episodic events such as storms on fluxes. Observations from fixed platforms and opportunistic research ship voyages are cost-effective. Initially, an easily accessible coastal observatory should be equipped, but eventually an open-ocean site should be selected to measure a range of fluxes. The French *SeaOrbiter* is a free-floating platform much like FLIP but for longer duration studies. It is one of the candidate platforms for opportunistic, extended flux studies in the open ocean. Research ships often perform direct flux measurements of heat and momentum that require the same equipment used to determine small-scale velocity fluctuations. These cruises should be augmented to measure CO_2 fluxes as well. Aside from measuring fluxes, accurate measurements should be taken of environmental forcing, such as friction velocity, wave slope, and surface turbulence parameters. Incorporating a remote-sensing component such as scatterometry is highly desirable. Estimated cost is $750,000 annually.

Perform upscaling studies (priority 2)

To calculate air-sea CO_2 flux fields, we need to quantify spatial and temporal variability in relevant properties from observations and satellite data. We then need to include this information, using statistical techniques, in the estimation of regional fluxes. Here we recommend support for experimental studies that will improve our ability to interpolate and extrapolate. Field observations should be supported to develop algorithms characterizing regional fluxes. Synthesis and modeling studies should include improved parameterizations using products that can be measured remotely. This requires incorporating spatial and temporal variability of surface parameters into regional flux estimates by statistical means to quantify variability as determined from satellites. Estimated cost is $350,000 per year.

Perform process studies of gas exchange (priority 3)

The two recently completed NOAA efforts, the GasEx 1998 and 2001 studies, have shown the feasibility of the direct flux measurements and have provided initial results on parameterization with forcing. Future studies should have a greater focus on parameterization using remotely sensed products. They should be collocated with intensive basin observations of ΔpCO_2. The recommendation is to perform one process study each in the North Atlantic, North Pacific, and Southern Ocean areas during a period when VOS are intensely studying the sea surface pCO_2 field. The estimated cost (per process study) is \$1.5 million and \$1 million in dedicated ship time.

3.3.4 Deploy moorings and carry out time series studies of pCO_2 and related biogeochemical properties in major biogeochemical provinces of the world's oceans

We recommend time-series studies utilizing both ships and autonomous platforms to characterize seasonal- to decadal-scale variability in ocean biogeochemistry. We urge that, wherever possible, time-series stations supporting CO_2 observations be joint with those of other programs such as CLIVAR (using, for instance, their proposed flux buoys). The time-series stations will provide the time-continuity that is lacking in the decadal surveys and will allow the program to detect changes in the oceanic system as they occur. The proposed observation program must be designed to detect such changes early, allowing response with additional observational assets, surveys, and in-depth process studies.

Continue time-series stations at HOT and BATS (priority 1)

We recommend continued support and augmentation to include autonomous platforms for the two current American time series at Bermuda (BATS) and Hawaii (HOT). This recommendation is based on the fact that these two sites are the most extensively studied and therefore are optimal to field-test the emerging new autonomous technology required for long-term monitoring (see below). This recommendation is in line with the recommendations given by independent advisory panels of the National Science Foundation and NASA. Estimated cost is \$2 million per year (including the cost of mooring).

Continue and formalize equatorial Pacific time series (priority 1)

We recommend that a time-series program be formalized for the equatorial Pacific based on the existing TAO mooring array and the ships servicing these moorings. This regional time-series site builds on the ongoing efforts of PMEL and MBARI for measuring upper ocean CO_2 concentrations and other properties. Implementing this recommendation will come at relatively modest cost because the new CO_2-oriented work can benefit optimally from the existing mooring infrastructure as well as the regular ship-based servicing in place. Estimated cost is \$600,000 per year (for four systems to observe pCO_2 and related properties, excluding the cost of mooring).

Implement time-series sampling in the boreal North Atlantic and North Pacific (priority 2)

We recommend that existing time-series stations in areas critical for detecting and documenting interannual to decadal ocean variability be augmented with CO_2 measurements (see Tables 4-1 and 4-3 in Chapter 4). Two critical areas are the high latitudes of the North Atlantic and North Pacific. In these regions, the dominant modes of extratropical climate variability, such as the Pacific Decadal Oscillation and the North Atlantic Oscillation, are most strongly expressed. A third critical area is the Southern Ocean, for which model simulations indicate high sensitivity to future climate changes.

Our specific selection of sites is based on the expectation that there will be large variations in biological and physical cycles on interannual to decadal timescales. It is also based on resource availability to service the sites and the existence of previous efforts to study the regions. Specifically, for the North Atlantic, we recommend continuing and augmenting the Labrador Sea time-series site Bravo and the Norwegian Sea time-series site Mike, where previous studies revealed large seasonal variations in the euphotic zone (Takahashi *et al.*, 1993). These sites are optimally placed to study the impact of the North Atlantic Oscillation on upper ocean variability in physics, chemistry, and biology. Accordingly, we also recommend the study of ancillary tracers of biogeochemical processes, as for the VOS studies outlined above. Estimated cost is $2 million annually (including the cost of mooring operations). The cost of dedicated ship time is estimated at $1 million per year (for 25 days of operation in each basin).

Implement time-series sites in the Southern Ocean (priority 3)

Toward the end of the plan's 5-year period, when autonomous technology will be more advanced, we recommend extending the existing set of time-series stations into the Southern Ocean, where model simulations clearly indicate the most dramatic long-term changes in response to global climate. Extending observational capabilities into this region is extremely important, since this region is not only sensitive, but represents an area where relatively small climate changes can result in large changes in CO_2 fluxes and ocean storage. Estimated cost is $2 million per year (including the cost of mooring and ship operations). The cost of dedicated ship time (50 days) is estimated at $1 million annually.

3.3.5 Design and implement a data management and access system that will make CO_2 measurements easily accessible on the web, including both discrete data and fields determined using interpolation schemes (priority 1)

The data obtained in this effort will be most useful if it can be provided to the community in a uniform collated format. Rapid dissemination (less than a year) is critical as well so that the data can be used as boundary conditions and constraints for models. Moreover, the data should be available for the

biennial assessment (see Chapter 6). It is critical that this data management system is in place at the time the data is being gathered in the field rather than after the fact. Estimated cost is $400,000 per year.

3.3.6 Develop improved autonomous sensors for sea surface analysis of pCO_2 and related properties

The ability to autonomously measure pCO_2 and other properties of biogeochemical interest will greatly extend our knowledge of air-sea CO_2 fluxes and mediating processes. We recommend the following development efforts to extend these capabilities.

Improve autonomous pCO_2 instruments (priority 2)

We recommend that resources be devoted to a small number of efforts to improve and test instruments for measuring sea surface pCO_2 on VOS, moorings, floats, and drifters. Development efforts should achieve some or all of the following: improving accuracy, durability (and extending the duty cycle), data handling, and ease of use; and lowering costs. We strongly encourage SBIR initiatives to produce pCO_2 systems and other seagoing instruments at competitive cost. Estimated cost is $400,000 annually.

Develop improved sensors for measuring ancillary geochemical properties (priority 2)

Improved sensors should be developed for measuring such ancillary properties as NO_3^-, SiO_2, and DOC. Development of samplers may also be appropriate. We recommend funding projects that show the greatest promise within the available resources. Estimated cost for this effort is $1 million annually.

3.3.7 Develop formalisms for interpolating air-sea CO_2 fluxes in time and space, and seasonal and annual averages, from local flux values (priority 3)

The calculation of air-sea fluxes from sea surface pCO_2 fields, gas exchange parameterizations, and wind speed (or another satellite property) needs to be developed, to calculate the basin-scale flux fields that are the primary product of the recommended observations. Estimated cost is $300,000 per year.

3.3.8 Deploy drifters with pCO_2 sensors to map pCO_2 fields of otherwise inaccessible regions and regions where large seasonal pCO_2 variations are linked to large biogeochemical fluxes (priority 3)

This work has several objectives:

- Map the pCO_2 fields in important regions of the North Atlantic, equatorial and North Pacific, and Southern Oceans that are not accessible by using ships of opportunity.
- Carry out Lagrangian experiments (in which observing platforms move with surface water bodies) to determine timescales of pCO_2 variability at local spatial scales, and distinguish biological and physical influences.
- Acquire a data set to enhance understanding of the information content from a large array of pCO_2 drifters, for planning future observations.

We suggest a series of experiments, addressing the three objectives listed above, involving about 20 drifters. Possible sites and more specific objectives include the following.

Improve knowledge of the pCO_2 field of the Southern Ocean

Drifters released along a meridional line would flow to the east and monitor seasonal changes in pCO_2 and other properties over a broad zonal reach. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

Study the springtime pCO_2 drawdown in the North Atlantic during the bloom

Drifters could be released during springtime, in a grid that would give continuous records of sea surface pCO_2 during the period of the bloom over a large part of the basin. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

Improve knowledge of the synoptic pCO_2 field in the equatorial Pacific

Drifters starting in two N-S lines would flow eastward and westward parallel to the equator, giving a detailed picture of the evolution of regional pCO_2 variations and their relation to mesoscale physics and satellite chlorophyll fields. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

These three experiments are intended as examples of opportunities, rather than projects specifically recommended for implementation.

Chapter Four

Integrated Studies in the Water Column

4.1 Overview

The ocean is the primary realm removing anthropogenic CO_2 from the atmosphere, particularly on multidecadal to centennial timescales. Anthropogenic CO_2 enters the ocean at the surface but is rapidly mixed down into the thermocline. There it resides for many decades until it is gradually transferred to the deep ocean. Accurately characterizing the evolving inventory and distribution of anthropogenic and natural (total) CO_2 in the ocean interior is fundamental for several reasons. First, it gives basic information about the evolving disposition of anthropogenic CO_2 that is not remaining in the atmosphere. Second, the distribution of anthropogenic CO_2 in the ocean interior reflects the governing processes of surface uptake and redistribution by ocean circulation. The anthropogenic CO_2 distribution thus allows us to test and improve models of processes controlling ocean uptake, thereby improving our predictive capabilities. Third, the distribution of anthropogenic CO_2 reflects regional uptake rates of CO_2 at the sea surface and subsequent horizontal transports. In this way, the oceanic distribution of anthropogenic CO_2 gives an independent constraint on basin-scale ocean uptake and redistribution for comparison with air-sea flux estimates. These regional constraints on ocean uptake are also important for quantifying continental-scale CO_2 uptake. Fourth, secular climate change is projected to alter large-scale ocean circulation and marine biogeochemistry, leading to corresponding changes in the background natural ocean carbon cycle and the partitioning of carbon between the ocean and atmosphere.

We recommend three components to the program for ocean interior measurements.

1. A series of repeat ocean transects, involving reoccupation of selected meridional and zonal World Ocean Circulation Experiment (WOCE) lines, in which CO_2 system properties will be measured along with hydrographic properties, nutrients, and transient tracers.

2. Time series stations, including autonomous sampling from moorings, that provide data on monthly to seasonal timescales for measurement of hydrography, CO_2 properties, nutrients, and (at appropriate intervals) transient tracers.

3. Support for the development of autonomous platforms and instruments that measure properties of interest in the ocean interior, and for deployment as these capabilities become operational. Such equipment will allow us to greatly improve the spatial and temporal resolution of our measurements.

These efforts should provide important information on several essential subjects:

- The evolving distribution of both natural and anthropogenic CO_2 in the ocean interior. Meridional ocean sections, supplemented by zonal lines and time series, will give this information. The evolving time-dependent CO_2 distribution reflects the sum of oceanic processes and is therefore a first-order constraint on models used to predict ocean CO_2 uptake.

- Transport of CO_2 in the ocean interior. Zonal lines provide the primary constraints on meridional transport of natural and anthropogenic CO_2. Patterns of transport reflect processes of uptake and redistribution.

- Interannual and decadal variability in the oceanic distribution of CO_2 and bioactive tracers. There is evidence that oceanic ventilation and rates of biogeochemical processes vary during events such as the Pacific Decadal Oscillation (PDO), North Atlantic Oscillation (NAO), and El Niño-Southern Oscillation (ENSO). Understanding these variations will allow us to document the influence of interannual and decadal variability on ocean uptake of fossil CO_2, and governing processes.

- Improved constraints on air-sea CO_2 fluxes. Interior ocean CO_2 fluxes depend, in part, on basin-scale uptake rates of anthropogenic CO_2. The data thus give a rate that can be compared with air-sea CO_2 fluxes measured by sea surface studies. They also give a critical independent constraint for inverse calculations of CO_2 uptake by the land biosphere.

- Improved constraints on ocean biogeochemical models. All the information listed in the items above is critical for the validation of ocean biogeochemical models used to predict future carbon distributions and fluxes.

Ocean interior studies should be a continuing effort that exploits strong linkages with the Climate Variability and Predicitability (CLIVAR) program and other complementary programs to make efficient use of ship time, moorings, and autonomous platforms.

4.2 Background

Two intertwined approaches have been used to constrain the current ocean uptake of anthropogenic CO_2 from the distribution of properties in the subsurface ocean. In the first approach, the composition of subsurface waters is used to calculate the concentration of anthropogenic CO_2 and its rate of increase. In the second, models describing the large-scale mixing and transport of the oceans are used to predict the present and future uptake rates of anthropogenic CO_2 and its oceanic distribution. In the past, the modeling approach has received the most attention. Models of increasing complexity

have been used to calculate that the global oceanic uptake rate of anthropogenic CO_2 was about 2 Pg C/yr in the 1980s, rising to about 2.4 Pg C/yr at present (Orr *et al.*, 2001).

The other approach, estimating the large-scale anthropogenic CO_2 distribution from observations, is currently hampered by the lack of high-quality historical CO_2 data. We lack an adequate baseline to infer directly the change in CO_2 inventory over time. As a result, the (small) anthropogenic CO_2 concentration must be inferred using an estimate of its pre-anthropogenic value calculated from the modern concentrations of CO_2 and other properties. Chen and Millero (1978) and Brewer (1978) first outlined methods for this calculation; Gruber *et al.* (1996) have recently developed a modified approach. More recently, a number of alternative, albeit more indirect, means to estimate anthropogenic CO_2 have been proposed. These involve efforts to balance the global budget for ^{13}C of CO_2 (Heimann and Maier Reimer, 1996), or linking anthropogenic CO_2 to chlorofluorocarbons (Watanabe *et al.*, submitted, 2001; Gruber *et al.*, in preparation, 2001). All of these approaches require a global database of high-quality CO_2 measurements along with concentration data for other bioactive and hydrographic properties. The global CO_2 survey of the World Ocean Circulation Experiment/Joint Global Ocean Flux Program (WOCE/JGOFS) provided such a data set for the first time, making a major contribution to our understanding of ocean carbon uptake. These data, interpreted as described above, are yielding information about the oceanic distribution of anthropogenic CO_2 in the ocean, and basin- to global-scale inventories of these properties (Gruber *et al.*, 1996; Gruber, 1998; Feely *et al.*, 1999; Sabine *et al.*, 1999; Sabine *et al.*, 2001).

The reconstructed distribution of anthropogenic CO_2 in the oceans shows a strong surface- to deep-ocean gradient (Fig. 4-1). This is as expected for a tracer that invades the ocean from the surface; however, this surface- to deep-ocean gradient is not uniform. There are large differences between the North Atlantic, where anthropogenic CO_2 can be traced down to the bottom, and the tropical Pacific, where no anthropogenic CO_2 can be detected below 600 m. The highest concentrations and deepest penetration of anthropogenic CO_2 are associated with the Subtropical Convergence Zones. This distribution is consistent with that expected based on current knowledge of large-scale ocean circulation.

A second major finding evolving from the WOCE/JGOFS CO_2 survey is the success in reconstructing the change of inorganic carbon over time by comparing these high-quality data with historical data (Wallace, 1995; Slansky *et al.*, 1997; Peng *et al.*, 1998; Sabine *et al.*, 1999). Despite the lower quality of the historical data, the estimated changes over time are consistent with the trends expected based on the total anthropogenic CO_2 concentrations computed from the new hydrographic data alone. These results clearly demonstrate that the ingrowth of anthropogenic CO_2 can be observed by a repeat sampling of interior ocean water masses. The ingrowth of anthropogenic CO_2 over time has also been directly observed in mixed layer samples at the Bermuda and Hawaii long-term observations sites (Winn *et al.*, 1996; Bates, 2001).

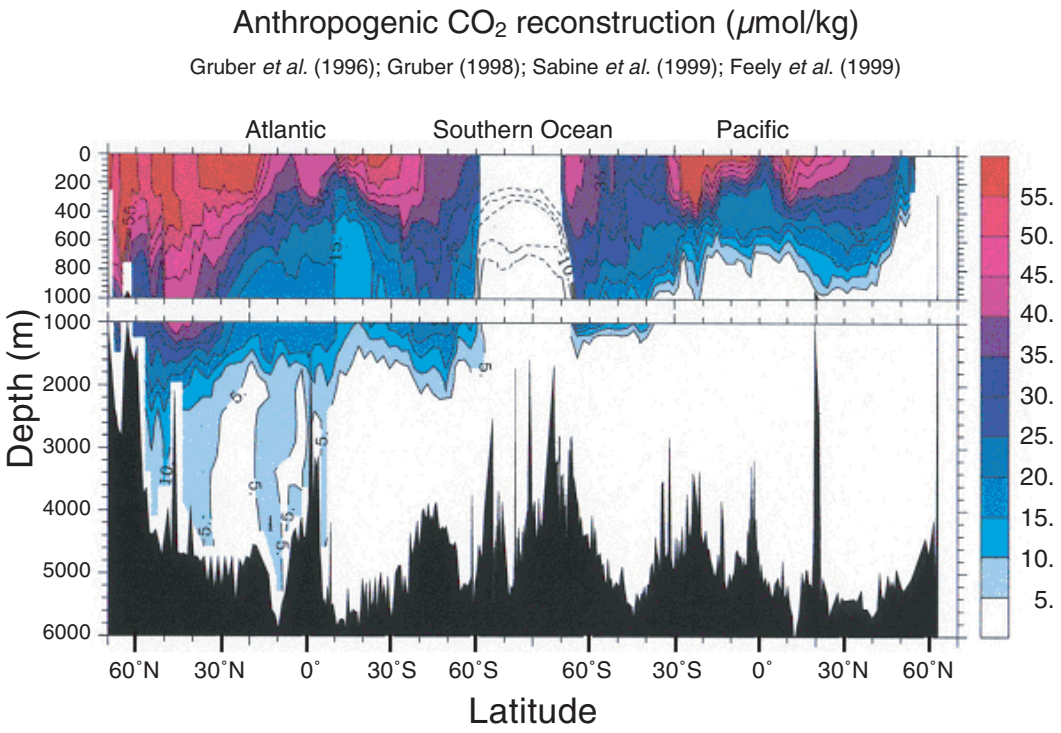


Figure 4-1: Distribution of anthropogenic CO_2 in the Atlantic and Pacific Oceans (after Gruber *et al.*, 2000).

The main factor controlling the current uptake of anthropogenic CO_2 by the ocean is the transport of this "excess" CO_2 from the surface into the interior of the ocean. Other anthropogenic tracers that follow the same pathway of ocean uptake provide powerful constraints on the oceanic CO_2 uptake. Such anthropogenic tracers include bomb radiocarbon and anthropogenic halocarbons. Their advantage over anthropogenic CO_2 is that they are entirely anthropogenic, or their natural abundance is at least better known. These tracers, together with estimates of the oceanic distribution of anthropogenic CO_2 and its rate of change, therefore, provide a critical target/test for ocean circulation models. The models do a good job of simulating the global ocean inventory of anthropogenic CO_2 (Orr *et al.*, 2001). However, they are less successful in computing regional distributions of anthropogenic CO_2 and other tracers in the oceans (Fig. 4-2; Gruber, 1998; Orr *et al.*, 2001; Dutay *et al.* 2001).

The discrepancies between data on transient tracer distributions and model predictions highlight ways in which the models can be improved. For example, recent intercomparisons of model output have allowed diagnosis of model characteristics that lead to divergent predictions (`http://www.ipsl.jussieu.fr/ocmip/`). These comparisons, and ongoing model improvements, will lead toward two advances in our understanding of the oceanic uptake of anthropogenic CO_2. Improved models will allow for more accurate interpolations of oceanic concentration fields, thereby giving well-constrained basin- and global-scale CO_2 inventories with sparser data sets. Further, more

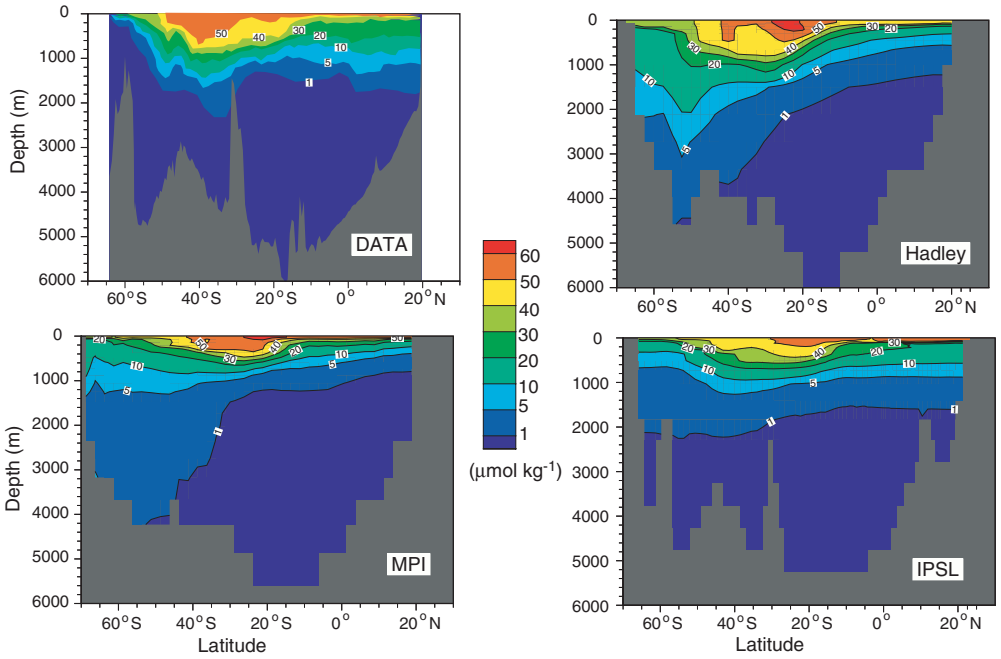


Figure 4-2: North-south section of anthropogenic CO_2 (μmol/kg) in the Indian Ocean at 92°E from observations (DATA) and from simulations by OCMIP models. Model abbreviations are: MPI = Max Planck Institüt für Meteorologie—Hamburg, Germany; Hadley = Hadley Centre for Climate Prediction and Research, Bracknell, England, UK; IPSL = Institute Pierre Simon LaPlace, France.

accurate models will lead to improved projections of ocean uptake rates of CO_2, and hence better predictions of the evolution of atmospheric CO_2 burdens.

Improvements in observations and modeling of ocean ventilation are essential components of a carbon-observing plan. To first order, the long-term oceanic uptake of anthropogenic CO_2 is regulated by water mass transport. In planning a decadal-scale observing program, a better understanding of carbon transport within the ocean's interior can help identify critical areas that need additional sampling and monitoring for those changes in overturning that may have serious consequences for future anthropogenic uptake. Preliminary 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) used data from three WOCE/JGOFS sections together with several pre-WOCE cruises in the South Atlantic between 10°S and 30°S to estimate meridional carbon transports in this region. Notable findings by Holfort and colleagues are that the net preindustrial 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 North Atlantic Deep Water has not yet been contaminated by the anthropogenic signal at this latitude. A study of ocean transport links the carbon flux es-

Table 4-1: Existing time-series stations in the oceans.

Existing time-series stations	Autonomous sensors	CO_2	Transient tracers
S/BATS/BTM, Bermuda/U.S.	yes	yes	no
HOT, Hawaii, U.S.	no	yes	no
Eq. Pacific, especially 0°, 155°W, 2°S, 170°W, U.S.	yes	yes	no
Station Papa, NE Pacific, Canada	no	yes	no
Mike, Norwegian Sea, Norway	no	no	no
KNOT, NW Pacific, Japan	no	yes	no
ESTOC, Canary Islands, Spain/Germany	no	yes	no
Bravo, Labrador Sea, Canada	no	no	no

timates provided by the surface observation program and the ocean storage derived from the ocean interior work proposed here. The "natural" 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.

As previously described in detail in Chapter 3, time-series studies within the oceans are required to delineate the interannual and decadal variability caused by long-term changes in ocean circulation and biology that occur in response to the penetration of anthropogenic temperature and CO_2 signals into the oceans. Time-series studies are similarly needed to assess the variability that is the result of natural climatic changes including ENSO, PDO, NAO, etc. At present, there are only a few places where long-term observations allow us to assess the magnitude of interannual variability (Table 4-1), prominent examples being the JGOFS studies at the Hawaiian Ocean Time-series site (HOT; e.g., Karl and Lukas, 1996; Karl, 1999) and Bermuda Atlantic Time-series Study site (BATS; e.g., Steinberg *et al.*, 2000; Bates, 2001). This important work has shown that variability is as much an implicit component of the ocean carbon cycle as it is of climate in general (Karl *et al.*, 2001).

From observations at the HOT site over the past three decades, Karl and coworkers (Karl, 1999; Karl *et al.*, 2001) have observed systematic changes in the community structure of phytoplankton that have been linked to phase changes in the Pacific Decadal Oscillation. They suggested that large-scale changes in the stability of the water column caused systematic shifts in the phytoplankton community leading to enhanced nitrogen fixation. Such changes can have profound impacts on the net exchange of carbon between the upper ocean and the ocean interior because nitrogen fixation will lead to increased export from the euphotic zone into the permanent thermocline. It also might impact the air-sea balance of CO_2 indirectly in that such a community structure change can lead to a net increase of the available fixed nitrogen for general phytoplankton growth and export.

Studies at BATS have also demonstrated interannual to decadal variabil-

ity in ecosystem responses to physical forcing and upper ocean biogeochemistry that may be linked to large-scale processes of ocean variability. Bates (2001) and Gruber *et al.* (in preparation, 2001) showed, for example, that biological production and air-sea fluxes of CO_2 are strongly correlated with sea-surface temperature variations, which are themselves to a significant degree controlled by interannual to decadal variations in the North Atlantic Oscillation. These changes not only manifest themselves in the upper ocean, but often show up even more strongly in the thermocline (Bates, 2001; Joyce and Robbins, 1996). The BATS results clearly show significant increases in interior ocean TCO_2 concentrations over time in subtropical mode waters ($\sim$2.3 μmol kg/yr) that may be related to changes in atmospheric conditions over the North Atlantic resulting in changes in water column ventilation processes (Bates *et al.*, 1996). Similar changes may be occurring elsewhere in the intermediate waters of the oceans.

Research from other long-term time-series programs such as the California Cooperative Fisheries Investigation (CalCOFI) (Roemmich and McGowan, 1995) and from Ocean Weather Station Papa (Takahashi *et al.*, 1993, 1997) all show that the view of a static ocean is mostly a result of the absence of oceanic data to document upper ocean ecosystem changes and that variability cannot be neglected. Interannual variations recorded at the few time-series stations are hardly local phenomenon. Rather, large-scale changes in the climate system affect the distribution of carbon and other bioactive tracers in a major way. An illustration comes from the recent finding that the thermocline oxygen content changed throughout the North Pacific basin in recent decades (Pahlow and Riebesell, 2000; Keller *et al.* 2001; Emerson *et al.*, in press; Watanabe *et al.*, submitted, 2001). These authors have analyzed hydrographic data in the North Pacific and discerned evidence for changes in nutrient and O_2 inventories in thermocline waters as well as the shallower waters of the deep ocean. The variations must be caused by changes in biogeochemical fluxes or by variations in ventilation rates. At present we cannot determine which. Either cause would have an effect on the net transfer of CO_2 across the air-sea interface and therefore directly on the ocean uptake rates of anthropogenic CO_2. We also do not know whether the biogeochemical changes are natural or are harbingers of future global climate change. The latter was interpreted as the reason for large-scale oxygen changes in the Southern Ocean (Matear *et al.*, 2000).

Global change simulations have examined the implications of global warming for the uptake of anthropogenic CO_2 during the coming century and beyond. A consistent finding in these studies is that warming and increased precipitation induce increased stratification, most notably in the Southern Ocean (Sarmiento *et al.*, 1998; Matear *et al.*, 1999). Increased stratification, in turn, has two counterbalancing effects on upper ocean biogeochemistry. The first is a reduction of upwelling and productivity, particularly in the low latitudes; the second is an increase in nutrient utilization (Bopp *et al.*, 2001). The Southern Ocean has a particularly large potential to modulate anthropogenic CO_2 uptake because of its large nutrient reservoir. In agreement with this expectation, modeling studies point to the Southern Ocean

as the critical region in which ocean change can cause large changes in anthropogenic CO_2 uptake (Sarmiento *et al.*, 1998; Matear *et al.*, 1999).

Understanding interannual to decadal variability linked to ocean ventilation is important for two reasons. First, the response of ocean chemistry and biogeochemistry to variability in the physical forcing gives mechanistic insight that can ultimately be expressed in predictive models. Second, global change may induce switches in ocean physics that are extensions of natural variability. One example is the possibility that the eastern tropical Pacific may become more El Niño-like as Earth warms, with corresponding increases in seawater temperature and reduced CO_2 distributions (McPhaden, 1999; Feely *et al.*, 2001). Thus, variability now expressed over decadal timescales may foreshadow century timescale evolution in the era of global change. Characterizing interannual variability is a major focus of our recommendations. Long-term continuous observations are critical in this respect.

This chapter recommends two approaches for the study of CO_2 in the ocean interior. The first involves periodic hydrographic studies to map out the long-term increase in the oceanic burden of anthropogenic CO_2 and other transient tracers. This work will also document snapshot variability in oceanic distributions of bioactive tracers reflecting decadal variability in carbon fluxes and ventilation rates. The second approach involves ongoing observations of bioactive tracers (and related properties) at time series stations where oceanic variability is likely to be manifested.

The program has several overarching objectives:

- Determine the large-scale decadal evolution of the anthropogenic CO_2 inventory to within 10% ($\sim$3 Pg C globally over the next decade) on a global and basin scale.
- Close the decadal basin-scale budget of carbon to within 0.1 Pg C/yr on the basis of inventory changes, lateral transport, and air-sea flux.
- Determine the response of the oceanic carbon system to interannual and interdecadal climate variability.
- Provide decadal time-scale changes in the distribution of CO_2 species, transient tracers, and other biogeochemical tracers to constrain models to improve their predictability.

Our stated objective is to determine the anthropogenic CO_2 burden of ocean interior waters to $\pm$3 Pg C. A daunting challenge comes from the fact that the total oceanic CO_2 inventory is about 12,000 times larger than this anthropogenic contribution (38,000 Pg C). The average concentration increase over the entire global oceans would be approximately 0.2 μmol/kg, at least 5 times less than the present analytical uncertainty. What makes this objective tractable is that decadal CO_2 invasion is concentrated almost entirely in the upper 10% or less of the oceans, which makes it possible to accurately constrain the changing inventory of these waters. Observations of CO_2 cannot address the possibility that underlying waters are repositories for small amounts of anthropogenic CO_2 that, in aggregate, comprise a significant part of the balance. We recognize this possibility and believe that

it should be addressed, to the extent possible, by measuring the abundance of halocarbons and other diagnostic tracers. However, we focus in our discussion on quantifying anthropogenic CO_2 inventories of shallower waters, which, we believe, dominate the mass balance.

An important constraint on the sampling system is that key variables must be measured over appropriate time and space scales. We are learning that the entire spectrum of dynamic processes in the oceans, ranging from episodic processes (hurricanes, mesoscale eddies, etc.) to basin-scale climatic changes (ENSO, PDO, NAO, etc.) are important, so complete reliance on infrequent ship-based observations is not an option (Dickey, 2001). Thus, the strategy is to put in place a global ocean-observing network of sampling platforms to provide observations in the form of repeat ship-based sections, time-series stations, moorings, gliders, and profiling floats, to document the continuing evolution of these fields in time and space. These basin-scale measurements, along with integrative models, encompassing the Atlantic, Pacific, Southern, and Indian Oceans will constrain the evolving uptake rates of anthropogenic CO_2 by the oceans, independent of atmospheric and sea surface measurements. The data on anthropogenic CO_2 and other transient tracers will provide critical targets for ocean circulation models and the basis for ocean inverse/data assimilation efforts. Finally, the results will provide improved constraints on the atmospheric inverse models used to calculate fossil fuel CO_2 sequestration rates by North America and other continental land masses.

4.2.1 Network design

To the extent possible, we should use objective criteria to determine the scope of the network for repeat ocean sections and to design the network. Therefore, two of us (C. Sabine and R. Feely) conducted a network design study to test a strategy for constraining the uptake rate and distribution of CO_2 from hydrographic data. For this study three-dimensional global anthropogenic CO_2 fields from the NCAR OCMIP-2 Model (1.8° by 3.6° by 25 levels) were examined for model years 1995 and 2005. First, the 1995 model fields were linearly interpolated onto a $1° \times 1°$ grid and subsampled at the WOCE/JGOFS station locations. The subsampled values were then mapped back to the full basin for each level using a loess interpolation function. Integrating the maps over the appropriate volumes, basin-wide inventories were determined. These inventories agreed very well (within 0.1 Pg C) with the inventories determined by summing up all of the boxes in the full ocean model. This agreement indicates that the WOCE/JGOFS sampling density was sufficient to adequately constrain the full basin inventories in the major oceans.

Can ocean inventories of anthropogenic CO_2 be accurately constrained with surveys coarser in scale than those of WOCE/JGOFS? If so, how many sections are necessary? At least two possible approaches can be considered to cover the extremes. The first approach assumes that ocean circulation and biological activity on the basin to global scale has and will continue to operate at steady state. Anthropogenic uptake, under this approach, is based

solely on the solubility pump. In this case, it might be possible to scale up the WOCE/JGOFS basin-wide inventories by resampling a few lines at a future date, deriving a function that describes the change in anthropogenic CO_2 along these lines, and using that function to estimate the new anthropogenic CO_2 concentrations from all of the original WOCE/JGOFS survey lines.

To investigate the feasibility of this approach, the changes in the NCAR anthropogenic CO_2 concentrations between model year 1995 and 2005 were compared with the 1995 concentrations. All of the model-based changes (for all depths and all oceans) fell along a single line showing a clear positive correlation with the 1995 concentrations. If these results held for the real ocean, it would imply that a single profile covering a range of anthropogenic CO_2 concentrations could be used to derive a function to scale up the WOCE/JGOFS data in the future. Unfortunately, the data do not appear to validate such an approach: anthropogenic CO_2 estimates for WOCE samples from the Indian Ocean do not vary linearly with estimates for GEOSECS samples of the same water mass. Therefore, we cannot expect to accurately constrain anthropogenic CO_2 inventories with a minimalist strategy involving simple scaling.

Ideally, the full WOCE/JGOFS survey should be repeated every decade, but the required resources are unlikely to be available. Therefore, we investigated the accuracy of inventories determined via intermediate sampling strategies using a second approach. Specifically, we subsampled anthropogenic CO_2 concentrations computed by the NCAR 2005 simulation. First, we examined inventories determined by running one zonal section through the center of each ocean basin. This second approach was tested for the Pacific by subsampling the NCAR 2005 model results along one N-S line and one E-W line. The interpolated basin-wide inventory for this limited data set generally agrees with the model inventory (60 vs. 65 Pg C). However, the regional distribution, calculated by loess interpolation, is very different. In fact, the anthropogenic CO_2 distribution is better reproduced by neglecting the zonal line and assuming that the meridional line represents constant zonal values. This interpolation approach gave a Pacific inventory of 63 Pg C (model = 65 Pg C). Differences between model inventories and zonal interpolation estimates were typically from 5 to 20 mol/m^2 (Fig. 4-3).

The largest differences were off the coast of North and South America and off Japan, where significant zonal gradients exist. The NCAR 2005 model was also subsampled using a sampling plan similar to that proposed by CLIVAR (Gould and Toole, 1999). This plan involves sampling about 4 to 11 lines per basin. The interpolated Pacific inventory based on four zonal lines and seven meridional lines was again approximately 63 Pg C, which is within our goal of 10%. Differences between the model and interpolated inventories were generally less than 5 mol/m^2. Zonal lines (with high resolution in the western boundary currents) are also critical in order to compute ocean horizontal transport. A few scenarios were tested where an additional zonal or meridional line was added, with very little effect on the final inventory. Similar studies were carried out for the other ocean basins with the same general results. Based on these findings, the proposed repeat section plan is

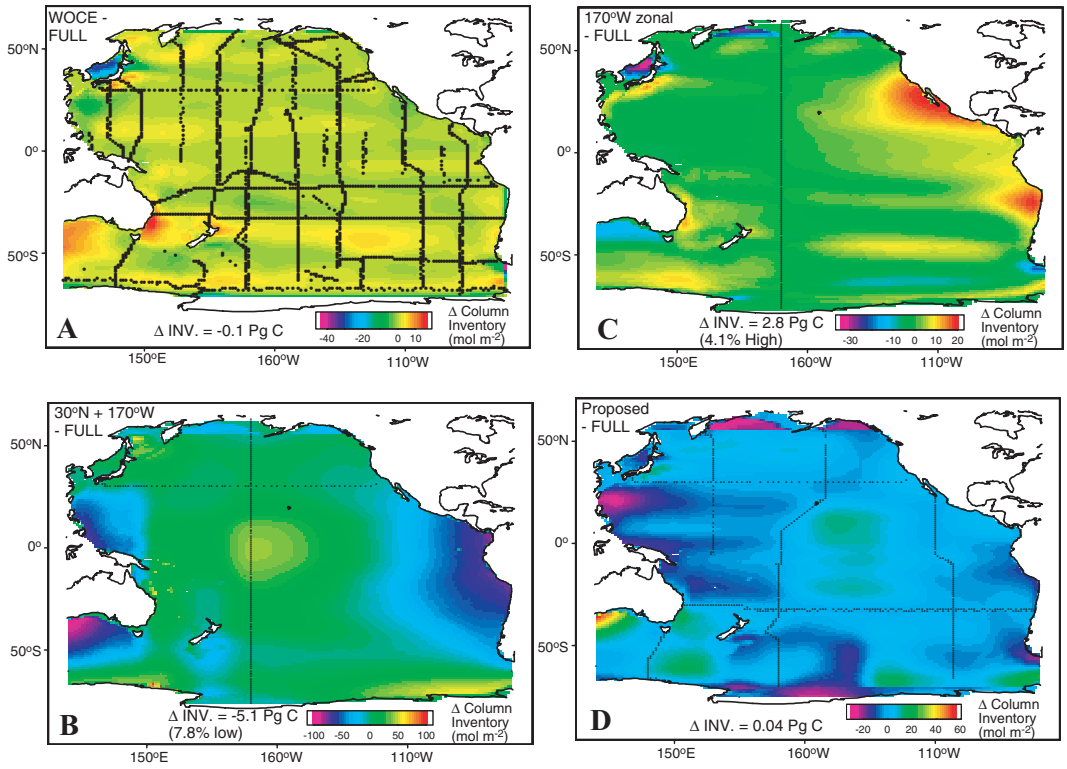


Figure 4-3: Maps of the difference between the Pacific anthropogenic CO_2, (A) column inventory from the NCAR model and the inventory determined by mapping the model values subsampled along the WOCE survey lines, (B) along one zonal and one meridonal section, (C) along one meridonal section assuming these values represent the zonal mean, (D) and along the repeat lines proposed in this document. Black dots on each map indicate sample locations. Note: color scales are different for each map.

likely to provide sufficiently accurate anthropogenic CO_2 inventories while requiring far fewer resources than the WOCE/JGOFS study (Fig. 4-4).

The difference between sampling along WOCE transects and sampling one meridional line per basin is simply that the former gives accurate information about distributions as well as inventories. We believe this distribution information is essential for three purposes: achieving confidence in inventories, understanding controls on anthropogenic CO_2 uptake and its distribution, and predicting future uptake rates.

Other countries are now committed to sampling some of the proposed CO_2 repeat transects. Interpolation of just the currently committed transects resulted in regional errors that were much larger than the full survey. Interpolation of only the U.S. transects proposed in this document also resulted in regional errors that were roughly twice the full survey errors. The best plan, of course, is a coordination and synthesis of repeat lines by the international community.

The results from this preliminary study depend somewhat on the distributions determined by the model as well as the choice of interpolation schemes. For example, the model is integrated with a repeat annual surface forcing, thus greatly reducing interannual to decadal variability. How the

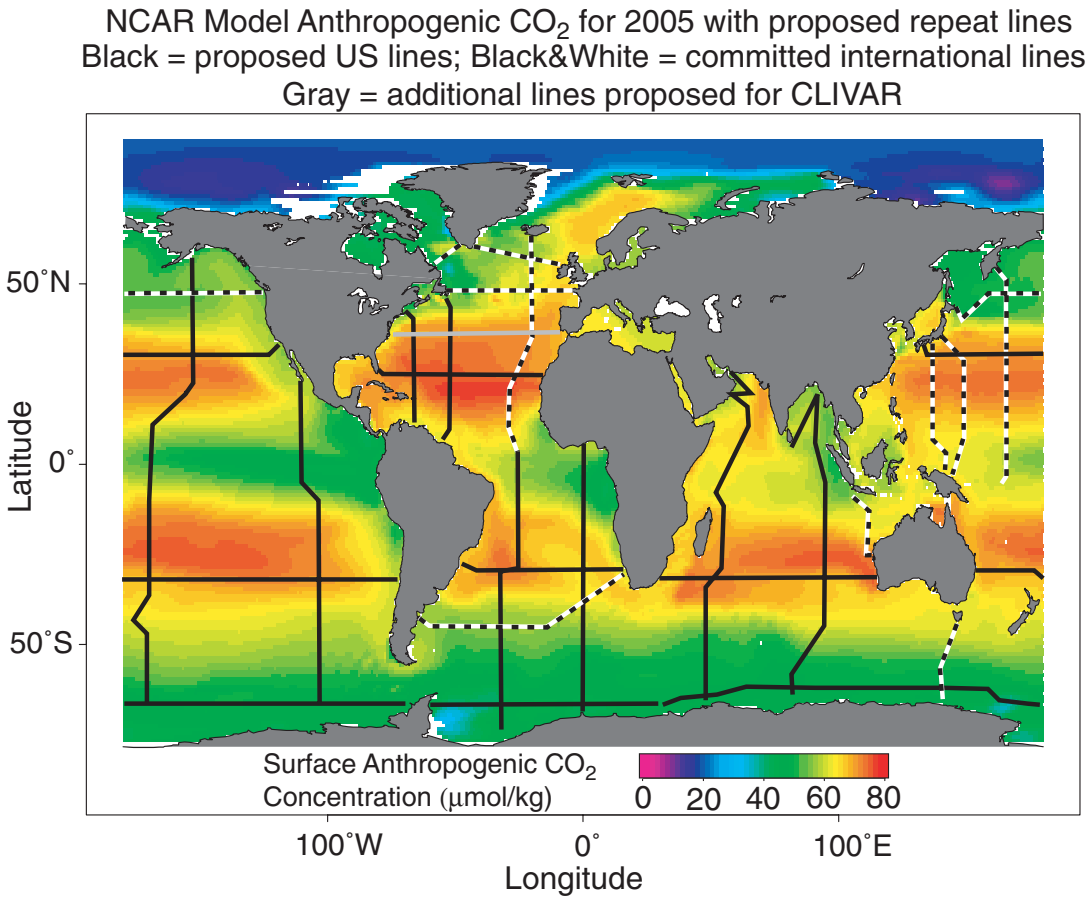


Figure 4-4: Locations of proposed repeat sections (black lines) for studies of circulation, transport anthropogenic CO_2 inventories. The grey lines are additional proposed CLIVAR cruise tracks and the black-and-white lines are committed repeat cruise tracks by similar international programs.

ocean will respond exactly to future changes in atmospheric CO_2 levels and climate change is also difficult to determine. The two scenarios examined here represent two end members: (1) steady-state circulation and biology and (2) a total redistribution of carbon, requiring a blind interpolation approach. The reality will likely be somewhere between these two extremes, suggesting that a conservative (oversampling) network design is prudent.

Even if the ocean circulation changes, the differences between two sequential 10-year repeat surveys will likely be restricted to the upper few hundred meters, where the thermocline waters are generally less than 10 years old. Thus, it is extremely unlikely that we will miss dramatic shifts in the ocean distribution of anthropogenic CO_2. The sampling strategy proposed in this document attempts to maximize the scientific return on resources, while maintaining the ability to detect and address potential surprises in the response of the ocean circulation and biology to future forcing.

4.3 Recommendations

We recommend as part of the ocean interior component of the plan two complementary and synergistic activities: large-scale repeat ocean sections, and time-series observations at fixed locations.

4.3.1 Repeat ocean sections

We recommend an ongoing program in which 15 repeat sections spanning the global ocean are resampled every 10 years. Properties to be measured include hydrography, redundant CO_2 system properties, nutrients, halocarbons, and emerging tracers of biology and physics.

We recommend that a subset of WOCE transects, shown in Fig. 4-4 and listed in Table 4-2, be reoccupied periodically for hydrographic and chemical studies. Our recommendations are formulated with the objective of characterizing the evolving ocean inventory of anthropogenic CO_2 among other properties. The recommended cruise tracks are based, in part, on the network design study described in the CLIVAR documents (Gould and Toole, 1999). We recommend that a modified version of their plan be adopted for characterizing the oceanic distribution of anthropogenic CO_2. Table 4-2 summarizes the objectives each cruise track will fulfill beyond the basic goal of mapping the transients and constraining the anthropogenic inventory. We recommend that each section be sampled from coast to coast. Such sampling is particularly important for zonal sections, which will be used for meridional transport calculations (Wunsch, 1996).

The requirements for ocean transport calculations should not add much of a burden to the repeat section work proposed here. Station spacing on the proposed sections should be 30 to 60 nautical miles to minimize aliasing by eddies and other mesoscale variability. The number of transects required to constrain the major oceans is estimated to be at least 2 to 4 meridional and 2 or 3 zonal sections per ocean (Taft *et al.*, 1995). Meridional sections are important for understanding variations in basin-scale circulation patterns and inventory changes. Repeat occupation of zonal sections allows for the detection of variability in the rates, pathways, and properties of deep and intermediate waters carried toward the equator from the high latitudes, and for detection of zonal variations in carbon storage. Attention must be given to potential biases resulting from seasonal variability in the transport. As a result, an intense period of seasonal sampling may be required to evaluate this issue. Ideally, the cruises should be coast to coast, located downstream of the deep and intermediate water formation regions. The required parameters are the same as those proposed to determine the inventory estimates. The transient tracers play a key role in the transport fluxes because they provide temporal information about ocean mixing and advection that is essential to interpreting anthropogenic CO_2 distributions.

Connections with climate programs such as CLIVAR are important for the success of the transport calculations. The repeat hydrographic survey transects proposed for CLIVAR are consistent with the requirements for the carbon measurement program outlined here (Gould and Toole, 1999;

Table 4-2: Suggested sections for whole water column hydrographic and tracer monitoring by the United States.

Atlantic Ocean	
24°N	Heat, freshwater and carbon/tracer fluxes/inventories
30°S	Heat, freshwater and carbon/tracer fluxes/inventories
52°W	Carbon/tracer invasion and transport in western gyre of N. Atlantic
66°W	Carbon/tracer invasion and transport in western gyre of N. Atlantic
0°	Carbon/tracer invasion and transport in eastern gyre of S. Atlantic
20–30°W	Carbon/tracer invasion and transport in western basin of S. Atlantic
67°S	Carbon/tracer invasion in the Southern Ocean
Pacific Ocean	
30°N	Heat, freshwater and carbon/tracer fluxes/inventories
32°S	Heat, freshwater and carbon/tracer fluxes/inventories
150–170°W	Carbon/tracer invasion and transport in eastern basin of N. Pacific, western basin of S. Pacific
105–110°W	Equatorial upwelling region and carbon/tracer invasion and transport in eastern basin of S. Pacific
67°S	Carbon/tracer invasion in the Southern Ocean
Indian Ocean	
55–65°E	Carbon/tracer invasion and transport in western basins of Indian Ocean; also choke point line south of Kerguelen
90°E	Carbon/tracer invasion and transport in eastern basins of Indian Ocean; also choke point line south of Broken Plateau
65°S	Carbon/tracer invasion in the Southern Ocean

Rintoul *et al.*, 1999). Potential benefits of a cooperative program include improved knowledge of the rate of change of heat and freshwater storage and fluxes. These can be directly related to carbon transports, linkages to CLIVAR-derived estimates of direct velocities (e.g., western boundary current moorings, floats, cables) required for transport calculations, and an assessment of changes in deep and shallow water-mass formation and overturning.

4.3.2 Properties to be analyzed on repeat sections

We recommend that samples be analyzed for a broad suite of hydrographic and chemical properties that are diagnostic of carbon inventories and fluxes. These can be divided into the following overlapping groups.

- Hydrographic properties (T and S)
- Major bioactive tracers (nutrients, O_2, TCO_2—total CO_2, TA—total alkalinity, pCO_2, DOC—dissolved organic carbon, DON—dissolved organic nitrogen, $\delta^{13}C$ of CO_2, and (at less frequent spacing/intervals) iron
- Transient tracers of ocean circulation (halocarbons, ^{14}C)

- Emerging tracers of mixing, biogeochemical processes, and deep water formation

These measurements will contribute in several ways. TCO_2, TA, nutrients, O_2, and halocarbons form the basic data set required for mapping the distribution of anthropogenic CO_2 in the oceans (e.g., Gruber *et al.*, 1996; Gruber, 1998; Feely *et al.*, 1999; Sabine *et al.*, 1999). Macronutrients (nitrate, phosphate, silicate) and micronutrients (e.g., iron) control the patterns and rates of ocean biogeochemistry and are sensitive indicators of climate change; iron is now thought to play a key role in limiting surface production in high-nitrate low-chlorophyll (HNLC) regions, but the oceanic distribution and budget is poorly characterized (Fung *et al.*, 2000). The balance of the global budget for ^{13}C of CO_2 between the atmosphere, oceans, and terrestrial biosphere provides an independent estimate of anthropogenic CO_2 uptake in the oceans, giving complementary information about its distribution (Quay *et al.* 1992; Tans *et al.*, 1993; Gruber and Keeling, 2001). DOC and DON are significant components the ocean carbon and nitrogen cycles because they make up approximately 20% of the global annual export flux to the interior ocean (Hansell and Carlson, 1988). At depth, the exported DOC is remineralized to CO_2, thus contributing to the CO_2 gradient created by the biological pump. We need to know the DOC and DON distributions in order to close the mass balance when calculating meridional fluxes from zonal sections.

The distribution of bioactive tracers serves to reflect both natural variations and anthropogenic changes in ocean ventilation rates and biogeochemical fluxes. Several studies have demonstrated variability in nutrient and O_2 concentrations of mode waters and thermocline waters linked to interannual hydrographic variability. For example, Bates (2001) and Gruber *et al.* (in preparation) demonstrated variability near Bermuda associated with the North Atlantic Oscillation. Karl *et al.* (2001) showed that the Pacific Decadal Oscillation induces significant variations in hydrography and nutrient properties, which may lead to long-term changes in the export flux of carbon. Several recent studies have demonstrated changes in North Pacific O_2 and nutrient concentrations of undocumented origin (Pahlow and Riebesell, 2000; Keller *et al.*, 2001; Emerson *et al.*, in press). Matear *et al.* (2000) predicted a large change in the ventilation of Southern Ocean waters, and argued that a comparison of O_2 concentrations measured in Eltanin and WOCE samples confirmed their model prediction.

Finally, calculations using the O_2 inventory of air to constrain anthropogenic CO_2 uptake by the oceans and land biosphere (e.g., Keeling and Shertz, 1992) require an assumption about the stability of the ocean O_2 inventory. Papers to date assume constancy. However work (cited above) showing variability in the O_2 concentration of thermocline waters challenges this assumption, suggesting that ocean changes may be quantitatively important. Measurements of O_2 concentrations in repeat ocean sections will give firm constraints on ocean O_2 inventory changes. They will allow one to use O_2 data to provide an independent estimate of ocean CO_2 uptake.

4.3.3 Transient tracers

Seawater distributions of anthropogenic chemicals constrain rates of oceanic mixing processes that influence the oceanic distribution of anthropogenic CO_2. Properties of interest include halocarbons, ^{14}C, $\delta^{13}C$ of CO_2, and anthropogenic CO_2 itself. Mapping the evolving distribution of these tracers provides unique and important information about ocean circulation. A noteworthy characteristic of transient tracers is that emission curves differ and, of particular interest, emissions of different chemicals begin at different times. Thus the periodic introduction of new chemicals effectively leads to repeat "dye experiments" which record changes in ocean circulation.

4.3.4 Emerging tracers of mixing and biogeochemistry

We are currently developing analytical methods and conceptual insights for new tracers that are important for understanding biogeochemical properties and their interaction with ocean circulation. The $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- record a variety of interesting biogeochemical and mixing processes (Sigman *et al.*, 2000). Of particular interest here, these properties constrain the rates at which vertical mixing and northward advection supply nutrients to shallow waters of the Southern Ocean. This is a critical issue with respect to the role of the Southern Ocean in global change. The $\delta^{18}O$ of O_2 is a nonlinear tracer that reflects the interaction of mixing and respiration in the oceans in a unique way (Bender, 1990; Maier-Reimer, 1993). The triple isotope composition of dissolved O_2 reflects the fraction of dissolved O_2 derived from photosynthesis. This property constrains rates of primary production, and provides a tracer of water mixed from the euphotic zone into mode waters and the thermocline (Luz and Barkan, 2000).

Heavy noble gases are undersaturated in deep ocean waters. Undersaturation comes about because gas exchange lags cooling in deep water formation regions. Observing the evolution of undersaturation is one measure of changes in the nature of intermediate and deep water formation as the oceans warm.

We recommend that such emerging tracers be measured wherever they can make a unique contribution to our understanding of the evolving distribution of bioactive tracers, mixing, and ventilation in the ocean.

4.3.5 Repeat time of ocean sections

We recommend a repeat time of 10 years. Future projections suggest that anthropogenic CO_2 in the oceans will increase by about 20–25% over the next decade. The rise in anthropogenic CO_2 in thermocline waters during this period is expected to be approximately 5 μmol/kg. With currently achieved precision and accuracy (about ± 1 μmol/kg), such an increase can be detected in individual samples and averaged in large data sets. Therefore inventory increases will be accurately constrained. Decadal surveys will reveal changes in ocean ventilation and biological production in the era of global warming, and will document changes in CO_2 sequestration that herald changes in the rate of atmospheric CO_2 increase. Decadal surveys will also constrain ocean O_2

inventories, allowing independent calculations of ocean and land biosphere CO_2 uptake from atmospheric O_2/N_2 studies. We can compare CO_2 invasion into individual basins estimated from global atmospheric data, regional air-sea fluxes of CO_2, and regional ocean inventory changes. In summary, timely updates of the CO_2 distribution in the ocean interior are essential to the evolving comprehensive analysis of the CO_2 balance. However, the ocean interior is unlike other realms in that it cannot be monitored continuously in a comprehensive manner. We believe that decadal updates are the minimal requirement for a "real-time" understanding of evolution of the carbon cycle. Finally, the repeat transects offer excellent opportunities to measure a wide range of ocean properties with great potential for process information, including chlorophyll, pigments, iron, etc. These ancillary measurements will provide critical information for prognostic modeling and interpolation.

4.3.6 Spatial resolution of ocean sections

Our network design study suggests that approximately 2 to 4 meridional and 2 or 3 zonal sections per ocean basin are required to constrain the distribution of anthropogenic CO_2 (see also Taft *et al.*, 1995; Gould and Toole, 1999). Meridional sections are important for understanding variations in basin-scale circulation patterns and anthropogenic CO_2 inventory changes. In the North Atlantic in particular, these should be weighted toward the western portion of the basin, because present knowledge of transport processes suggests that the maximum change in the anthropogenic CO_2 inventory will be found here. However, given our present incomplete knowledge of thermocline ventilation in the Pacific and Indian Oceans, we require additional lines in the central and eastern basins of these oceans as well. Repeat occupation of zonal sections allows the determination of zonal variations in anthropogenic CO_2 inventories, as well as the detection of changes in the rates, pathways, and properties of deep and intermediate waters carried toward the equator from the high latitudes. Zonal sections allow us to calculate transport (fluxes) of water and carbon required to balance the carbon budget within each basin. To satisfy inverse modeling requirements (Wunsch, 1996) for closing carbon budgets on a regional basis, all zonal sections should be coast-to-coast sections located downstream of the thermocline ventilation zones and the deep and intermediate water formation regions. Model results suggest that the region of maximum oceanic uptake of anthropogenic CO_2 is near 40°S–60°S in all oceans. Time series of zonal lines just equatorward of this latitude range are particularly necessary.

High-resolution hydrographic surveys currently offer the only direct method for estimating ocean transport of CO_2. Geostrophic currents are determined from the observed density field, often utilizing an inverse box model to estimate unknown reference level velocities. The net CO_2 transport is the integrated product of the distribution of the currents and CO_2 concentrations. Previous estimates of natural and anthropogenic CO_2 transport (Brewer *et al.*, 1979; Martel and Wunsch 1993; Holfort *et al.*, 1998) reveal that accurate estimates require sufficient spatial sampling of physical properties to resolve the mesoscale eddy field. While the CTD sampling

must be sufficient to resolve the eddy variations (∼55 km) for transport calculations, regression and interpolation analysis has demonstrated that we can accurately reconstruct the CO_2 field itself, especially below the seasonal thermocline, from a subsampled distribution of lower resolution (Goyet *et al.*, 1995).

Other countries have already committed to occupy lines in addition to those in Table 4-2 and Fig. 4-4. The British plan to occupy 32°S in the Indian Ocean, 45°S in the Atlantic and the northern hemisphere portion of 20°W; the Japanese will occupy 144°E and 165°E in the North Pacific, and 32°S in the South Atlantic and South Pacific; the Germans will occupy 48°N in the North Atlantic; and the Canadians will repeat a line through the subpolar gyre of the North Atlantic from Labrador via Greenland to Scotland, and line P in the northeastern Pacific. Additional lines in the northeastern Atlantic are planned by several countries, while the Australians will occupy a series of sections in the southwest Pacific and southeast Indian Oceans. Finally, the sections south of South America, Africa, and Australia across the Antarctic Circumpolar Current are visited frequently by ships serving the Antarctic bases; it seems likely that most of these sections will be reoccupied on a relatively frequent basis. Thus, the global coverage will likely be considerably more than shown in Fig. 4-4.

When possible, the occupations of these sections should be coordinated to reduce ambiguities in combined interpretation of estimates of inventory increases and lateral transport. For instance, one strategy, based partly on the premise that meridional sections are better for constraining inventories and zonal sections better for constraining transport, would allow best closure of ocean carbon budgets on a basin scale, assuming a 10-year repeat cycle. For each hemisphere of each ocean, meridional sections for inventory estimates should be occupied as closely as possible in time. Then, 5 years later zonal sections for lateral ocean carbon transport estimates should be taken, followed by a reoccupation of the meridional sections 5 years later. In this manner, the meridional sections yield a change in carbon inventory centered over a time interval that appropriately matches the carbon transport estimates derived from the zonal transects. In addition, the staggered occupation of meridional and zonal sections would improve temporal resolution where the zonal and meridional sections cross, likely for the most part in the subtropics.

4.3.7 Time-series observations of the properties of the ocean interior

Ocean interior concentrations of biogeochemical properties and transient tracers vary in response to changes in ventilation and biological activity on a wide range of timescales. Examples of interannual to decadal variations include the response of the ocean to El Niño events, the Pacific Decadal Oscillation, and the North Atlantic Oscillation. We recommend time-series observations at selected sites to observe and document such variability on timescales up to decades (Table 4-3 and Fig. 4-5). These time-series stations will provide the time continuity now lacking in the decadal surveys and will

Table 4-3: Proposed time-series stations as part of this program.

Location	Motivation	Activity	Priority
S/BATS/BTM, Bermuda/U.S.	NAO, Bermuda testbed mooring	Add autonomous instrumentation to ongoing time-series activity	1A
HOT, Hawaii, U.S.	PDO, ENSO, testbed mooring	Add autonomous instrumentation to ongoing time-series activity	1A
Eq. Pacific, especially 0°, 155°W; 2°S, 170°W, U.S.	ENSO variability, testbed mooring	Add autonomous instrumentation to TAO moorings	1A
Station Papa, NE Pacific/Canada	PDO	Add autonomous sampling platform	1B
Bravo, Labrador Sea/Canada	NAO, subarctic response	Add autonomous sampling platform	1B
Mike, Norwegian Sea/Norway	NAO, subarctic response	Add autonomous sampling platform	1B
Pacific sector of the Southern Ocean	Global warming, Antarctic Circumpolar Wave, ENSO connection	Add autonomous sampling platform	2A
Atlantic sector of the Southern Ocean	Global warming, Antarctic Circumpolar Wave, THC changes	Add autonomous sampling platform	2A
Western and eastern equatorial Pacific	ENSO	Add autonomous instrumentation to TAO mooring	2B
Eastern equatorial North Atlantic (Pirata Moorings)	Tropical Atlantic Dipole	Add autonomous instrumentation to Pirata mooring	2B
Western and eastern subtropical South Pacific	Southern Hemisphere subtropical gyre, extremely low Fe environment	Add mooring	2B
Western and eastern subtropical South Atlantic	Southern Hemisphere subtropical gyre	Add mooring	2B

1A = 1st priority, first 5-year period; 1B = 2nd priority, first 5-year period; 2A = 1st priority, 2nd 5-year period; 2B = 2nd or 3rd priority, second 5-year period.

allow the program to detect changes in the oceanic system as they occur. The proposed observation program must be designed to detect such changes early, allowing response with additional observational assets, surveys, and in-depth process studies.

These time-series observations, by extending from the surface ocean into the ocean interior, will also serve as "nodal points" linking the surface variations observed by the large-scale surface program and the large-scale ocean interior changes observed by deep hydrographic surveys. Such a linkage is crucial, since observation programs focused on physical oceanography have shown that a significant fraction of variability associated with decadal timescale changes occurs within the thermocline and can manifest itself back at the surface many years later. For example, Gu and Philander (1996) demonstrated that temperature anomalies can get subducted into the thermocline of the subtropical gyres and resurface back in the tropical Pacific more than a decade later, significantly influencing heat exchange. Furthermore, long-term changes are often more strongly manifested in subsurface

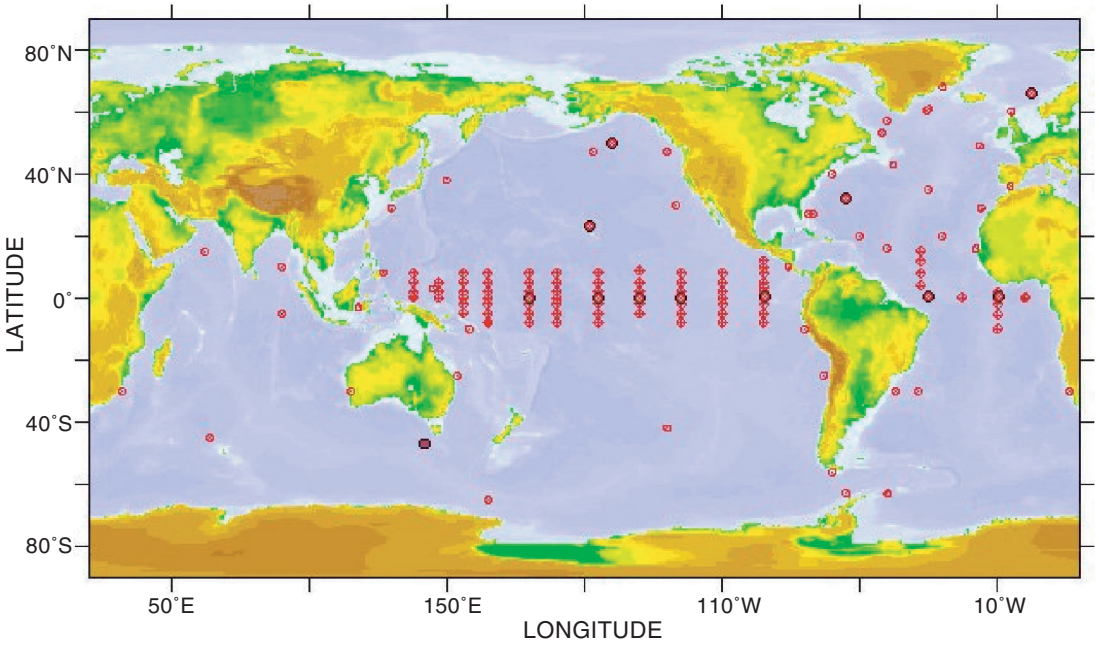


Figure 4-5: World map of existing and proposed mooring sites for long-term interdisciplinary observations. The black open circles show high-priority time-series mooring sites for the Carbon Cycle Science Program.

waters, because the large-scale transport and mixing act as low-pass filters (Deser *et al.*, 1996). By covering timescales from days to decades, these time-series observations will give crucial insight into the mechanisms that govern oceanic variability, insight that will improve assessments of future changes.

4.3.8 Sites for time series station

As in the case of surface measurements (Chapter 3), we recommend, for the first 5-year period, continued support and augmentation to include autonomous platforms and instruments for the two current American time series at Bermuda (BATS) and Hawaii (HOT) for the interior ocean time-series measurements (Table 4-3). We also recommend that a program be formalized for the equatorial Pacific based on the existing TAO mooring array and the ship servicing these moorings (Fig. 4-5).

The data for these three sites will provide critical information on changes in the composition of the interior ocean waters due to circulation and ecosystem changes resulting from ENSO and extratropical climate variability, such as the Pacific Decadal Oscillation and the North Atlantic Oscillation. In addition, for the first 5-year period, we recommend that existing time-series sites in critical high-latitude regions of the North Atlantic and North Pacific be augmented with CO_2 measurements. For the North Pacific, we recommend continuation and augmentation of the Canadian JGOFS time series at station Papa to document the influence of the Pacific Decadal Oscillation. In particular, this study will show how the recently observed change in

thermocline oxygen concentrations will evolve, and how they are connected with variations in carbon storage. Because this station is regularly serviced by research ships from Canada, optimal synergisms with ship-based observations can be exploited. We also recommend support and encouragement for interaction with the Japanese time-series studies in the northwestern Pacific. In the North Atlantic, we recommend continuation and augmentation of the Labrador Sea time-series site Bravo and of the Norwegian Sea time-series site Mike, where previous studies revealed large seasonal variations (e.g., Takahashi *et al.*, 1993). These sites are optimally placed to study the impact of the North Atlantic Oscillation on upper ocean and thermocline variability in physics, chemistry, and biology.

For the second 5-year period, when autonomous technology will become fully operational, we recommend extending the existing set of time-series stations into the Southern Ocean, where model simulations clearly indicate that long-term changes in response to global climate change will be most strongly manifested. Extending the observational capabilities into this sensitive area is extremely important because relatively small changes in thermohaline circulation and biogeochemistry can result in large regional changes in CO_2 fluxes and ocean storage. Also, for the second 5-year period, we recommend the addition of time-series stations in the tropical and subtropical South Atlantic and South Pacific. We envision that several of these new time-series sites will be maintained by our international collaborators and will only require specific augmentation with autonomous sensors.

Time-series measurements at fixed stations are currently conducted in two ways: (1) ship-based measurements at intervals of a month (occasionally a bit more frequently) and (2) autonomous sampling from moorings. To understand the long-term changes in the oceanic carbon cycle due to climate change, oceanographers have depended heavily on time-series ship-based data at a very limited number of specific locations in the major oceanic provinces. These have yielded important data sets referred to earlier.

Ship-based time-series measurements are impractical for measuring variability over intervals from a week to a month; they cannot be made during storms or high-sea conditions; and they are too expensive for remote locations. Instrumental advances over the past 15 years have led to autonomous moorings capable of sampling properties of chemical, biological, and physical interest with resolution as good as a minute and a duty cycle of a year or more (e.g., Dickey, 1991; Chavez *et al.*, 1999; Dickey and Falkowski, 2001). This work has provided a growing body of evidence that episodic phenomena are extremely important causes of variability in CO_2 and related biogeochemical properties and processes. We therefore recommend that the new time-series observation sites be focused on autonomous sampling technology with ship-based support as required.

Because one of the problems in defining the spatial and temporal variability of carbon uptake in the ocean interior is lack of data, strategies are needed to increase spatial coverage and sampling frequency at reduced per datum cost. Particular emphasis should be placed on the development of new technology, particularly instruments for measuring CO_2 and related properties on research ships, moorings, profiling floats, and gliders (Goyet *et*

al., 1992; DeGrandpre *et al.*, 1995; Friederich *et al.*, 1995; Tokar and Dickey, 2000; Varney, 2000). It is recommended that a portion of this program should be devoted to the development of new automated systems that can be interchangeably mounted on moorings and profiling floats, or used as autonomous systems on volunteer observing ships. For example, the proposed distribution of PALACE and ARGO floats in the Atlantic and Pacific under the CLIVAR program could serve as the primary vehicles for the CO_2 sensors (Davis *et al.*, 2000). A combination of surface drifters and CO_2 sensors on profiling floats and gliders could allow us to observe and quantify the coupled evolution of near-surface and mid-water carbon fields. Recent technological advances in methodology for in situ carbon measurements could make this a reality. For example, the recent development of high-precision in situ methods for TCO_2, TA, and pCO_2 by Robert Byrne and colleagues at the University of South Florida use a compact spectrophotometric analysis system (SEAS; Byrne *et al.*, 2001). The system is capable of spectral analysis from 400 to 750 nm in both absorbance and fluorescence modes. The sample cell is configured to use long pathlength liquid core waveguides (10 to 500 cm) for pH, pCO_2, TCO_2, and TA. The system is deployed with the Bottom Stationed Ocean Profiler (BSOP) or other similar profilers. These devices have been designed to carry SEAS sensors and other instruments, and telemeter chemical and physical data after each cycle. As discussed in Chapter 3, a strong program of autonomous CO_2 sensor and related instrument and platform development and field testing is needed during the first 5-year period of the program. Thus, we strongly endorse the similar recommendations in Chapter 3.

While some CO_2 sensors have been deployed or are ready for deployment on moorings and profiling floats (DeGrandpre *et al.*, 1995), other sensors need further testing under field conditions before they can be considered fully operational (Byrne *et al.*, 2001). The time-series sites provide an excellent opportunity for calibration and field testing during site reoccupations by the surface ship, when the in situ measurements can be compared with shipboard measurements.

4.3.9 Properties to be analyzed at time-series sites

Autonomous observations should focus on characterizing dissolved bioactive constituents and biogeochemical processes in the upper ocean and the thermocline. Properties of particular interest to the CO_2 problem include TCO_2, TA, pCO_2, nutrients, O_2, DOC/DON, particulate organic and inorganic carbon, halocarbons, bio-optical parameters, and bioactive trace metals such as iron. Of these, TCO_2, TA, pCO_2, nutrients, O_2 and halocarbons are directly relevant for determining the distribution of CO_2. POC/PIC and trace metal concentrations are of great interest to process studies of the ocean carbon cycle. Many of these properties can be measured using a combination of in situ analyzers and moored samplers. Observing platforms could be moorings, profiling floats, or even gliders. At the present time, the technology is evolving rapidly, and we make no specific recommendations about sensors, samplers, and platforms. However, the autonomous units must certainly

Table 4-4: Priorities and cost estimates for the interior ocean program.

Element of the implementation plan	Priority	Ship time* ($/year)	Science ($/year)
First 5-Year Period			
Meridional and Zonal Sections (Atlantic and Pacific Oceans)	1	$2,000,000	$2,100,000
Augmenting HOT, BATS, and Equatorial Pacific with autonomous sensors	1	$500,000	$1,500,000
Augmenting high-latitude time-series sites with CO_2 measurements	2	$500,000	$1,100,000
Develop/improve sensors for measurements of two CO_2 system properties	2		$500,000
Second 5-Year Period			
Meridional and Zonal Sections (Southern Oceans)	1	$1,500,000	$2,200,000
Meridional and Zonal Sections (Atlantic, Pacific, and Indian Oceans)	1	$1,500,000	$1,500,000
Augmenting Southern Ocean time-series sites with autonomous sensors	1	$500,000	$1,500,000
Instrumented profiling floats and gliders	2	$800,000	$1,500,000
Augmenting tropical and subtropical time-series sites with autonomous sensors	3	$500,000	$1,500,000

*Ship-time costs are estimated at $20,000 per day.

fulfill two requirements. First, they must be efficient in the sense that they need to operate for long periods of time at the required level of *accuracy and precision*. Second, the analytical uncertainty needs to be smaller than the likely amplitude of interannual timescale variations. The required accuracy depends on the site, resolution attained, and precise objectives. As a guide, accuracy and precision should be about ± 1 μmol/kg for O_2, ± 2 μmol/kg for TCO_2 and TA, and ± 0.2 μmol/kg or $\pm 1\%$ for nutrients (whichever is smaller). As was the case with the WOCE/JGOFS global survey, we recommend continued support for a strong standards and intercalibration effort as a necessary component throughout the duration of the program.

4.3.10 Priorities for the ocean interior

Monitoring the evolving fossil CO_2 inventory is an essential long-term component of any effort to understand oceanic CO_2 exchange. We recommend an integrated approach involving a network of repeat sections and time-series stations using ships, moorings, profiling floats, and gliders to document the continuing large-scale evolution of these fields. This activity would be an ongoing effort and could exploit strong linkages with other efforts such as the transport studies and CLIVAR (Climate Variability and Predictability program) within GOOS (Global Ocean Observing System) and GCOS (Global Climate Observing System) to make efficient use of ship time. This ongoing ocean interior component of the Carbon Cycle Science Program will consist of three major research activities phased over two 5-year periods (Table 4-4).

4.3.11 The first 5 years

- **Conduct meridional and zonal sections in the Atlantic and Pacific (priority 1).** Several of the Atlantic and Pacific transects were occupied more than 7 years ago, and can provide valuable data quickly.

- **Augmentation of existing U.S. time-series sites in the North Atlantic, North Pacific, and equatorial Pacific with autonomous sensors (priority 1).** We strongly recommend that autonomous time-series measurements be tested and "proven" at these sites before they are deployed in large numbers. This means that the instruments have repeatedly demonstrated their ability to maintain the required levels of precision and accuracy for the planned duration of the deployments.

- **Augmentation of high latitude time series sites with CO_2 measurements (priority 2).** We recommend that existing time-series sites in critical high-latitude regions of the North Atlantic and North Pacific be augmented with CO_2 measurements.

- **Development of new instrumentation for two CO_2 parameters and CO_2-related species on moorings, profiling floats and gliders (priority 2).** We recommend that systems that measure at least two components of the carbon system simultaneously be given high priority for development.

4.3.12 The second 5 years

- **Expansion of the global surveys to the Southern Ocean (priority 1).**

- **Implementation of meriodional and zonal sections in the Pacific, Atlantic and Indian Oceans (priority 1).**

- **Expansion of the time-series stations in the Southern Ocean (priority 1).**

- **Deployment of instrumented profiling floats and gliders (priority 2).**

- **Expansion of the time-series stations in the tropical and subtropical regions of the South Atlantic and South Pacific (priority 3).**

It is assumed that the program resources will grow over the 10-year period to support these enhanced research activities. It is also envisioned that the field and modeling program will continue beyond the 10-year effort described here. This implementation plan concentrates on the first 10 years of the program. Future implementation plans will be developed as needed as the program evolves over the next decade.

4.4 Summary

The Ocean Interior Program consists of repeated and nearly continuous systematic full water column sampling of CO_2 and CO_2-related parameters, tracers, and hydrography to determine the large-scale decadal evolution of the anthropogenic CO_2 inventory in the oceans. It will provide necessary data required to improve global circulation and biogeochemistry models on global and basin scales, close the decadal basin-scale budget of carbon using information on the basis of inventory changes and lateral transport, and determine the response of the oceanic carbon system to interannual and interdecadal climate variability. Our strategy is to put in place a global ocean-observing network of sampling platforms to make observations, including repeat ship-based sections, and time-series stations using moorings, profiling floats, and navigated gliders. This approach documents the continuing evolution of these fields and provides a powerful constraint for model parameterizations of the carbon system in the oceans.

Chapter Five

Synthesis and Modeling

5.1 Overview

Despite near-term advances in in situ measurements and remote sensing, observations of carbon in the ocean and atmosphere alone will remain too sparse to adequately characterize the time-space variability of the global carbon cycle and the net carbon fluxes among reservoirs. Numerical modeling including data assimilation will therefore play a pivotal role in the synthesis and interpretation of carbon cycle data. Modeling considerations should also be incorporated from the beginning in developing a global observational strategy, with particular focus on the network design for sampling and timely public access to data. This research is essential to help answer the first fundamental question raised by the U.S. Carbon Cycle Science Plan (CCSP), namely, what has happened to the carbon dioxide already emitted by human activities? The second basic question raised by this plan is, what are the likely future trends in atmospheric CO_2 concentrations? This question can be answered only with prognostic models. Improving such models must therefore be one of the principal goals of carbon cycle research over the next decade.

Three classes of models are envisioned here as essential to a global ocean-atmosphere-land carbon cycle observing strategy.

1. Prognostic (forward) atmospheric circulation/transport models and oceanic circulation/biogeochemistry models.

2. Diagnostic (inverse) versions for the same types of atmosphere and ocean models.

3. Data assimilation models for atmosphere and ocean biogeochemistry.

Two other categories of models are also discussed here and are essential from a broader perspective on carbon cycle research.

1. Land-surface biogeochemical models.

2. Comprehensive (coupled) ocean-atmosphere-land climate and carbon cycle models.

Significant progress can be achieved in carbon cycle modeling over the next 5–10 years. First, the development and evaluation of biogeochemical models are grounded by field data at a fundamental level, and the recent and ongoing expansions of the observational base for carbon will accelerate numerical modeling. Second, data assimilation is emerging as a new and powerful tool in biogeochemistry, providing the tools to combine data and

models into a coherent description of the carbon system. Third, coupled carbon cycle models are maturing to a point where we can study the dynamics of the Earth system as a whole.

During the 5-year ramp-up phase, the synthesis and modeling component should include the following research foci and infrastructure elements that are common to all three observing domains:

- Augmented/new carbon data centers to undertake or coordinate the compilation, quality control, and distribution of in situ and remote-sensing data relevant to the carbon cycle, as well as derived synthesis products (e.g., surface fluxes and assimilation fields) produced by the research community.
- Process and inverse modeling studies to design optimal sampling networks and assess the utility and tradeoffs among existing and emerging measurement and platform technologies.
- Ongoing development and improvement of atmospheric transport and oceanic circulation and biogeochemical models used to diagnose carbon sources and sinks; direct evaluation of simulations against observations must be integral to the model development effort.
- Comparison and reconciliation of independent estimates of regional air-sea CO_2 fluxes from direct observations, atmospheric inversions, and oceanic inversions; this central effort compares results from all three observing domains.
- Hindcast simulations and data synthesis of the ocean/atmosphere/land carbon cycle variability over the recent historical period (1950s–present) using atmospheric reanalysis products and ocean state estimations.
- Pilot data assimilation studies to investigate the methods, data needs, and general feasibility of ocean/atmosphere/land carbon data assimilation systems. In the longer term, synthesis and modeling must evolve to full data assimilation systems to provide ongoing evaluations of carbon sources and sinks and the underlying mechanisms.
- High-resolution physical circulation and biogeochemical models for specific process studies and to provide context for regional campaigns and field experiments.
- Prognostic coupled climate model development and simulations to improve projections of the carbon cycle's future evolution under various scenarios for emissions, land use, and other areas.

The carbon cycle is embedded in the physical climate system; close collaboration with the weather, physical oceanographic, and climate communities is imperative, both for observational systems and modeling, and will be synergistic and mutually beneficial. Similar strong linkages must be established with the terrestrial carbon cycling community. The remainder of this

chapter covers the general synthesis and modeling elements for an ocean-atmosphere observing system and topics that relate more specifically to the other chapters of this report (on observing CO_2 in the atmosphere, surface ocean, and the ocean interior). This chapter's recommendations on modeling and synthesis are more general than those in the observation chapters, and cost estimates for recommended activities have been omitted here.

5.2 Recommendations

5.2.1 Carbon data management and distribution

The proposed carbon data center(s) would act as the collection point for the various types and levels of data streams. For many types of data, particularly for those collected via spaceborne platforms, such centers are already in existence and do not need to be duplicated. However, for many other observations—for example, those associated with the rapidly increasing number of underway pCO_2 data and airborne CO_2—such a center(s) needs to be established and supported. The data synthesis at these sites might include quality control procedures beyond the initial quality control at the level of individual measurements and observational networks. This includes, for example, investigating the internal consistency of the data as well as testing for long-term data precision and accuracy. High priority should also be given to fully documenting the various data products and streams (metadata). The data centers would be responsible for publicly distributing the data electronically (most likely via the web) in a timely fashion, following the models set up by CDIAC, JGOFS, WOCE, and others. Data and funding policies need to be established at the program's beginning to ensure prompt data submittal and release. Finally, data centers would serve as repositories and distribution points for synthetic data products (e.g., flux estimates, interpolated fields, assimilation output) developed as part of the project.

5.2.2 Sampling network design

The creation of a global carbon cycle observing system faces daunting challenges, among them the wide range of relevant time-space scales, from synoptic to decadal, and from mesoscale and regional to basin/continental scale. Fortunately, a set of relatively new sensor, sampling, and platform technologies (e.g., airborne sampling and autonomous sensors on moorings and drifters) are greatly expanding our view of atmospheric and oceanic biogeochemistry. Nevertheless, the optimal mix of these new and more traditional methods for an improved sampling network are not well known. A number of atmospheric inversion studies using relatively coarse resolution transport models have explored the impact on surface carbon flux estimates of expanding the ground-based air-sampling network and/or adding airborne and satellite measurements. More work is likely required, however, at fine spatial resolution and incorporating more sophisticated dynamics (e.g., diurnal cycle, planetary boundary layer) to refine surface CO_2 flux estimates. For

the ocean, preliminary sampling requirements have been defined for surface pCO_2 and carbon inventory sections using statistical methods (see Appendix D, Appendix E, and Chapter 4). Again, more detailed study using formal inverse techniques and high-resolution process models is warranted, particularly as new data sets become available.

5.2.3 Ocean and atmosphere prognostic model—data evaluation

Focused research on forward or prognostic atmospheric transport and ocean biogeochemical models is required to better quantify surface CO_2 fluxes, develop a fundamental understanding of processes controlling those fluxes, and improve future climate projections. Particular emphasis should be placed initially on physical circulation, because carbon is redistributed horizontally and vertically by constantly varying atmospheric and oceanic transport. Therefore, synthesis of observations and interpretation of data require adequate representation of advection and mixing as well as their variations. Atmospheric and oceanic constituents have source and sink distributions and lifetimes different from temperature, humidity, salinity, and other traditional physical circulation parameters. The simulation of tracer distributions therefore demands different strengths and tolerates weaknesses in general circulation models (e.g., TransCom, the Ocean Carbon Model Intercomparison Project [OCMIP]).

In particular, the IGBP-GAIM TransCom and OCMIP intercomparions reveal large discrepancies in model simulations of the vertical and horizontal structure of tracers in both atmosphere and ocean. These discrepancies result largely from uncertainties in the representation of subgrid processes in the models, and the required improvements in the models are often parallel in atmospheric and oceanic models. Examples include, but are not limited to, diurnal and seasonal dynamics of the atmospheric planetary boundary layer and the oceanic mixed layer; mixing and transport of tracers by clouds and deep/intermediate water formation; flow over orography and boundary currents; and diapycnal and isopycnal mixing.

The OCMIP intercomparison has also begun to evaluate the biogeochemical components of ocean models using the rich database from the JGOFS/WOCE global CO_2 survey (e.g., nutrients, DIC, oxygen). The treatment of biology in these models is woefully crude, however, and a new round of model-data evaluation is called for, one that incorporates biology in ways intended to better predict or describe the sea surface pCO_2 field based on mechanistic principles.

5.2.4 Reconciliation of air-sea CO_2 flux estimates

Air-sea fluxes of CO_2 can be derived in three independent ways: inversion of atmospheric CO_2 concentrations using atmospheric transport models (ATMs), inversion of interior oceanic carbon system observations using oceanic circulation/biogeochemistry models, and direct in situ observation of air-sea ΔpCO_2 and wind speed or sea surface roughness, proxies for gas

transfer velocity. Confrontation of these independent estimates would challenge both the models and measurements. Reconciling these independent estimates would provide confidence in the regional carbon sinks inferred from the atmospheric CO_2 data. The construction and intercomparison of these estimates represents the intersection of the three axes of the entire observation program, and hence is a major focus.

Inverse or diagnostic models are routinely used to estimate air-sea fluxes of CO_2 (and other biogeochemical gases such as O_2) from the atmospheric surface sampling network data. The atmospheric transport research community has a rich history in this area, and inverse techniques have the advantage of quantifying regional (subbasin to basin-scale) flux magnitudes as well as the associated uncertainties. The resulting model-generated products provide the input needed for scientific and political assessments and the initial conditions for short-term and long-term predictions using prognostic models. Similar methods can be applied to ocean circulation models and subsurface carbon observations, but work on these applications is just beginning. The more traditional, direct oceanic air-sea flux approach requires spatial and temporal interpolation of the sparse in situ pCO_2 data and estimates of air-sea gas transfer from wind speed (as determined by atmospheric analysis, satellite scatterometry, etc.) and/or satellite surface roughness. The most straightforward interpolation methods involve statistical objective analysis. The next level of sophistication incorporates information from more densely sampled and/or remotely sensed ocean properties (e.g., sea surface temperature and salinity, ocean color) using either empirical or theoretical relationships (full data assimilation is discussed in more detail below).

5.2.5 Hindcast simulations

The Earth's climate exhibits significant subannual, interannual, and decadal variability across a range of spatial scales from regional to global, with much of the nonseasonal signal associated with regional climate modes such as the El-Niño/Southern Oscillation (ENSO), North Atlantic Oscillation (NAO), Antarctic Circumpolar Wave, and the like. The observed growth rate of atmospheric CO_2 contains considerable temporal variability on similar scales, which can be partitioned with inverse techniques into land and ocean contributions based on spatial patterns and atmospheric $\delta^{13}C$ and O_2/N_2 data. Even more information can be derived by examining the spatial and temporal variability patterns of marine and terrestrial ecosystems. Natural climate variability offers a ready-made set of perturbation and/or sensitivity studies that can clarify the physical and biological mechanisms governing carbon cycle dynamics. In addition to replicating the large-scale geographic patterns of the mean state and seasonal cycle, particular emphasis should be placed on evaluating the ability of prognostic models to hindcast the atmosphere/ocean/land carbon cycle and biogeochemical responses to interannual to decadal natural variability. The experience gained from this research will feed into the continued development and improvement of prognostic models for simulating the future evolution of carbon dioxide under a range of emissions scenarios.

5.2.6 Data assimilation

Data assimilation models have roots in numerical weather prediction, in which synoptic meteorological observations are continuously fed into numerical weather models to produce a global, gridded, synoptic description of the atmospheric circulation every 4 or 6 hours. The assimilation models thus merge diverse data streams into a single framework, interpolating and extrapolating observations spatially and temporally, and imposing internal consistency among the various parameters in the analyzed products.

The development of assimilation models will contribute centrally to the formulation of a strategy for constraining regional carbon budgets. It is crucial to use a diversity of approaches and models to derive and reconcile these estimates, and data assimilation provides a coherent framework for conducting such work. The results from the atmospheric inversions also should be evaluated with the fluxes predicted from maturing terrestrial carbon simulations, to assess flux magnitudes and patterns, and to isolate the physical and biogeochemical driving factors.

To accomplish this task, data assimilation models must be expanded to incorporate carbon observations, including related tracer and remote-sensing data. The initial focus will likely be on assimilating atmospheric (or ocean) CO_2 concentration data alone, but with time more integrated systems will evolve that fold in biological data streams, such as satellite-derived terrestrial vegetation indices and surface ocean color. Data assimilation models already capture much of the variability in the physical climate system on synoptic to interannual timescales, and so the assimilated carbon products would be dynamically consistent with the temporally evolving atmospheric and oceanic circulation. Additional data products would include optimal estimates of all the carbon state variables and fluxes resolved in the numerical simulation (e.g., net community production and surface CO_2 fluxes). As emphasized below, the infrastructure costs of full-scale, numerical data assimilation are large, and it is presently unclear whether the best course would be to incorporate carbon into the (mostly) operational atmosphere and ocean data assimilation efforts or to develop a parallel data assimilation system more specifically tailored for carbon cycle studies.

Assimilation of ocean carbon observations into atmosphere and ocean models is a new area of research, and an initial research phase is strongly encouraged before making the transition toward a more operational mode. In the research phase, a diversity of approaches and numerical models must be used. The intercomparison of these methods and models and assessment of the realism of the "analyzed" carbon products will challenge and accelerate the development of the biogeochemical parameterizations. The meteorological community has an extensive history with atmospheric data analysis and assimilation models, which form a core component of the operational weather forecasts (e.g., NCEP, ECMWF). These techniques have also been expanded to seasonal and interannual climate prediction issues (e.g., ENSO), incorporating coupled upper ocean, atmosphere, and land physical models and satellite remote-sensing data (e.g., the NASA Goddard DAO assimilations). The CLIVAR program and Global Ocean Data Assimilation

Experiment (GODAE) have attempted to elevate global ocean state estimation from its current experimental status to a quasi-operational tool for climate research and prediction. A number of hindcasting ocean state estimation projects are also underway (e.g., ECCO—Estimating the Circulation and Climate of the Ocean). The development of a carbon data assimilation program should build on and leverage collaborations with NOAA, CLIVAR, GODAE, and NASA.

5.2.7 Prognostic (forecast) simulations

Coupled carbon and climate models are needed for projecting the influence of terrestrial and oceanic processes on the rate of atmospheric CO_2 growth and climate change; they are also needed to identify carbon/biogeochemistry metrics that may be early (fast response) signals of slow climate change. Coupled models will also serve as the framework for integrated global carbon cycle data assimilation. The United States needs to develop the capability for a comprehensive climate system modeling program built on high-end, global models that cover a number of areas:

- The coupling of all components of the climate system.
- All processes that determine the composition of CO_2 and other radiatively and chemically important trace constituents in the atmosphere.
- Future climate change over the next several centuries under a range of social, political, and economic scenarios.
- A systematic set of tracers and diagnostics that can be used to evaluate the model performance for regional assessment.

The carbon cycle must be an integral component of such an effort, which must build on and leverage process-level research on the physical, chemical, and biological mechanisms governing the climate system. One critical source of process-level information is the large-scale tracer observations that, interpreted with models, reflect carbon fluxes and their relation to forcing.

5.2.8 Modeling studies for atmospheric CO_2

As outlined in the chapter on needed atmospheric observations, there is much more information on continental and basin scale carbon exchange in even the current atmospheric data stream than we are able to extract with current transport models. As the observing system is expanded to include more continental locations and satellite derived CO_2 fields, models will increasingly be called on to quantify CO_2 surface flux information from the atmospheric concentration data on finer regional scales. There are three basic synthesis and modeling needs specific to the atmospheric observation component:

- Improve atmospheric tracer model representation of the synoptic wind field, diurnal cycle, and vertical mass transport.
- Incorporate carbon data assimilation into global atmosphere models.

- Develop high-resolution mesoscale atmosphere-land carbon cycle models to support regional field campaigns.

Improve tracer model representation of the synoptic wind field, the diurnal cycle, and vertical mass transport to better resolve the high-frequency variability observed in continuous measurements and observations in continental interiors

Most atmospheric observations to date have focused on remote background locations, which could be analyzed with the coarse-resolution atmospheric transport derived from GCMs. Newer stations in continental locations are much more strongly influenced by local to regional sources and sinks. Terrestrial fluxes are strongly variable in both space and time, as is atmospheric transport over land. Taken together, this variability in fluxes and transport produces much "noisier" time series of tracer concentration at continental observing locations than in the remote marine boundary layer. Current sampling protocols are dominated by discrete sampling, providing a single measurement from a highly variable concentration field. Such measurements are only representative when they are averaged over many samples, for example, as monthly means. Present inverse modeling studies optimize monthly mean concentration fields simulated by global ATMs over grid cells of more than 10^5 km^2 through depths of hundreds to thousands of meters. Data used in these inversions are typically monthly mean concentrations calculated from discrete samples. The analysis therefore inappropriately compares simulated mass-weighted means sampled continuously to the mean of a handful of point measurements taken from a continuously varying field.

More information is in principle extractable from highly variable concentration data, but requires accurate knowledge of the upstream trajectory of the air being sampled. Many of the current models being used for inversion studies do not even use "real" winds, relying on correct simulation of the climatological transport operator to optimize a fit to the climatology of observed CO_2. Some models do calculate tracer transport using analyzed winds, produced by weather forecasting centers. Wind fields generated in this way are also model simulations, though they have been made consistent with observations in an optimal way through data assimilation methods. Unfortunately, these wind fields are largely unconstrained by data in some areas of the world with few soundings (notably large areas of the Pacific and Southern Oceans). In addition, forecast and analysis centers typically do not archive vertical mass transport due to unresolved physical processes such as moist convection and turbulence. In ATMs driven by analyzed winds, these mass fluxes are usually estimated independently, using algorithms that are different than the ones used in the "parent" forecast model. The resulting inconsistency in transport between the resolved advection (estimated by the forecast model) and the vertical mass fluxes (estimated by the physical parameterization in the off-line ATM) reduces the realism of the simulated tracer field.

Making the most out of future observations that include high-frequency time series, such as records from continuous analyzers on tall towers, will

require not only accurate transport by "real winds," but also accurate simulation of vertical structure. Meeting this goal will require dedicated efforts to advance the state of the art of simulating diurnal variations in surface ventilation and entrainment at the top of the planetary boundary layer and the effects of vertical transports in cumulus clouds. ATMs used for inversion of continuous records may require high vertical resolution near the surface, but the height of the top of the planetary boundary layer varies from 100 m under very stable conditions to several kilometers under strongly convective conditions. The challenge then is to resolve strong tracer gradients and entrainment processes at whatever height they occur in the lower troposphere. Of course, the representation of planetary boundary layer entrainment and cumulus convection is also of paramount importance in weather and climate modeling, and it is the subject of very active research in the physical climate community. Models used for numerical weather prediction are already using advanced physical parameterizations and running on grids of as small as 50 km (or equivalent spectral resolution).

High time-resolution flux estimates may be obtained from continuous, high-frequency data through the use of realistic transports obtained from operational weather analyses. The most serious impediment to this kind of analysis today is the lack of subgrid-scale mass fluxes. A top priority for inverse model development should be to obtain both winds and convective transports from Numerical Weather Prediction (NWP) centers at the highest possible resolution, preferably on an hourly time step. This achievement will allow analysis of actual cases from continuous analyzers as opposed to time means. Shifts in concentration during frontal passage, wind shifts, or other weather events would then become part of the signal in the inversion, rather than being treated as noise. Weather analysis and reanalysis products have typically been provided on a 6-hour basis, and subgrid-scale mass fluxes have not been included. Extending these products to hourly time resolution and including parameterized transports would dramatically increase data storage and transmission requirements. But recent advances in both areas have exceeded Moore's Law, and such increases are now both technically feasible and economical. Realistic model transports at high temporal and spatial resolution will enable inversion analysis to move toward direct assimilation of concentration data for surface flux estimation. Assimilation methods have already been explored using existing ATMs (Bruhwiler *et al.*, 1999; Dargaville *et al.*, 2000; Rayner *et al.*, 2000). Applying these methods to highly resolved transports from a new generation of reanalysis products would substantially improve flux estimates and exploit the new information being provided from continental observations. These improvements could be obtained in the next 2 years and should be strongly encouraged, but will require significant effort and resources from one or more NWP centers.

Develop techniques and methods for carbon data assimilation into global atmospheric models

Real-time assimilation of satellite and in situ CO_2 estimates in operational weather forecasting would provide an ideal framework for estimation of re-

gional surface CO_2 fluxes by mass balance. Carrying tracer concentrations as a prognostic variable in the assimilation provides strong constraints from the "memory" in the atmosphere and would reduce artificial noise from poorly constrained CO_2 retrievals. Assimilated CO_2 concentrations in operational NWP models would produce fully populated, global gridded data, filling the gaps left by clouds, yet remaining optimally consistent with existing observations. Correct knowledge of atmospheric CO_2 also has recently been shown to improve the retrieval of temperature profiles from infrared spectroscopy, reducing forecast initialization error by as much as 1 K over some regions (Engelen *et al.*, in press). Achieving this goal will require the commitment of operational NWP centers and their sponsors. Such a program is technically feasible and could be implemented as early as 2002, when satellite CO_2 estimates begin to be available from the Atmospheric Infrared Sounder (AIRS) aboard EOS-Aqua. The operational centers (for example, NCEP, ECMWF, and NASA DAO) have the requisite human resources and skill, computing infrastructure, and data-handling capability, but the centers have correctly argued that such analyses are beyond their weather forecasting mandate. Significant new resources would be required to accomplish routine CO_2 data assimilation, yet the scientific return is potentially enormous, especially later in the decade when higher quality global satellite products are expected to become available.

Spaceborne CO_2 data alone, however, will not solve all of the problems, and a major need in the next 5 years will be to analyze possible bias in trace gas products derived from satellite retrievals. This will entail substantial field sampling programs (see section on atmospheric observations), but also may require models to extrapolate data into unobservable "gaps." Sensors relying on reflected sunlight, for example, will see only daytime conditions, which are likely to have systematically lower CO_2 concentrations over vegetated land than the true mean. Similarly, almost any spaceborne estimate of CO_2 concentration will be biased to clear sky conditions, which may result in small but systematic errors over time. To counter these biases, models used for data analysis, assimilation, and flux estimation will need better parameterizations of high frequency surface flux and vertical mixing variability, for example, accounting for diurnal cycles over land.

Develop high-resolution mesoscale atmosphere-land carbon cycle models to support regional field campaigns

In addition to developing and improving *global* ATMs for inverse calculation of surface carbon fluxes by data assimilation, there is a need for model development in support of regional field campaigns. Such campaigns (e.g., BOREAS, LBA, COBRA, and SAFARI2000) are an important test of the ability of simulation models to scale from locally observable processes (flux tower scale) to larger regions. They provide an opportunity to apply the same sort of mass-balance constraint on such upscaled models that can be obtained at continental scale through inverse modeling, but at much finer scales for specific cases. Aircraft sampling can strongly constrain predictive models of carbon and other trace gas fluxes, but only if trajectories are

known in considerable spatial and temporal detail for the actual flight days and times. Even the very best global meteorological data analysis products have insufficient resolution to be very useful for this purpose. Mesoscale atmospheric models can be driven from globally gridded data, with "nests" down to 1 km or finer for this purpose, and operational analysis and forecasts from such models can therefore be very useful in support of field campaigns. Such models can resolve features of circulation and transport, for example moist convection and entrainment at the top of the planetary boundary layer, that must be parameterized in global models. Case studies from field campaigns in which fine-scale analyses are well constrained by observations can also be used as test beds for improved parameterizations of these processes in global models.

Most mesoscale atmospheric models in current use can be run from analyzed fields at larger scale and are thus already available for use in field campaigns. Very few, if any, however, are coupled to ecophysiological process models that predict spatial and temporal variations of photosynthesis and respiration. Intensive field campaigns, such as those conducted by CarboEurope and the proposed North American Carbon Experiment, would be excellent tests of such models. As computer power increases, it will be possible to simulate coupled interactions among weather, hydrology, and biogeochemistry at scales of a few kilometers over continental-sized regions for periods of up to a year. Such a simulation would be very expensive to run, but could be tested quite rigorously against data from surface, airborne, and spaceborne platforms. These tests, which would provide significant insight, algorithm development, and even code for the development of the global coupled assimilation models, could be accomplished in the next 5 years. By the end of the decade, these fine-scale models would likely merge with the more ambitious global coupled models and be run routinely at global scale on grids of 10 km or less.

5.2.9 Modeling studies for upper ocean physics/biogeochemistry and sea surface pCO_2

There are four basic synthesis and modeling challenges specific to the surface CO_2 observations component:

- Improve quantification of the time/space correlation scales for surface pCO_2, surface air-sea CO_2 flux, and other relevant physical and biogeochemical properties as the basis for the design of sampling programs.
- Relate observed and historical patterns and variability in pCO_2 and ancillary tracers (TCO_2, TA, O_2, nutrients, isotopic composition of these species) to the underlying biological and physical mechanisms.
- Develop empirical and mechanistically based numerical methods for extrapolating in situ pCO_2 data and air-sea flux estimates to basin-scale.
- Initiate surface ocean color and pCO_2 data assimilation studies.

The objectives are of course related in that improved understanding of the governing dynamics provides a more rigorous basis for time/space extrapolation and data assimilation.

Quantify the time/space correlation scales of surface pCO_2, surface air-sea CO_2 flux, and other relevant physical and biogeochemical properties via synthesis of in situ and remotely sensed data and high-resolution process models

Appendices E and F present preliminary sampling density requirements for a surface pCO_2 observing system based on statistical analyses of existing underway pCO_2 and time-series data. These estimates need to be refined over the first 5 years of the program using a combination of new surface data from instrumented moorings, drifters, and volunteer observing ship lines and directed modeling studies. An important question involves identifying the degree to which pCO_2 is correlated with the gas exchange coefficient, which might result, for example, from strong winds and the ensuing vertical mixing. The key is to better characterize the relevant time and space correlation scales for surface pCO_2, air-sea CO_2 flux, and other biogeochemical fields. Time/space scales are fundamental to basin-scale extrapolation as well (see below). An iterative procedure is envisioned whereby new scale estimates are applied and the resulting skill of basin extrapolations (compared, for example, to independent data withheld from the analysis) is used to guide revised scale estimates and sampling requirements.

Surface pCO_2, air-sea CO_2 flux, and ocean biology vary on a wide range of scales driven primarily by ocean/atmosphere physics: synoptic events (e.g., storms), submesoscale fronts, mesoscale eddies, and gyre circulation and climatic modes. Present measurement technologies typically limit the high-resolution sampling of pCO_2 to one dimension, either in space (e.g., a VOS underway line) or time (e.g., a moored time-series record). In a research mode, it is possible to make two-dimensional and partial three-dimensional surveys with dedicated seasoar surveys along a grid of transect lines. Analyses of satellite surface fields of physical properties (e.g., sea surface temperature, sea surface height) and biological properties (e.g., ocean color) suggest that the mesoscale (roughly 10–100 km) is a dominant scale of variability.

Eddy-resolving numerical models can provide a more complete picture of the time-evolving three-dimensional fields of the upper ocean and the relationship of pCO_2 to remotely sensed properties. A number of eddy-resolving biogeochemical process models have been developed (e.g., McGillicuddy and Robinson, 1997; Mahadevan and Archer, 2000). The Mahadevan and Archer work is particular interesting because it uses idealized tracers to show the relationship between time and space scales across the submesoscale and mesoscale, more slowly evolving tracers having longer space scales. Eddy-resolving, basin-scale ecosystem models have also been constructed (e.g., Oschlies and Garcon, 1999), but some caution is warranted because very high resolution ($\sim 1/10^{\circ}$) is required to properly capture the statistics of the eddy field and the eddy-mean flow interaction (Smith *et al.*, 2000). Some

encouraging, very simple biogeochemical studies are being conducted on this scope (McGillicuddy *et al.*, in preparation). Even higher resolution submesoscale processes may also be important. Carbon system dynamics need to be incorporated into these classes of models to explore the high-frequency space/time variability in surface pCO_2.

Develop improved empirical and mechanistically based methods for extrapolating in situ pCO_2 data and air-sea flux estimates to basin scale

At the simplest level, the basin-scale extrapolation problem can be viewed as one of objectively analyzing a sparsely sampled field in space and time. The Takahashi *et al.* (1997, 1999) climatology, for example, is constructed using inhomogeneous and anisotropic correlation scales derived in part from the surface circulation field of an ocean general circulation model. Additional information can be incorporated using empirical relationships with satellite sea surface temperature, ocean color, and climatological nutrient fields. The advent of regular satellite sea surface height observations and, soon, the ARGO profiling float array provide additional information on eddy kinetic energy and thermocline structure, key for estimating subsurface nutrient and DIC inputs to the upper ocean. The incorporation of the in situ and satellite data into numerical models of low or moderate complexity will provide a foundation for interpolating between observations and deriving accurate basin-scale pCO_2 fields and air-sea fluxes.

These statistical approaches should be augmented using more mechanistic, process models to examine the cross-correlations among key physical, chemical, and biological variables. For example, 1-D studies (Keeling *et al.*, 1997) have shown that the surface concentration of oxygen, and presumably CO_2, varies with wind speed due to surface gas exchange, turbulent mixing, and biology (which is impacted by the mixing). Cross-correlation on synoptic or storm timescales that will vary regionally is significant. The eddy-resolving models together with moorings, high-resolution survey data, and surface drifters will allow for a more thorough investigation of this and other potential aliasing factors. Prognostic basin-scale biogeochemical models can also be used to construct more robust large-scale relationships of pCO_2 to other variables.

Relate observed and historical patterns and variability in pCO_2 and ancillary tracers (TCO_2, TA, O_2, nutrients, isotopic composition of these species) to the underlying biological and physical mechanisms

Prognostic models can provide consistent and complete hindcasts of three-dimensional biological and physical fields to explore dynamical relations, and through model-data evaluation improve the parameterizations of the marine carbon cycle. A number of three-dimensional marine ecosystem models are available on regional to global scales, many of them including an active carbon cycle (e.g., Six and Maier-Reimer, 1996). Only recently, however, have

these models begun to incorporate more sophisticated treatment of ecosystem dynamics beyond simple phytoplankton-zooplankton-nutrient-detritus food webs. In particular, models for the high-nitrate low-chlorophyll (HNLC) regions such as the subpolar and Equatorial Pacific and the Southern Ocean will require some treatment of iron limitation (e.g., Moore *et al.*, 2001). Calcification, nitrogen fixation, community structure, subsurface biogeochemical dynamics, and numerical advection schemes are other important concerns (Doney, 1999). Further, these models are typically either non-eddy-resolving or eddy-permitting, and at least for the near term, mesoscale eddy effects (e.g., eddy nutrient pumping) will have to be included using some form of subgrid-scale parameterization. A key aspect of the modeling component will be the ongoing evaluation and improvement of the basic ecosystem and biogeochemical model components.

A basic premise of present modeling is that physics forces ocean biogeochemistry; if we knew the physics well and had the proper ecological and biogeochemical models, we could predict large-scale biogeographic spatial patterns, the seasonal cycle, and interannual climate variability. An assumption is that intrinsic biological modes may affect individual species but do not greatly impact carbon fluxes. Getting the physics right is therefore fundamental. Physical hindcasts that cover the past several decades are becoming common (1950s to present, but with the bulk of the evaluation/forcing observations from about 1970 on). These simulations can take one of two forms: unconstrained forward models (e.g., Doney *et al.*, 2001), and state estimation/data assimilation models (e.g., Stammer *et al.*, 2001). The resulting physical fields should be used to drive simulations of pCO_2 variability in order to evaluate biogeochemical model skill, separate the relative importance of physical and biological processes on the variability of pCO_2 and ancillary tracers, and explore the response of ocean pCO_2 and other properties to regional, interannual climate modes (ENSO, PDO, NAO, etc.). As mentioned above, these simulations will also serve as the basis for surface pCO_2 extrapolation products.

Initiate surface ocean color and pCO_2 data assimilation studies

Biogeochemical data assimilation is in its infancy, and a three-phased approach is likely warranted. As outlined above, the first phase will involve assimilation of the much-better-sampled physical variables and off-line ecological and biogeochemical simulations. The second phase will include active assimilation of satellite ocean color as well as physics. The third phase will involve the assimilation of in situ pCO_2 data and other tracers such as mixed layer nutrient concentrations and biological O_2 supersaturation. This rationale is driven by the fact that a biogeochemistry model is only as good as the underlying physics and is limited by the current paucity of in situ surface pCO_2 (and related) data. At this time, the most effective strategy may be to use the emerging field data sets indirectly to improve the ecosystem and biogeochemistry models. Inversion of the subsurface carbon, nutrient, and oxygen fields is also important in that it provides complementary climatological estimates of export production and surface air-sea fluxes.

A number of recent parameter optimization studies have been conducted for marine biogeochemical box and one-dimensional models, particularly with time-series data (e.g., Matear, 1995; Fasham and Evans, 1995; Hurtt and Armstrong, 1996; Fennel *et al.*, 2001). Applications to three-dimensional models are more limited, but include efforts to assimilate satellite ocean color data into ecosystem models (e.g., Ishizaka, 1990). Presently, the appropriate methods for assimilating biological and chemical data are an open research question, which should be explored during the initial phase of the project. The utility of data assimilation will continue to grow with the import and refinement of numerical methods from meteorology and physical oceanography to interdisciplinary problems (Robinson, 1996) and with the availability of automated software systems for generating the required model adjoints (Giering and Kaminski, 1998).

5.2.10 Modeling studies of CO_2 in the ocean interior

There are four synthesis and modeling challenges specific to the ocean interior observation component:

- Extrapolate ocean interior observations on repeat ocean transects, time-series stations, and autonomous platforms to determine the ocean carbon inventory and its changes in space and time, including interannual variability.
- Use ocean interior observations to infer air-sea fluxes of carbon and transport of carbon within the oceans, and their variability in space and time.
- Relate the observed patterns and variability of carbon and other tracers to the underlying biological mechanisms with the aim of developing improved models.
- Continue improving and assessing tracer transport characteristics in oceanic general circulation models, especially those used to diagnose carbon sources and sinks.

Extrapolate ocean interior observations to determine the ocean carbon inventory and its changes in space and time, including interannual variability

The primary aim of the ocean interior measurement program is to provide constraints on the changes in the ocean carbon inventory in space and through time. However, because of the difficulty of obtaining direct measurements, the observations are and will always be relatively sparse in space and time. Furthermore, they exhibit considerable seasonal and interannual variability. The use of such measurements to determine long-term inventory changes has thus required the development of a number of methods to determine the excess (anthropogenic) dissolved inorganic carbon either by estimating and removing the background preindustrial CO_2 field (e.g., Brewer, 1978; Chen and Millero, 1979; Goyet *et al.*, 1999; Gruber *et al.*,

1996) or computing the temporal change in ocean CO_2 directly by differencing one set of cruises and another (Wallace, 1995, 2001). Recent comparisons of methods for detecting excess dissolved inorganic carbon showed significant disagreements between different approaches (Wanninkhof *et al.*, 1999; Coatanoan *et al.*, 2001). All the methods involve assumptions that can be tested with model simulation results. A good example is the calculation of the preindustrial, dissolved inorganic carbon disequilibrium, which, if incorrect, could significantly bias the thermocline anthropogenic CO_2 estimate. Furthermore, as model simulations improve, it will be possible to use data assimilation to obtain an independent estimate of the change in inventory through time. Finally, it is important that the measurement strategy be continually tested and improved through time. Model simulations have played and will continue to play a key role in this regard.

Use ocean interior observations to infer air-sea fluxes of carbon and transport of carbon within the oceans, and their variability in space and time

Analogous to the atmospheric transport and inversion studies, the air-sea fluxes of biogeochemical species (including CO_2) can be derived in theory by inversion of interior oceanic carbon system observations using oceanic circulation and biogeochemical models (e.g., Gruber *et al.*, 2001; Gloor *et al.*, 2001). This relatively new approach in oceanography has many similarities to the atmospheric calculations, but some significant differences and unique problems as well. For example, the mixing timescale of the troposphere is only a few years; by contrast the mixing timescale of the deep ocean is several thousand years. The stability of the ocean circulation over such periods, an implicit assumption of the current inverse approach, is not well assured. The inversion of ocean interior observations has to date been conducted for a single circulation model, and considerably more work is warranted to explore the sensitivity to the physical and biogeochemical model framework, underlying assumptions and experiment formulation, and the inversion techniques. Furthermore, this work should be more closely tied to and related with more traditional box inverse models and Greens function analysis, which have been used for some time in the oceanographic community to infer ocean circulation, biogeochemical rates and transport (Schlitzer, 1999), and transient tracer uptake.

Relate the observed patterns and variability of carbon and other tracers to the underlying biological mechanisms with the aim of developing improved models

Many of the modeling issues raised with regard to surface pCO_2 apply to ocean interior CO_2 simulations as well. The subsurface distributions of CO_2, alkalinity, oxygen, and nutrients are strongly driven by the so-called biological pump, and more mechanistic parameterizations are needed for surface net community production, dissolved and particulate organic matter export fluxes, and subsurface remineralization. Despite important recent advances

in our understanding of the role of particulate as well as dissolved organic matter in the export of carbon from the surface into the ocean interior (e.g., Armstrong *et al.*, 2001; Carlson and Ducklow, 1995; Hansell and Carlson, 1998; Kirchman *et al.*, 1993), more realistic export fluxes will require better treatment of, for example, planktonic functional groups (e.g., nitrogen fixers, calcifiers), dissolved organic carbon and nutrient cycling, and mesoscale eddies. We have an even poorer understanding of the biological and physical processes that occur in the subsurface waters of the main thermocline, the so-called twilight zone, where most of exported organic matter is remineralized. The National Science Foundation has prepared plans to study these processes in future years. The interior measurements proposed in this plan will provide information on the mechanisms involved in the vertical transport, transformation, and remineralization of organic matter that will complement the proposed subsurface biogeochemical observations. Together these data will be important constraints when developing more realistic biogeochemical models as well as improved physical circulation (see the next recommendation).

Continue improving and assessing tracer transport characteristics in oceanic general circulation models, especially those used to diagnose carbon sources and sinks

The constantly varying oceanic circulation redistributes carbon horizontally and vertically, and so the synthesis and interpretation of observations require adequate representation of transport and mixing and their variations. Oceanic constituents have source/sink distributions and lifetimes different from temperature, salinity, and other traditional physical circulation parameters. Thus, simulations of tracer distributions reveal different strengths and weaknesses of the general circulation models, as amply revealed by OCMIP. In particular, the OCMIP intercomparisons reveal large discrepancies in model simulations of the vertical structure of tracers in the ocean, as discussed in the introduction to this section. Oceanic data useful for testing and improving oceanic models include the chlorofluorocarbons and radiocarbon as well as traditional hydrographic tracers and nutrient distributions.

5.2.11 Modeling studies of the global coupled carbon-climate system

There are two basic synthesis and modeling challenges specific to the global coupled carbon-climate system component:

- Improve and evaluate global coupled carbon-climate models.
- Develop techniques for carbon data assimilation into global coupled models.

Improve and evaluate global coupled carbon-climate models

The advent of global coupled carbon-climate models is a very recent advance (e.g., Cox *et al.*, 2000), and considerable effort is required to develop a robust set of models, diagnostics, and model-data evaluation metrics so that coupled models can be used with confidence for interannual variability and future climate scenarios. In addition to all of the problems associated with developing and validating the individual biogeochemical models, a number of issues arise unique to the coupled system. First, the climate of coupled physical models is typically degraded relative to either the observed state and/or uncoupled component models, which have been "tuned" to match observations (Blackmon *et al.*, 2001). The additional complexity associated with the coupled system suggests that the solutions to such problems will not be simple or direct. These physical errors will propagate through the biogeochemical and carbon systems as well. Second, the variability in the coupled solutions can only be compared with observations in a statistical sense, greatly complicating model validation exercises. Third, similar to the physical system, coupling will lead to new dynamical behaviors and model-data error patterns associated with exchanges of carbon among the reservoirs that do not occur in the uncoupled model components.

Develop techniques for carbon data assimilation into global coupled models

An ambitious program of assimilation of chemical tracer data into coupled atmosphere-land-ocean models can be envisioned in the middle of the decade. Rather than simply estimating regional surface fluxes from mass-balance considerations in a well-observed (and well-simulated) atmosphere (as outlined in the atmospheric section above), this approach would optimize parameters in underlying biogeochemical and biogeophysical models that describe the processes responsible for the fluxes. The atmospheric observations, therefore, would be used quantitatively to better constrain some of the poorly known parameters controlling regional surface CO_2 fluxes in present simulations. Such parameters might include the temperature sensitivity of soil respiration, the wind-speed dependence of the air-sea gas exchange coefficient, and the photosynthetic capacity of forest canopies. Assimilation into global coupled models would provide improved time-resolved maps of surface carbon exchange, but also lead to progressive improvements in the predictive capability of the process models over time. This kind of work has already begun for hydrological models (Land Data Assimilation System, Walker and Houser, 2001), and has been demonstrated with simple atmosphere-land biosphere models (Rayner *et al.*, 1999).

The first goal would be to better parameterize "fast" ecophysiological responses and transport processes so that the coupled assimilation system produces synoptic to seasonal CO_2 surface fluxes that match observed short-term changes in atmospheric CO_2 and that reasonably extrapolate to unobservable parts of the diurnal cycle or cloud field. The parameters in such a model would be optimized over time and space. The mass-balance analysis

would then be used to estimate the "slower" ecological components of the fluxes (due to forest regrowth, fires, harvest, etc.). In the longer term, these slow processes could be parameterized in the assimilation model as well.

As more skill with the data assimilation methods is acquired, other data constraints could be added toward the end of the decade such as terrestrial and marine biomass and productivity, in situ surface CO_2 flux estimates (e.g., from Ameriflux sites and ocean moorings, VOS and drifters). Ideally, such a coupled model with embedded biology would predict quantities that are directly observable, including temperature, wind, atmospheric CO_2, surface ocean pCO_2, and spectral radiance at the top of the atmosphere, the latter the result of the radiative interactions with vegetation, phytoplankton, and atmospheric trace gases such as CO_2 and CO. The assimilation system would then seek to minimize a generalized cost function that includes deviations of each of the predicted quantities from the actual observations stream, which would be suitably defined to include both observations made at the surface, by automated in situ sensors, and from space. Such a system would enable near-real-time analysis of the elements of the carbon cycle on land and in the oceans, and the processes that give rise to sources and sinks. It would be invaluable both for monitoring variability and for learning about the coupled Earth system. Most important, it would enable the development of falsifiable predictive models about the future behavior of the carbon cycle and the climate system.

Constructing the coupled data assimilation system described above will require either (1) convincing the major operational centers (and their sponsors) that such an expensive expansion of their mission is worthwhile; or (2) recreating the massive infrastructure and human resources currently used in those centers for the service of the carbon cycle research effort. Which of these two paths to follow is a difficult choice. Option 1 would obviously be less expensive, building on a huge, sustained, and successful ongoing program or programs. Considerable restructuring would be required at the highest levels of the weather forecasting organizations, however, which would not be easy or perhaps even desirable to accomplish. A major parallel data assimilation effort in Earth System Science would be very expensive to build, but would be more flexible and would not risk dilution or disruption of the operational infrastructure that has become so important to meteorology and commerce. Such a specialized assimilation system in parallel with the operational centers would have the tremendous luxury of being able to perform at a significant time lag, because real-time analysis or forecasts of carbon fluxes will probably never be necessary. This approach would also accommodate an observing system that includes time-consuming postprocessing of satellite imagery and sample collection for later laboratory analysis. These types of data would be impossible to process in the assimilation system if the fluxes had to be determined on an operational timetable.

Chapter Six

Biennial Assessment of the State of the Carbon Cycle Studies

6.1 Background

The continuing societal need for knowledge about the carbon cycle—to understand climate change and similar critical issues and to formulate the knowledge needed to formulate policy responses—requires an ongoing research and observation program. The outline of this program involves a permanent observing system and, while still indistinct, must be taken into account at the outset.

Continuing observational systems have a number of characteristic features:

- They are developed through scientific research, but their permanence is owed to the value they bring to society.
- The process of building these systems is a research enterprise that gradually becomes more and more operational as the science matures.
- Operational systems prove their value by providing useful information products, developed through a process that requires societal input to determine its information needs. The elicitation of societal needs requires a valuable and continuing dialog of scientists and the society they serve.
- These operational products are combinations of the observations, the models used to interpret and enhance the observations, and the data systems that make the resulting information readily and usefully available.

To maximize these systems' benefits in the area of carbon cycle science, we recommend the preparation and publication of a biennial assessment on the status of the science. This assessment would consist of two principal parts, one covering the research program, the other covering research results.

6.2 Assessing the State of Carbon Cycle Research

The biennial report would assess the status of several major areas of carbon cycle research:

- Atmospheric and oceanic observations of CO_2 and ancillary tracers.

- Process-level studies of CO_2 biogeochemistry and CO_2 anthropogenic sequestration. These studies will improve knowledge of land and ocean biogeochemistry, atmospheric and oceanic circulation, gas exchange across the air-sea interface, and enhance our ability to model all these processes.

- Modeling studies. One section of the biennial report would evaluate the current state and recent improvements of carbon cycle models and their consistent coupling to comprehensive climate models.

- Current observational approaches and sites. The report would also summarize current observational approaches and sites based on atmospheric flask samples, tall towers, aircraft sampling and aircraft campaigns, tracks of ships and drifters, ocean buoys, and transects recently occupied and planned for ocean interior studies.

6.2.1 Assessing research results

The report would assess research results in several areas:

- Recent advances in process-level understanding of biogeochemistry, atmosphere and ocean circulation, and gas exchange.

- Estimates of the anthropogenic sources and sinks of carbon for the previous biennium, including industrial output, land use changes, and purposeful sequestration rates.

- Estimates of global CO_2 fluxes between atmosphere and oceans, and between atmosphere and continental biosphere.

- Estimates of regional CO_2 fluxes between atmosphere and oceans, and between atmosphere and the continental biosphere.

- New estimates of the total global and continental-scale carbon budgets.

- Interannual variability in global and regional CO_2 sequestration rates, and their relation to physical forcing.

The biennial assessment will address the carbon cycle on a global scale, but the focus of land biosphere discussions will be North America. The assessment should be written at a level appropriate for scientists interested in the carbon cycle and climate. It should also contain a full summary, written at the technical level of a *Scientific American* article, to inform the general public and provide information useful to policy makers.

The biennial assessment will thus serve a number of purposes.

For U.S. society, it will provide baselines and future projections to compare options about how society can best address issues relating to the carbon cycle such as climate change science and impacts on ecosystem health, hydrologic systems, and human health and welfare. Continual advances made over time through the assessment would demonstrate to the public that progress is being made, providing tangible fulfillment of the social contract

the public makes to support research for ultimate social benefit. Because assessments would be regularly updated and available, they will inform the public and provide unbiased scientific information for use by decision makers at all levels considering carbon cycle issues in their policy formulation.

For the researcher, the biennial assessment will provide sources and perspectives of data not otherwise available. The biennial assessment would thus provide a step toward an ultimate climate observing system in return for the researcher's ongoing and systematic production of the assessment's inputs and products. The assessment will also give researchers a report card on how well their programs are doing and how satisfied society is with the result.

In summary, the biennial assessment will be valuable to a wide range of users, and provide a high level of reward and accountability for the carbon cycle science research community.

Chapter Seven

Summary

In the preceding chapters, we have laid out a plan for large-scale U.S. measurements of CO_2 in the fluid realms of the surface Earth. The measurements are formulated to allow us to track the distribution of fossil fuel CO_2 in the oceans and atmosphere, improve our understanding of underlying controls on inventories and fluxes, and to advance our ability to predict the future distribution of fossil CO_2 in the oceans, atmosphere, and land biosphere. This document represents the implementation plan for the large-scale CO_2 observing component of the U.S. Carbon Cycle Science Plan.

The implementation plan recommends an integrated study of CO_2 accumulation and transfer in the atmosphere, the surface ocean, and the ocean interior. The atmosphere is of interest as the medium from which CO_2 is lost to both the land biosphere and the oceans. It is also, of course, the reservoir that impacts climate via the greenhouse effect. The sea surface is of interest as the interface between atmosphere and ocean interior. The interior is of interest as the ultimate repository of most anthropogenic CO_2.

A number of common features exist in the programs that we recommend for each of these realms. First, plans for each realm involve analytical and other advances in instrumentation. The atmospheric plan calls for development of an advanced CO_2 analyzer that would be the keystone of several new field efforts. Sea surface and ocean interior plans call for the development of autonomous sensors that will provide continuous long-tem measurements on a variety of platforms. Perhaps foremost among these seawater instruments are ones that will measure two variables in the CO_2 system.

Second, the backbone of each observing system is an ongoing network aimed at comprehensively documenting the evolving CO_2 distribution. The specific observing plan for each realm depends on the accessibility to sampling and the time and space scales of variability. Observations for the atmosphere involve continued sampling at remote stations as well as an intensive program of aircraft sampling. Much of the sampling is to be done on synoptic timescales, with continuous sampling on tall towers supporting the study of boundary layer mixing. Sea surface pCO_2 studies will be focused around volunteer observing ships (VOS) making continuous measurements on repeat crossings. These will be supplemented by moored autonomous instruments and shipboard sampling at traditional time series study stations. The sea surface observations will access all timescales from diurnal, to seasonal, to interannual. Accessibility is much poorer than for atmospheric measurements, but mean values and variability can be characterized with fewer observing platforms. Ocean interior CO_2 concentrations are most difficult to measure, while changing most slowly. We recommend observing ocean interior CO_2 with repeat ocean hydrographic sections occupied once per decade. As is the case for sea surface studies, these will be supplemented with time series measurements at fixed locations. The combined interior data

set will record both interannual variability and the continuing accumulation of anthropogenic CO_2.

A third common feature is that measurements in all three realms will have process content related to biogeochemistry and ocean/atmosphere physics. Atmospheric studies emphasize continental measurements in the lower atmosphere that reflect the dynamics of boundary layer mixing, given the diurnal cycle of CO_2 uptake and release by the biosphere. Sea surface CO_2 studies include two important process components. The first involves measurements of chemical and isotopic tracers constraining net and gross production rates. These results, in turn, inform us about the quantitative impact of upper ocean biology on sea surface TCO_2 and pCO_2. The second is the study of gas exchange coefficients and their dependence on wind speed or a related property. These studies will allow us to reduce the large uncertainties this term currently introduces into air-sea CO_2 fluxes. Ocean interior studies address ocean physics issues by providing information on the distribution of halocarbons and anthropogenic CO_2. These data challenge tracer transport models that predict patterns of these properties. In addition, information on interannual variability in the atmosphere, surface ocean, and interior ocean holds key process-level information: in each case, it reflects the biological response to changes in physical forcing (expressed as weather/climate on land, and mainly as mixing in the ocean).

The fourth, related, common point is the essential interaction between data collection and modeling. To deduce carbon fluxes from CO_2 distributions, we need models describing both physical transport and interactions with the biosphere. Neither the physical nor biogeochemical models are adequate in any of the three realms. Perhaps the most satisfactory models concern upper ocean physics, while the least satisfactory describe remineralization of biogenic matter in the thermocline (these nominations could certainly be debated). The models themselves need to be technically upgraded to give better inherent descriptions of the processes they represent. As well, models need to incorporate results of observations, described above, so that they correctly represent rates of all important biogeochemical and physical processes. Thus, for all three realms, we envision an interactive process in which models are used to interpret data, and data are used to improve models. Simultaneously, physical and biogeochemical models will become more sophisticated in basic approach. Thus, for example, in all three realms, there is a progression from one-dimensional to two- and three-dimensional models; from steady-state to time-dependent models; and from forward models, to inverse models, and on to data assimilation models. Analogously, there is a progression from empirical parameterizations of biogeochemical processes to quantitative representations of fundamental rate processes.

Fifth, progress in each realm requires interfacing our large-scale observations with small-scale studies of fundamental biosphere processes that are being independently planned. Studies in all three realms also need to deal with the problem of scaling. One aspect of this problem is experimental. This aspect involves the need to study processes at scales ranging from the level of organisms, to that of local and coherent ecosystems, to scales of continents and ocean basins, to the globe. This plan deals with the larger

scales. However, success requires interfacing with programs to study fundamental processes on the scales of organisms and local ecosystems. This topic, implicit rather than explicit in our recommendations, will receive attention as process studies and observations progress from planning to action. A second aspect of the scaling problem relates to models. Models must be able to describe CO_2 fluxes and distributions at the large scale in a way that reflects the fundamental processes observed in organism/ecosystem studies of the biosphere, as well as the basic transport processes of the atmosphere and oceans. A related issue, both implicit and explicit in this document, involves international cooperation. Implementation of the various national plans needs to be coordinated so that the international effort is synergistic.

Sixth, the recommended studies in each realm are redundant wherever possible. We regard this characteristic as essential, since each approach gives fluxes with large uncertainties. The most important point of overlap concerns rates of CO_2 uptake at the sea surface. Atmospheric measurements, sea surface pCO_2 measurements, and ocean interior measurements all constrain rates of CO_2 uptake by the oceans at basin or smaller scales. Comparing these redundant measurements will be an important focus of the program. Good agreement will verify the independent estimates. It would also validate continental CO_2 uptake estimates based on atmospheric data alone.

Finally, the studies we recommend have the dual objectives of characterizing distributions and fluxes in each realm as well as gaining process level insight. The two together allow us to track evolving inventories of anthropogenic CO_2 while also deepening our understanding of basic biogeochemical processes, as needed for prediction.

References

Armstrong, R.A., C. Lee, J.I. Hedges, S. Honjo, and S.G. Wakeham (2002): Remineralization of organic carbon in the deep ocean: a mechanistic model of transport and protection by inorganic materials. *Deep-Sea Res. II, 49*(1–3), 219–236.

Bainbridge, A.E. (1981): *GEOSECS Atlantic Expedition Vol. 1, Hydrographic Data 1972–1973*. U.S. Government Printing Office, Washington D.C., 121 pp.

Barber, R.T., M.P. Sanderson, S.T. Lisdley, F. Chai, J. Newton, C.C. Trees, D.G. Foley, and F.P. Chavez (1996): Primary productivity and its regulation in the equatorial Pacific during and following the 1991–1992 El Niño. *Deep-Sea Res. II, 43*, 933–969.

Bates, N.R. (2001): Interannual variability of oceanic CO_2 and biogeochemical properties in the western North Atlantic Subtropical Gyre. *Deep-Sea Res. II, 48*, 1507–1528.

Bates, N.R., A.H. Knap, and A.F. Michaels (1996): Seasonal and interannual variability of the ocean carbon dioxide sytem system at the U.S. JGOFS Bermuda Atlantic Times-series Site. *Deep-Sea Res. II, 43*, 247–383.

Bates N.R., A.H. Knap, and A.F. Michaels (1998a): The effect of hurricanes on the local and global estimates of air-sea exchange of CO_2. *Nature, 395*, 58–61.

Bates, N.R., T. Takahashi, D.W. Chipman, and A.H. Knapp (1998b): Variability of pCO_2 on diel to seasonal time scales in the Sargasso Sea. *J. Geophys. Res., 103*, 15,567–15,585.

Bender, M.L. (1990): D18O of dissolved O_2 in seawater: a unique tracer of circulation and respiration in the deep sea. *J. Geophys. Res., 95*, 22,243–22,252.

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. Am. Meteorol. Soc.*, submitted.

Bock, E.J., T. Hara, N.M. Frew, and W.R. McGillis (1999): Relationship between air-sea gas transfer and short wind waves. *J. Geophys. Res., 104*, 25,821–25,831.

Bopp, L., P. Monfray, O. Aumont, J.-L. Dufresne, H. Le Treut, L. Terray, and J.C. Orr (2001): Potential impact of climate change on marine export production. *Global Biogeochem. Cycles, 15(1)*, 81–99.

Bosquet, P., P. Peylin, P. Ciais, C. LeQuere, P. Friedlingstein, and P.P. Tans (2000): Regional changes in carbon dioxide fluxes of land and oceans since 1980. *Science, 290*, 1242–1346.

Brewer, P.G. (1978): Direct observation of the oceanic CO_2 increase. *Geophys. Res. Lett., 5*, 997–1000.

Brewer, P.G., C. Goyet, and D. Dyressen (1979): Carbon dioxide transport by ocean currents at 25°N latitude in the Atlantic Ocean. *Science, 246*, 477–479.

Broecker, W.S., J.R. Ledwell, T. Takahashi, R. Weiss, L. Merlivat, L. Memery, T.-H. Peng, B. Jahne, and K.O. Munnich (1986): Isotopic versus micrometeorologic ocean CO_2 fluxes: A serious conflict. *J. Geophys. Res., 91*, 10,517–10,527.

Broecker, W.S., D. Spencer, and H. Craig (1982): *GEOSECS Pacific Expedition Vol. 3, Hydrographic Data 1973–1974*. U.S. Government Printing Office, Washington D.C., 137 pp.

Byrne, R.H., E. Kaltenbacher, E.T. Steimle, and X. Liu, Design of autonomous in-situ spectrophotometric systems for measurement of nutrients and CO_2-system parameters. *Proceedings of the International Workshop on Autonomous Measurements of Biogeochemical Parameters in the Ocean,* February 20–22, Honolulu, HI, in press.

Carlson, C.A., and H.W. Ducklow (1995): Dissolved organic carbon in the upper

ocean of the central equatorial Pacific Ocean, 1992: Daily and finescale vertical variations. *Deep-Sea Res. II, 42*, 639–656.

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 Niño. *Science, 286*, 2126–2131.

Chen, C.-T., and F.J. Millero (1979): Gradual increase of oceanic CO_2. *Nature, 277*, 205–206.

Ciais, P., P.P. Tans, M. Trolier, J.W.C. White, and R.J. Francey (1995): A large Northern Hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. *Science, 269*, 1098–1102.

Coatanoan, C., C. Goyet, N. Gruber, C.L. Sabine, and M. Warner (2001): Comparison of two approaches to quantify anthropogenic CO_2 in the ocean: Results from the northern Indian Ocean. *Global Biogeochem. Cycles, 15(1)*, 11–26.

Cox P.M., R.A. Betts, C.D. Jones, S.A. Spall, and I.J. Totterdell (2000): Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature, 408*, 184–187.

Dacey, J.W.H., J.B. Edson, P.H. Holland, and W.R. McGillis (1999): In situ estimation of air-sea gas transfer using DMS. *13th Symposium on Boundary Layer and Turbulence*, January 10–15, 1999, Dallas, TX, AMS, Boston, MA, 425–426.

Dargaville, R.J., R.M. Law, and F. Pribac (2000): Implications of interannual variability in atmospheric circulation on modeled CO_2 concentrations and source estimates. *Global Biogeochem. Cycles, 14*, 931–943.

Davis, R.E., W.S. Kessler, R. Lukas, R.A. Weller, D.W. Behringer, D.R. Cayan, D.B. Chelton, C. Eriksen, S. Esbensen, R.A. Fine, I. Fukumori, M.C. Gregg, E. Harrison, G.C. Johnson, T. Lee, N.J. Mantua, J.P. McCreary, M.J. McPhaden, J.C. McWilliams, A.J. Miller, H. Mitsudera, P.P. Niiler, B. Qiu, D. Raymond, D. Roemmich, D.L. Rudnick, N. Schneider, P.S. Schopf, D. Stammer, L. Thompson, and W.B. White (2000): Implementing the Pacific Basin Extended Climate Study (PBECS). U.S. CLIVAR Report, 109 pp. Available from the U.S. CLIVAR Project Office.

DeGrandpre, M.D., T.R. Hammer, S.P. Smith, and F.I. Sayles (1995): In situ measurements of seawater pCO_2. *Limnol. Oceanogr., 40*, 969–975.

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

Dickey, T. (1991): The emergence of concurrent high-resolution physical and bio-optical measurements in the upper ocean and their applications. *Rev. Geophys., 29*, 383–413.

Dickey, T. (2001): The role of new technology in advancing ocean biogeochemical research. *Oceanography, 14*(4), 108–120.

Dickey, T., and P. Falkowski, Solar energy and its biological-physical interactions in the sea. Chapter 9 in *The Sea*, Vol. 12, A. Robinson *et al.* (eds.), in press.

Doney, S.C. (1999): Major challenges confronting marine biogeochemical modeling. *Global Biogeochem. Cycles, 13*, 705–714.

Doney, S.C., S. Yeager, G. Danabasoglu, W.G. Large, and J.C. McWilliams, Modeling oceanic interannual variability (1958–1997): Simulation design and model—data evaluation, submitted.

Dutay, J.-C., *et al.*, Evaluation of ocean model ventilation with CFC-11: Comparison of 13 global ocean models. *Ocean Modelling*, in press.

Emerson, S., P.D. Quay, C. Stump, D. Wilbur, and R. Schudlich (1995): Chemical tracers of productivity and respiration in the subtropical Pacific Ocean. *J. Geophys. Res., 100*, 15,873–15,887.

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*(3), 535–554.

Esbensen, S.K., and Y. Kushnir (1981): The heat budget of the global ocean: An atlas based on estimates from surface marine observations. Oregon State University, Corvalis, OR.

Fairall, C.W., J.E. Hare, J.B. Edson, and W.R. McGillis (2000): Parameterization and micrometeorological measurements of air-sea gas transfer. *Bound.-Layer Meteorol., 96*, 63–105.

Fan, S., M. Gloor, S. Pacala, J. Sarmiento, and P. Tans (1998): A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models. *Science, 282*, 442–446.

Fasham, M.J.R., and G.T. Evans (1995): The use of optimisation techniques to model marine ecosystem dynamics at the JGOFS station at 47°N and 20°W. *Philos. Trans. R. Soc. Lond., B348*, 206–209.

Feely, R.A., C.L. Sabine, R.M. Key, T.-H. Peng, and R. Wanninkhof (1999): The U.S. global CO_2 survey in the North and South Pacific Oceans: Preliminary synthesis results. In *2nd International Symposium, CO_2 in the Oceans*, extended abstracts, pp. 20–26, Center Global Env. Res., Tsukuba, Japan.

Feely, R.A., J. Boutin, C.E. Cosca, Y. Dandonneau, J. Etcheto, H.Y. Inoue, M. Ishii, C. Le Quere, D. Mackey, M. McPhaden, N. Metzl, A. Poisson, and R. Wanninkhof. Seasonal and interannual variability of CO_2 in the equatorial Pacific. *Deep-Sea Res. II*, in press.

Feely, R.A., C.L. Sabine, T. Takahashi, and R. Wanninkhof (2001): Uptake and storage of carbon dioxide in the oceans: The global CO_2 survey. *Oceanography, 14*(4), 18–32.

Fennel, K., M. Losch, J. Schroter, and M. Wenzel (2001): Testing a marine ecosystem model: Sensitivity analysis and parameter optimization. *J. Mar. Syst., 28*, 45–63.

Francey, R.J., P.P. Tans, C.E. Allison, I.G. Enting, J.W.C. White, and M. Trolier (1995): Changes in the oceanic and terrestrial carbon uptake since 1982. *Nature, 373*, 326–330.

Frew, N.M., D.M. Glover, E.J. Bock, C. Goyet, S.J. McCue, and R.J. Healy (1999): Estimation of global air-sea transfer of CO_2 using TOPEX/Poseidon dual-frequency backscatter. *IUGG Abstracts*, Birmingham, UK.

Friederich, G.E., P.G. Brewer, R. Herline, and F.P. Chavez (1995): Measurements of sea surface partial pressure of CO_2 from a moored buoy. *Deep-Sea Res. I, 42*, 1175–1186.

Fung, I.Y., S.K. Meyn, I. Tegen, S.C. Doney, J. John, and J. Bishop (2000): Iron supply and demand in the upper ocean. *Global Biogeochem. Cycles, 14*(1), 281–295.

Garcon, V.C., A. Oschlies, S.C. Doney, D. McGillicuddy, and J. Waniek (2001): The role of mesoscale variability on plankton dynamics in the North Atlantic. *Deep-Sea Res. I, 48*, 2199–2226.

Giering, R., and T. Kaminski (2001): Recipes for adjoint code construction. *Trans. Math. Software, 24*, 437–474.

Gloor, M., S.M. Fan, S. Pacala, and J. Sarmiento (2000): Optimal sampling of the atmosphere for purpose of inverse modeling: A model study. *Global Biogeochem. Cycles, 14*, 407–428.

Gloor, M., N. Gruber, J.L. Sarmiento, R.A. Feely, C.L. Sabine, and C. Roedenbeck, Reconstructing preindustrial and contemporary air-sea CO_2 fluxes by an inversion of ocean interior carbon data. *Science*, submitted.

Gould, W.J., and J.M. Toole (1999): Investigating ocean climate variability: the need for systematic hydrographic observations within CLIVAR/GOOS. In *Oceanobs 99:* the International Conference on the Ocean Observing System for Climate, Saint-Raphael, France, Session 3B.

Goyet, C., C. Coatanoan, G. Eischield, T. Amaoka, K. Okunda, R. Healy, and S.

Tsunogai (1999): Spatial variation of total CO_2 and total alkalinity in the northern Indian Ocean: A novel approach for the quantification of anthropogenic CO_2 in seawater. *J. Mar. Res., 57*.

Goyet, C., D. Davis, E.T. Pelzter, and P.G. Brewer (1995): Development of improved space sampling strategies for ocean chemical properties: total carbon dioxide and dissolved nitrate. *Geophys. Res. Lett., 22*, 945–948.

Goyet C., D.M. Walt, and P.G. Brewer (1992): Development of a fiber optic sensor for measurement of pCO_2 in sea water: design criteria and sea trials. *Deep-Sea Res. I, 39*, 1015–1026.

Gruber, N. (1998): Anthropogenic CO_2 in the Atlantic Ocean. *Global Biogeochem. Cycles, 12*, 165–191.

Gruber, N., and C.D. Keeling (2001): An improved estimate of the isotopic air-sea disequilibrium of CO_2: Implications for the oceanic uptake of anthropogenic CO_2. *Geophys. Res. Lett., 28*(3), 555–558.

Gruber, N., C.D. Keeling, and T.F. Stocker (1998): Carbon-13 constraints on the seasonal inorganic carbon budget at the BATS site in the northwestern Sargasso Sea. *Deep-Sea Res. I, 45*, 673–717.

Gruber, N., J.L. Sarmiento, and T.F. Stocker (1996): An improved method for detecting anthropogenic CO_2 in the oceans. *Global Biogeochem. Cycles, 10*(4), 809–837.

Gruber, N., J. Bullister, J.-C. Dutay, J.C. Orr, C. Sabine, and R. Slater, What the CFC's can tell us about the ocean uptake of anthropogenic CO_2. *J. Geophys. Res.*, in preparation.

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

Gu, D., and S.G.H. Philander (1996): Interdecadal climate fluctuations that depend on exchanges between the tropics and extratropics. *Science, 275*, 805–807.

Hansell, D.A., and C.A. Carlson (1998): Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature, 395*, 263–266.

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.

Holfort, J., K.M. Johnson, B. Schneide, 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.

Houghton, J.T., G.J. Jenkins, and J.J. Ephraums, eds. (1998): *Climate Change: The IPCC Scientific Assessment*. Cambridge University Press, Cambridge, UK, 365 pp.

Hurtt, G.C., and R.A. Armstrong (1996): A pelagic ecosystem model calibrated with BATS data. *Deep-Sea Res. II, 43*, 653–683.

Ishizaka, J. (1990): Coupling of Coastal Zone Color Scanner data to a physical-biological model of the Southeastern U.S. continental shelf ecosystem, 3, nutrient and phytoplankton fluxes and CZCS data assimilation. *J. Geophys. Res., 95*, 20,201–20,212.

Joyce, T.M., and P. Robbins (1996): The long-term hydrographic record at Bermuda. *J. Climatol., 9*, 3121–3131.

Kaminski, T., M. Heimann, and R. Giering (1999): A coarse grid three-dimensional global inverse model of the atmospheric transport, 2: Inversion of the transport of CO_2 in the 1980's. *J. Geophys. Res., 104,* 18,555–18,581.

Karl, D.M. (1999): A sea of change: Biogeochemical variability in the North Pacific Subtropical Gyre. *Ecosystems, 2*, 181–214.

Karl, D.M., R. Bidigare, and R.M. Letelier (2001): Long-term changes in plankton

community structure and productivity in the North Pacific Subtropical Gyre: The domain shift hypothesis. *Deep-Sea Res. II, 48*, 1449–1470.

Karl, D.M., and R. Lukas (1996): The Hawaii Ocean Time series (HOT) program: Background, rationale, and field implementation. *Deep-Sea Res. II, 43*, 129–156.

Keeling, C.D. (1968): Carbon dioxide in surface waters, 4: Global distribution. *J. Geophys. Res., 73*, 4529–4542.

Keeling, C.D., T.P. Whorf, M. Wahlen, and J. Vanderplicht (1995): Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. *Nature, 375*, 666–670.

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

Keeling, R.F., B.B. Stephens, R.G. Najjar, S.C. Doney, D. Archer, M. Heimann (1998): Seasonal variations in the atmospheric O_2/N_2 ratio in relation to the kinetics of air-sea gas exchange. *Global Biogeochem. Cycles, 12*, 141–163.

Keller, K., R.D. Slater, M. Bender, and R.M. Key, Decadal scale trends in North Pacific nutrient and oxygen concentrations: Biological or physical explanation. *Global Biogeochem. Cycles*, in press.

Kirchman, D.L., C. Lancelot, M.J.R. Fasham, L. Legendre, G. Radach, and M. Scott (1993): Dissolved organic matter in biogeochemical models of the ocean. In *Towards a Model of Ocean Biogeochemical Processes*, G.T. Evans and M.J.R. Fasham (eds.), Springer-Verlag, New York, 209–226.

Lapitan, R.L., R. Wanninkhof, and A.R. Mosier (1999): Methods for stable gas flux determination in aquatic and terrestrial systems. In *Scaling of Trace Gas Fluxes between Terrestrial and Aquatic Ecosystems and the Atmosphere*, A.F. Bouwman (ed.), Elsevier, Amsterdam, 27–66.

Levitus, S., J.I. Antonov, T.P. Boyer, and C. Stephens (2000): Warming of the world ocean. *Science, 287*, 2225–2229.

Liss, P.S., and L. Merlivat (1986): Air-sea gas exchange rates: Introduction and synthesis. In *The Role of Air-Sea Exchange in Geochemical Cycling*, P. Buat-Menard (ed.), Reidel, Boston, 113–129.

Louanchi, F., and R.G. Najjar (2000): A global monthly climatology of phosphate, nitrate, and silicate in the upper ocean: spring-summer export production and shallow remineralization. *Global Biogeochem. Cycles, 14*, 957–977.

Louanchi, F., D.P. Ruiz-Pino, C. Jeandel, C. Brunet, B. Schauer, A. Masson, M. Fiala, and A. Poisson (2001): Dissolved inorganic carbon, alkalinity, nutrient and oxygen seasonal and interannual variations at the Antarctic Ocean JGOFS-KERFIX site. *Deep-Sea Res. I, 48*, 1581–1603.

Luz, B., and E. Barkan (2000): Assessment of oceanic productivity with the triple-isotope composition of dissolved oxygen. *Science, 288*, 2028–2031.

Mahadevan, A., and D. Archer (2000): Modeling the impact of fronts and mesoscale circulation on the nutrient supply and biogeochemistry of the upper ocean. *J. Geophys. Res., 105*, 1209–1225.

Maier-Reimer, E. (1993): Geochemical cycles in an ocean general circulation model—preindustrial tracer distributions. *Global Biogeochem. Cycles, 7*, 645–677.

Martel F., and C. Wunsch (1993): The North Atlantic circulation in the early 1980's—an estimate from inversion of a finite difference model. *J. Phys. Oceanogr., 23*, 898–924.

Matear, R.J. (1995): Parameter optimization and analysis of ecosystem models using simulated annealing: A case study at Station P. *J. Mar. Res., 53*, 571–607.

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

Matear, R.J., A.C. Hirst, and B.I. McNeil (2000): Changes in dissolved oxygen in the Southern Ocean with climate change. *Geochem. Geophys. Geosyst., 1.*

McGillicuddy, D.J., Jr., and A.R. Robinson (1997): Eddy-induced nutrient supply and new production. *Deep-Sea Res. I, 44*, 1427–1450.

McGillis, W.R., J.B. Edson, J.E. Hare, and C.W. Fairall (2001a): Direct covariance air-sea CO_2 fluxes. *J. Geophys. Res., 106*, 16,729–16,746.

McGillis, W.R., J.B. Edson, J.D. Ware, J.W.H. Dacey, J.E. Hare, C.W. Fairall, and R. Wanninkhof (2001b): Carbon dioxide flux techniques performed during GasEx 98. *Mar. Chem., 75*, 267–280.

McNeil, C.L., and L. Merlivat (1996): The warm oceanic surface layer: Implications for CO_2 fluxes and surface gas measurements. *Geophys. Res. Lett., 23*, 3575–3578.

McPhaden, M.J. (1999): Genesis and evolution of the 1997–98 El Niño. *Science, 283*, 950–954.

Moore, J.K., S.C. Doney, J.A. Kleypas, D.M. Glover, and I.Y. Fung (2002): Iron cycling and nutrient limitation patterns in surface waters of the world ocean. *Deep-Sea Res. II, 49*(1–3), 463–508.

Myneni, R.B., C.D. Keeling, C.J. Tucker, G. Asrar, and R.R. Nemani (1997): Increased plant growth in the northern high latitudes. *Nature, 386*, 698–702.

Nightingale, P.D., G. Malin, C.S. Law, A.J. Watson, P.S. Liss, M.I. Liddicoat, J. Boutin, and R.C. Upstill-Goddard (2000): In-situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Global Biogeochem. Cycles, 14*, 373–387.

Orr, J.C., E. Maier-Reimer, U. Mikolajewicz, P. Monfray, J.L. Sarmiento, J.R. Toggweiler, N.K. Taylor, J. Palmer, N. Gruber, C.L. Sabine, C. Le Quere, R.M. Key, and J. Boutin (2001): Global oceanic uptake of anthropogenic carbon dioxide as predicted by four 3-D ocean models. *Global Biogeochem. Cycles, 15,* 43–60.

Oschlies, A., and V. Garcon (1998): Eddy-induced enhancement of primary production in a model of the North Atlantic Ocean. *Nature, 394,* 266–269.

Pahlow, M., and U. Riebesell (2000): Temporal trends in deep ocean Redfield ratios. *Science, 287*, 831–833.

Peng, T.-H., R. Wanninkhof, J.L. Bullister, R.A. Feely, and T. Takahashi (1998): Quantification of decadal anthropogenic CO_2 uptake in the ocean based on dissolved inorganic carbon measurements. *Nature, 396*, 560–563.

Quay, P.D., B. Tilbrook, and C.S. Wong (1992): Oceanic uptake of fossil fuel CO_2: ^{13}C evidence. *Science, 256*, 74–79.

Rayner P.J., I.G. Enting, R.J. Francey, and R. Langenfelds (1999): Reconstructing the recent carbon cycle from atmospheric CO_2, delta ^{13}C and O_2/N_2 observations. *Tellus, 51B*, 213–232.

Rayner, P.J., and R.M. Law (1999): The interannual variability of the global carbon cycle. *Tellus, 51B*, 233–248.

Rinoul, S.R., and J.L. Bullister (1999): A late winter hydrographic section from Tasmania to Antarctica. *Deep-Sea Res. I, 46*, 1417–1454.

Robertson, J.E., and A.J. Watson (1992): Thermal skin effect of the surface ocean and its implications for CO_2 uptake. *Nature, 358*, 738–740.

Robinson, A.R. (1996): Physical processes, field estimation and an approach to interdisciplinary ocean modeling. *Earth Sci. Rev., 40*, 3–54.

Roemmich, D., and J. McGowan (1995): Climatic warming and the decline of zooplankton in the California current. *Science, 267*, 1324–1326.

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 of the Indian Ocean. *Global Biogeochem. Cycles, 13*, 179–198.

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.

Sarmiento, J., and S. Wofsy (1999): *A U.S. Carbon Cycle Science Plan*. USGCRP, Washington, D.C., 69 pp.

Sigman D.M., M.A. Altabet, D.C. McCorkle, R. Francois, and G. Fischer (2000): The delta ^{15}N of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior. *J. Geophys. Res., 105*, 19,599–19,614.

Six, K.D., and E. Maier-Reimer (1996): Effects of plankton dynamics on seasonal carbon fluxes in an ocean general circulation model. *Global Biogeochem. Cycles, 10*, 559–583.

Slansky, C.M., R.A. Feely, and R. Wanninkhof (1997): The stepwise linear regression method for calculating anthropogenic CO_2 invasion into the North Pacific Ocean. In *Biogeochemical Processes in the North Pacific*, S. Tsunogai (ed.), Proceedings of the International Marine Science Symposium on Biogeochemical Processes in the North Pacific, 12–14 November 1996, Mutsu, Japan, Japan Marine Science Foundation, 70–79.

Smith, R.D., M.E. Maltrud, F.O. Bryan, and M.W. Hecht (2000): Numerical simulation of the North Atlantic at 1/10 deg. *J. Phys. Oceanogr., 30*, 1532–1561.

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., C. Wunsch, R. Giering, C. Eckert, P. Heimbach, J. Marotzke, A. Adcroft, C.N. Hill, and J. Marshall, The global ocean circulation during 1992–1997 estimated from ocean observations and a general circulation model. *J. Geophys. Res.*, submitted.

Steinberg, D.K., C.A. Carlson, N.R. Bates, R.J. Johnson, A.F. Michaels, and A.H. Knap (2001): Overview of the U.S. JGOFS Bermuda Atlantic Time-series Study BATS: A decade-scale look at ocean biology and biogeochemistry. *Deep-Sea Res. II, 48*, 1405–1447.

Strutton, P.G., and F.P. Chavez (2000): Primary productivity in the equatorial Pacific during the 1997–1998 El Niño. *J. Geophys. Res., 105*, 26,089–26,101.

Sweeney, C., D.A. Hansell, C.A. Carlson, L.A. Codispoti, L.I. Gordon, J. Marra, F.J. Millero, W.O. Smith, and T. Takahashi (2000): Biogeochemical regimes, net community production and carbon export in the Ross Sea, Antarctica. *Deep-Sea Res. I, 47*, 3369–3394.

Taft, B., J. Bullister, R.A. Feely, G. Johnson, and R. Wanninkhof (1995): NOAA ocean carbon and tracer program: an integrated approach to decadal ocean climate change studies, mms., 26 pp. plus 14 figs.

Takahashi, T. (1961): Carbon dioxide in the atmosphere and in Atlantic Ocean water. *J. Geophys. Res., 66*, 477–494.

Takahashi, T., R.A. Feely, R.F. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi (1997): Global air-sea flux of CO_2, An estimate based on measurements of sea-air pCO_2 difference. *Proc. Natl. Acad. Sci., 94*, 8929–8299.

Takahashi, T., J. Olafsson, J.G. Goddard, D.W. Chipman, and S.C. Sutherland (1993): Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochem. Cycles, 7*, 843–878.

Takahashi, T., R.H. Wanninkhof, R.A. Feely, R.F. Weiss, D.W. Chipman, N. Bates, J. Olafsson, C. Sabine, and S.C. Sutherland (1999): Net sea-air CO_2 flux over the global oceans: An improved estimate based on the sea-air pCO_2 difference. In *Proceedings of the 2nd International Symposium, CO_2 in the Oceans* (ISSN 1341–4356), Yukihiro Nojiri (ed.), Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Japan, 9–14.

Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tillbrook, N.

Bates, R. Wannikhof, R.A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri, Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. *Deep-Sea Res. I*, in press.

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.

Tokar, J.M., and T.D. Dickey (2000): Chemical Sensor Technology—Current and Future Applications. In *Chemical Sensors in Oceanography*, M.S. Varney (ed.), Gordon and Breach Scientific Publishers, Amsterdam, 303–329.

Van Scoy, K.A., K.P. Morris, J.E. Robertson, and A.J. Watson (1995): Thermal skin-effect and the air-sea flux of carbon dioxide—a seasonal high-resolution estimate. *Global Biogeochem. Cycles, 9*, 253–262.

Varney, M.S., ed. (2000): *Chemical Sensors in Oceanography*. Gordon and Breach Scientific Publishers, Amsterdam, 333 pp.

Wallace, D.W.R. (1995): Monitoring global ocean inventories. In *OOSDP Background Rep. 5*, Ocean Observ. Syst. Dev. Panel, Texas A&M University, College Station, Texas, 54 pp.

Wallace, D.W.R. (2001): Storage and transport of excess CO_2 in the oceans: the JGOFS/WOCE Global CO_2 Survey. In *Ocean Circulation and Climate: Observing and Modeling the Global Ocean*, G. Siedler, J. Gould, and J. Church (eds.), Academic Press, New York.

Walker, J.P., and P.R. Houser (2001): A methodology for initializing soil moisture in a global climate model: Assimilation of near-surface soil moisture observations. *J. Geophys. Res., 106*, 11,761–11,774.

Wanninkhof, R. (1992): Relationship between gas exchange and wind speed over the ocean. *J. Geophys. Res., 97*, 7373–7381.

Wanninkhof, R., and L. Bliven (1991): Relationship between gas exchange, wind speed and radar backscatter in a large wind-wave tank. *J. Geophys. Res., 96*, 2785–2796.

Wanninkhof, R., S.C. Doney, T.-H. Peng, J. 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.

Wanninkhof, R., S.C. Doney, T. Takahashi, and W.R. McGillis (2001): The effect of using time-averaged winds on regional air-sea CO_2 fluxes. In *Gas Transfer at Water Surfaces*, M. Donelan, W. Drennan, E. Saltzman, and R. Wanninkhof (eds.), AGU, Washington, D.C.

Wanninkhof, R., and W.R. McGillis (1999): A cubic relationship between air-sea CO_2 exchange and windspeed. *Geophys. Res. Lett., 26*, 1889–1892.

Watanabe, Y., T. Ono, and A. Shimamoto, Total carbonate increase in the western north Pacific using chemical tracer's age. *Mar. Chem.*, submitted.

Watson, A.J., R.C. Upstill-Goddard, and P.S. Liss (1991): Air-sea exchange in rough and stormy seas, measured by a dual tracer technique. *Nature, 349*, 145–147.

Weiss, R.F., W.S. Broecker, H. Craig, and D. Spencer (1983): *GEOSECS Indian Ocean Expedition*, vol. 5, Hydrographic Data 1977–1978. U.S. Government Printing Office, Washington D.C., 48 pp.

Winn, C.D., F.T. Mackenzie, C.J. Carrillo, C.L. Sabine, and D.M. Karl (1994): Air-sea exchange in the North Pacific subtropical gyre: Implications for the global carbon budget. *Global Biogeochem. Cycles, 8*(2), 157–163.

Wong, C.S., and Y.-H. Chan (1991): Temporal variations in the partial pressure and flux of CO_2 at ocean station P in the subarctic northeast Pacific Ocean. *Tellus, 43B*, 206–223.

Wunsch, C. (1996): *The Ocean Circulation Inverse Problem*. Cambridge University Press, Cambridge, UK, 442 pp.

Zhang, J.R., and P.D. Quay (1997): The total organic carbon export rate based on

^{13}C and ^{12}C of DIC budgets in the equatorial Pacific region. *Deep-Sea Res. I, 44*, 2163–2190.

Zhang, J.Z., R. Wanninkhof, and K. Lee (2001): Enhanced new production observed from the diurnal cycle of nitrate in an oligotrophic anticyclonic eddy. *Geophys. Res. Lett., 28*, 1579–1582.

Appendix A

Participant List
Global Carbon Cycle Observation Workshop

Boulder, Colorado
8–10 November 2000

*Michael Bender
Department of Geosciences
Princeton University
Princeton, NJ 08544
Tel: 609-258-2936
Fax: 609-258-0796
Email: Bender@princeton.edu

Mary-Elena Carr
Jet Propulsion Laboratory
MS 300-323
4800 Oak Grove Dr.
Pasadena, CA 91109-8099
Tel: 818-354-5097
Fax: 818-393-6720
Email: mec@pacific.jpl.nasa.gov

Piers Chapman
U.S. WOCE Office
3146 TAMU
Dept. of Oceanography
College Station, TX 77843
Tel: 979-845-8194
Fax: 979-845-0888
Pchapman@tamu.edu

Francisco Chavez
Monterey Bay Aquarium Research Institute
P.O. Box 628
7700 Sandholdt Rd.
Moss Landing, CA 95350
Tel: 831-775-1709
Fax: 831-775-1620
Email: chfr@mbari.org

Michael DeGrandpre
Department of Chemistry
Chem-Pharm Building
The University of Montana
Missoula, MT 59812
Tel: 406-243-4118
Fax: 406-243-4227
Email: mdegrand@selway.umt.edu

Scott Denning
Dept. of Atmospheric Science
Colorado State University
Fort Collins, CO 80523-1371
Tel: 970-491-6936
Fax: 970-491-8449
Email: denning@atmos.colostate.edu

Tommy Dickey
Ocean Physics Laboratory
University of California Santa Barbara
6487 Calle Real, Suite A
Santa Barbara, CA 93117
Tel: 805-893-7354
Fax: 805-967-5704
Email: tommy.dickey@opl.ucsb.edu

Lisa Dilling
NOAA, Office of Global Programs
1100 Wayne Ave., Suite 1210
Silver Spring, MD 20910
Tel: 301-427-2089 x106
Fax: 301-427-2073
Email: dilling@ogp.noaa.gov

* denotes that participant is a member of the core committee.

*Scott Doney
Climate and Global Dynamics
National Center for Atmospheric Research
P.O. Box 3000
Boulder, CO 80307-3000
Tel: 303-497-1639
Fax: 303-497-1700
Email: doney@ncar.ucar.edu

Christopher W. Fairall
R/ETL7
NOAA, Environmental Technology Laboratory
325 Broadway
Boulder, CO 80305
Tel: 303-497-3253
Fax: 303-497-6101
Email: Chris.Fairall@noaa.gov

*Richard Feely
NOAA, Pacific Marine Environmental Laboratory
7600 Sand Point Way NE
Seattle, WA 98115
Tel: 206-526-6214
Fax: 206-526-6744
Email: feely@pmel.noaa.gov

Rana Fine
University of Miami
RSMAS/MAC - S/A 261
4600 Rickenbacker Causeway
Miami, FL 33149-1098
Tel: 305-361-4764
Fax: 305-361-4917
Email: fine@rsmas.miami.edu

*Inez Fung
Center for Atmospheric Sciences
307 McCone Hall #4767
University of California, Berkeley
Berkeley, CA 94720-4767
Tel: 510-643-9367
Fax: 510-643-9377
Email: inez@atmos.berkeley.edu

Manuel Gloor
Max-Planck Institüt für Biogechemie
Postfach 100164
D-07701, Jena Germany
Tel: 0049-3641-686-725
Fax: 0049-3641-686-710
Email: mgloor@bgc-jena.mpg.de

Anand Gnanadesikan
302 Sayre Hall, Forrestal Campus
Princeton University
Princeton, NJ 08544-0710
Tel: 609-258-6619
Fax: 609-258-2850
Email: gnana@princeton.edu

*Nicolas Gruber
Institute of Geophysics & Planetary Physics
& Department of Atmospheric Sciences
5853 Slichter Hall
University of California, Los Angeles
Los Angeles, CA 90095-4996
Tel: 310-825-4772
Fax: 310-206-3051
Email: gruber@splash.Princeton.edu

*Ed Harrison
NOAA, Pacific Marine Environmental Laboratory
7600 Sand Point Way NE
Seattle, WA 98115
Tel: 206-526-6225
Fax: 206-526-6744
Email: harrison@pmel.noaa.gov

Gregory Johnson
NOAA/Pacific Marine Environmental Laboratory
7600 Sand Point Way, NE Bldg. 3
Seattle, WA 98115-6349
Tel: 206-526-6806
Fax: 206-526-6744
Email: gjohnson@pmel.noaa.gov

Kenneth Johnson
Monterey Bay Aquarium Research Institute
7700 Sandholdt Road
Moss Landing, CA 95039
Tel: 831-775-1985
Fax: 831-775-1620
Email: johnson@mbari.org

Mike Johnson
NOAA, Office of Global Programs
1100 Wayne Avenue, Suite 1210
Silver Spring, MD 20910
Tel: 301-427-2089 x169
Fax: 301-427-2073
Email: johnson@ogp.noaa.gov

*Ralph Keeling
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, CA 92093-0236
Tel: 858-534-7582
Fax: 858-534-2997
Email: rkeeling@ucsd.edu

Arne Kortzinger
Alfred-Wegner-Institute for Polar and Marine Research
Duesternbrooker Weg 20
D-24105, Germany
Tel: 49-471-4831-1851
Fax: 49-471-4831-1425
Email: akoertzinger@awi-bremerhaven.de

Ricardo Letelier
College of Oceanic & Atmospherics Sciences
Oregon State University
104 Ocean. Admin. Bldg.
Corvallis, OR 97331-5503
Tel: 541-737-3890
Fax: 541-737-2064
Email: letelier@OCE.ORST.edu

Chuck McClain
NASA/GSFC
Office of Global Carbon Studies
Code 970.1
Bldg. 28 Rm 107W
Greenbelt, MD 20771
Tel: 301-286-5377
Fax: 301-286-0268
Email: chuck@seawifs.gsfc.nasa.gov

Wade McGillis
Woods Hole Oceanographic Institute
Mail Stop 9
Woods Hole, MA 02543
Tel: 508-289-3325
Fax: 508-457-2132
Email: wmcgilliswhoi.edu

Ken Mooney
NOAA, Office of Global Programs
1100 Wayne Ave., Suite 1210
Silver Spring, MD 20910
Tel: 301-427-2089 x104
Fax: 301-427-2073
Email: mooney@ogp.noaa.gov

*Keith Moore
National Center for Atmospheric Research
Advanced Studies Program
P.O. Box 3000
Boulder, CO 80307-3000
Tel: 303 497-1692
Fax: 303 497-1646
Email: jkmoore@cgd.ucar.edu

Paulette Murphy
Ocean Climate Laboratory
NODC/NOAA, Rm. 4240
Silver Spring, MD 20910-3282
Tel: 301-713-3290 x208
Fax: 301-713-3303
Email: pmurphy@nodc.noaa.gov

Yukihiro Nojiri
Global Warming Mechanism Laboratory
National Institute for Environmental Studies
Tsukuba, Ibaraki 305-0053, Japan
Tel: 81-298-50-2499
Fax: 81-298-50-2569
Email: nojiri@nies.go.jp

Paul Quay
School of Oceanography
University of Washington
Room G, Marine Science Bldg.
P.O. Box 357940
Seattle, WA 98195
Tel: 206-685-8061
Fax: 206-685-3351
Email: pdquay@u.washington.edu

Don Rice
Chemical Oceanography Program
Division of Ocean Sciences
National Science Foundation
Arlington, VA 22230
Tel: (703) 292-8582
Fax: (703) 292-9085
Email: drice@nsf.gov

Paul Robbins
Scripps Institution of Oceanography
Mail Stop 0230
SIO/UCSD
9500 Gilman Dr.
La Jolla, CA 92093-0230
Tel: 858-534-6366
Fax: 858-534-9820
Email: probbins@ucsd.edu

Chris Sabine
NOAA, Pacific Marine Environmental Laboratory
7600 Sand Point Way, NE
Seattle, WA 98115
Tel: (206) 526-4809
Fax: (206) 526-6744
Email: sabine@pmel.noaa.gov

*Ed Sarachik
Atmospheric Sciences
University of Washington
Box 351640
Seattle, WA 98195-1640
Tel: 206-543-6720
Fax: 206-685-3397
Email: sarachik@atmos.washington.edu

*Jorge Sarmiento
AOS Program
Princeton University
Sayre Hall, Forrestal Campus
P.O. Box CN710
Princeton, NJ 08544-0710
Tel: 609-258-6585
Fax: 609-258-2850
Email: jls@splash.princeton.edu

*Britt Stephens
NOAA, Climate Monitoring and Diagnostics Laboratory
Mail Code R/CMDL1
325 Broadway
Boulder, CO 80305
Tel: 303-497-6999
Fax: 303-497-5590
Email: Britton.B.Stephens@noaa.gov

Colm Sweeney
Lamont-Doherty Earth Observatory
Columbia University
Box 1000, Route 9W
Palisades, NY 10964
Tel: 845-365-8768
Fax: 845-365-8165
Email: csweeney@ldeo.columbia.edu

*Taro Takahashi
Lamont-Doherty Earth Observatory
Columbia University
61 Route 9W
P.O. Box 1000
Palisades, NY 10964-8000
Tel: 845-365-8537
Fax: 845-365-8155
Email: taka@ldeo.columbia.edu

*Pieter Tans
NOAA/OAR/CMDL
325 Boulder R/CMDL1
Boulder, CO 80305
Tel: (303) 497-6678
Fax: (303) 497-6975
Email: ptans@cmdl.noaa.gov

Bronte Tilbrook
CSIRO Marine Research
Castray Esplanade
Hobart, Tasmania 7001
Australia
Tel: 61-3-6232-5273
Fax: 61-3-6232-5000
Email: Bronte.Tilbrook@marine.csiro.au

*Rik Wanninkhof
NOAA/AOML/OCD
4301 Rickenbacker Causeway
Miami, FL 33149
Tel: 305-361-4379
Fax: 305-361-4392
Email: Wanninkhof@aoml.noaa.gov

Kathy Watson
NOAA, Office of Global Programs
1100 Wayne Ave., Suite 1210
Silver Spring, MD 20910
Tel: 301-427-2089 x110
Fax: 301-427-2222
Email: watson@ogp.noaa.gov

Bob Weller
Woods Hole Oceanographic Institution
Mail Stop 29
Woods Hole, MA 02543
Tel: 508-289-2508
Fax: 508-457-2163
Email: rweller@whoi.edu

Appendix B

Commissioning Letter

November 30, 1999

Professor Michael Bender
Department of Geosciences
Guyot Hall
Princeton University
Princeton, NJ 08544
USA

Dear Michael,

The U.S. Carbon Cycle research community has recently completed a Carbon Cycle Science Plan (CCSP). This plan calls for an integrated approach to carbon cycle research focused around 2 questions: (1) What has happened to the CO_2 that has already been emitted by human activities (past anthropogenic CO_2); and (2) What will be the future atmospheric CO_2 concentrations resulting from both past and future emissions? Large scale atmospheric and oceanic in situ observations and modeling are called for to support several of the scientific goals of the CCSP, including quantifying and understanding the Northern Hemisphere terrestrial and global oceanic sinks and their associated physical and biogeochemical processes, and providing improved projections of atmospheric CO_2 concentrations.

As a contribution to the interagency process to develop an integrated carbon cycle program, NOAA is seeking assistance from the scientific community to define an implementation strategy to provide global information on the evolving distribution of CO_2. I am pleased that you are willing to lead this planning effort to develop an initial implementation plan for large scale oceanic and atmospheric observations in support of the CCSP. In your role as Chair, I would ask that you:

- Establish a working group composed of scientific experts from the relevant disciplines
- Define the scope of scientific issues to be addressed by the observing system
- By fall 2000, outline an implementation vision and strategy for the next 10 years. This strategy might consider:
  - Building on existing networks and technology where appropriate;
  - Specifying needs for new technology development;
  - Priorities for sequencing of implementation activities;
  - Links to complementary international activities;
  - Opportunities for collaboration with complementary programs such as CLIVAR and GOOS; and
  - Interactions with modeling and process research.

While NOAA is taking the lead on soliciting this strategy from the community, your working group should consider how this strategy will implement the CCSP objectives in a multi-agency framework. You are encouraged to interact with other planning efforts underway to implement the CCSP, such as OCTET, SOLAS, EDOCC, and others that might be appropriate.

NOAA will provide support for meetings of the working group, a workshop of experts, if necessary, and publication of the final implementation plan. Please submit a planning letter outlining your expected resource requirements for the working group activities.

Thank you for agreeing to lead this important activity, and I look forward to seeing the results.

Sincerely yours,

Lisa Dilling
NOAA GCC Program Manager

cc. Elliott Spiker

Appendix C

Acronyms

$\delta^{13}C$	Ratio of stable carbon isotopes, $^{13}C/^{12}C$
ADCP	Acoustic Doppler Current Profiler
AIRS	Atmospheric Infrared Sounder
ARGO	Global array of temperature/salinity profiling floats
ATM	Atmospheric Transport Model
BATS	Bermuda Atlantic Time Series
BBRS	Bermuda Biological Research Station
BOGCM	Biogeochemical Ocean General Circulation Model
BOREAS	Boreal Ecosystem-Atmosphere Study
BSOP	Bottom Stationed Ocean Profiler
CalCOFI	California Cooperative Oceanic Fisheries Investigation
CCSP	U.S. Carbon Cycle Science Plan
CDIAC	Carbon Dioxide Information Analysis Center (DOE)
CLIVAR	Climate Variability and Predictability (WCRP program)
CMDL	Climate Monitoring and Diagnostics Laboratory (NOAA)
CO_2	Carbon dioxide
COBRA	CO_2 Budget and Rectification Airborne Study
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CU-INSTAAR	Colorado University/Institute of Arctic and Alpine Research
CTD	Conductivity/temperature/depth profiler
DAO	Data Assimilation Office (NASA)
DIC	Dissolved inorganic carbon
DMS	Dimethylsulfide
DOC	Dissolved organic carbon
DOE	Department of Energy
DON	Dissolved organic nitrogen
ECCO	Estimating the Circulation and Climate of the Ocean
ECMWF	European Center for Medium-Range Weather Forecasting
ENSO	El Niño/Southern Oscillation
EOS	Earth Observing System (NASA)
EU	European Union
FLIP	Floating instrument platform (SIO)
GAIM	Global Analysis, Integration, and Modeling (IGBP)
GCM	General circulation model
GCOS	Global Climate Observing System (WMO)
GCTM	Global chemistry transport model
GEOSECS	Geochemical Ocean Sections Program
GMCC	Geophysical Monitoring for Climatic Change (NOAA)
GODAE	Global Ocean Data Assimilation Experiment
GOOS	Global Ocean Observing System (WMO)
HNLC	High-nitrate, low-chlorophyll
HOT	Hawaii Ocean Time-series Program
IGBP	International Geosphere-Biosphere Programme
IR	Infrared
JGOFS	Joint Global Ocean Flux Program (IGBP program)
LBA	Large Scale Biosphere-Atmosphere Experiment in Amazonia (NASA)
LTER	U.S. Long Term Ecological Research network (NSF)

MBARI	Monterey Bay Aquarium Research Institute
MLO	Mauna Loa Observatory
N_2	Gaseous nitrogen
NAO	North Atlantic Oscillation
NASA	National Aeronautics and Space Administration
NCAR	National Center for Atmospheric Research
NCEP	National Centers for Environmental Prediction (NWS)
NDVI	Normalized Difference Vegetation Index
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
NWP	Numerical Weather Prediction
NWS	National Weather Service
O_2	Gaseous oxygen
OAR	Oceanic and Atmospheric Research (NOAA)
OCMIP	Ocean Carbon Model Intercomparison Project (IGBP)
OCTET	Ocean Carbon Transformation Exchange and Export
OGP	Office of Global Programs (NOAA)
Omelet	Amalgam of various ocean community plans for carbon cycle research (NSF)
PALACE	Profiling Autonomous Lagrangian Current Explorer
PBECS	Pacific Basin Extended Climate Study
PBL	Planetary Boundary Layer
pCO_2	Partial pressure of carbon dioxide
PDO	Pacific Decadal Oscillation
PIC	Particulate inorganic carbon
PMEL	Pacific Marine Environmental Laboratory (NOAA)
POC	Particulate organic carbon
PON	Particulate organic nitrogen
QuickSCAT	Quick scatterometer (NASA)
RIOMAR	Transport, transformation, and fate of carbon in river-dominated ocean margins
SAFARI2000	Southern African Regional Science Initiative (NASA)
SBIR	Small Business Innovation Research
SEAS	Spectrophotometric Analysis System
SeaWiFS	Sea-viewing wide field-of-view sensor (NASA)
SKYHI	Troposphere-Stratosphere-Mesosphere General Circulation Model
SSS	Sea surface salinity
SST	Sea surface temperature
TA	Total alkalinity
TAO	Tropical Atmosphere-Ocean Array
TCO_2	Total dissolved inorganic carbon
TEM	Terrestrial Ecosystem Model
TOPEX	Topographical Experiment for Ocean Circulation (joint U.S.-French satellite)
TOS	The Oceanographic Society
TransCom	Atmospheric Tracer Transport Model Intercomparison
TSG	Thermosalinograph
US SOLAS	U.S. Surface Ocean–Lower Atmosphere Study
VOS	Volunteer observing ships
WCRP	World Climate Research Programme
WITN	WITN station tall-tower observation site in North Carolina
WLEF	WLEF station tall-tower observation site in Wisconsin
WMO	World Meteorological Organization
WOCE	World Ocean Circulation Experiment
XBT	Expendable bathythermograph

Appendix D

Spatial and Temporal Variability of Surface Water pCO_2 and Sampling Strategies

Colm Sweeney, Taro Takahashi, and Anand Gnanadesikan
in collaboration with
Rik Wanninkhof, Richard A. Feely, Gernot Friedrich, Francisco Chaves,
Nicolas Bates, Jon Olafsson, and Jorge Sarmiento

D.1 Introduction

The difference between the partial pressure of CO_2 (pCO_2) in surface ocean water and that in the overlying air represents the thermodynamic driving force for the CO_2 transfer across the sea surface. The direction of the net transfer flux of CO_2 is governed by the pCO_2 differences, and the magnitude of the flux may be expressed as a product of the pCO_2 difference and the gas transfer coefficient. Presently the only practical means for estimating the net sea-air CO_2 flux over the global oceans is a combination of the sea-air pCO_2 difference and the CO_2 gas transfer coefficient. Although an eddy correlation method aboard a ship at sea (Wanninkhof and McGillis, 1999) was successfully deployed over the North Atlantic during the recent GASEX–99 program, its applications is still limited. The objective of this report is (1) to analyze the spatial and temporal variability of surface water pCO_2 based on the available field observations, and (2) to recommend sampling frequencies in space and time needed for estimating net sea-air CO_2 flux in regional scales with a specified uncertainty and a known sea-air gas transfer coefficient on wind speed. It should be noted that the sampling frequencies needed for investigation of governing processes such as photosynthesis and upwelling are not addressed in this report.

D.2 General Background

Over the global oceans, the pCO_2 in surface ocean water is known to vary geographically and seasonally over a wide range between about 150 μatm and 500 μatm, or about 50% below and above the 2001 atmospheric pCO_2 level of about 360 μatm (or 370 ppm in CO_2 mole fraction concentration in dry air).

D.2.1 Factors that determine variability of pCO_2

The pCO_2 in mixed layer waters, which exchange CO_2 directly with the atmosphere, is affected by temperature, the total CO_2 concentration, and the alkalinity. While the water temperature is regulated by physical processes

(i.e., solar energy input, sea-air heat exchanges, and mixed layer thickness), the latter two are primarily controlled by biological processes (i.e., photosynthesis and respiration) and by upwelling of subsurface waters enriched in CO_2 and nutrients. The pCO_2 in surface ocean waters doubles for every 16°C temperature increase. For a parcel of seawater with constant chemical composition, pCO_2 would increase by a factor of 4 when it is warmed from polar water temperatures of about –1.9°C to equatorial water temperatures of about 30°C. However, the total CO_2 concentration in surface waters ranges from about 2150 μmol/kg in polar waters to 1850 μmol/kg in equatorial waters. If a global mean Revelle factor of 10 is used, this reduction of TCO_2 should cause a reduction of pCO_2 by a factor of 4.5. Thus, on a global scale, the effect of biology and upwelling on surface water pCO_2 is similar in magnitude but often opposite in direction to the temperature effect. The increasing effect on seawater pCO_2 of summer warming of water is commonly opposed by the lowering effect of photosynthesis during summer months. The decreasing effect on pCO_2 of winter cooling of water is counteracted by the increase in the total CO_2 concentration caused by winter convective mixing of deep waters rich in CO_2. It is therefore the interactions of the three major effects (i.e., temperature, upwelling, and biological utilization of CO_2) that determine the annual mean pCO_2 and variability about the mean in space and time.

D.2.2 Variability of surface water pCO_2

The spatial variability of the surface water pCO_2 is demonstrated in Fig. D-1 using about 700,000 pCO_2 observations made in the past 40 years by Takahashi *et al.* (1999). The standard deviation of observed pCO_2 values in each $4^\circ \times 5^\circ$ pixel was computed for each month, and the mean of the monthly standard deviation values have been plotted in color. The white areas indicate the pixels with no observations. The map, therefore, shows the magnitude of mean pCO_2 variability over the period of a month within each pixel area. It should be noted that some pixels have observations in all 12 months, whereas some pixels have observations only in one or more months. Small spatial variability (magenta-blue) is found mainly in the subtropical oceans, whereas large variability (green-yellow-orange) is found in the equatorial Pacific and the high-latitude oceans of both hemispheres, where concentrations of nutrients are large and productivity is high. The large pCO_2 variability in these areas may be attributed to mesoscale variability in biology as well as physical features such as eddies and internal waves.

Large spatial variability also has been observed in the areas affected by major western boundary current systems (Gulf Stream, Labrador Current, Brazil-Malvinas Confluence areas, Kuroshio, and Oyashio), along which eddies and filaments are formed. *Sampling strategies for surface water pCO_2 must be formulated by taking these areas of large spatial variability into consideration.*

The seasonal variability of surface water pCO_2 varies geographically and has a peak-to-peak amplitude which is as large as 280 μatm in some regions. Seasonal amplitudes exceeding 100 μatm have been observed in the

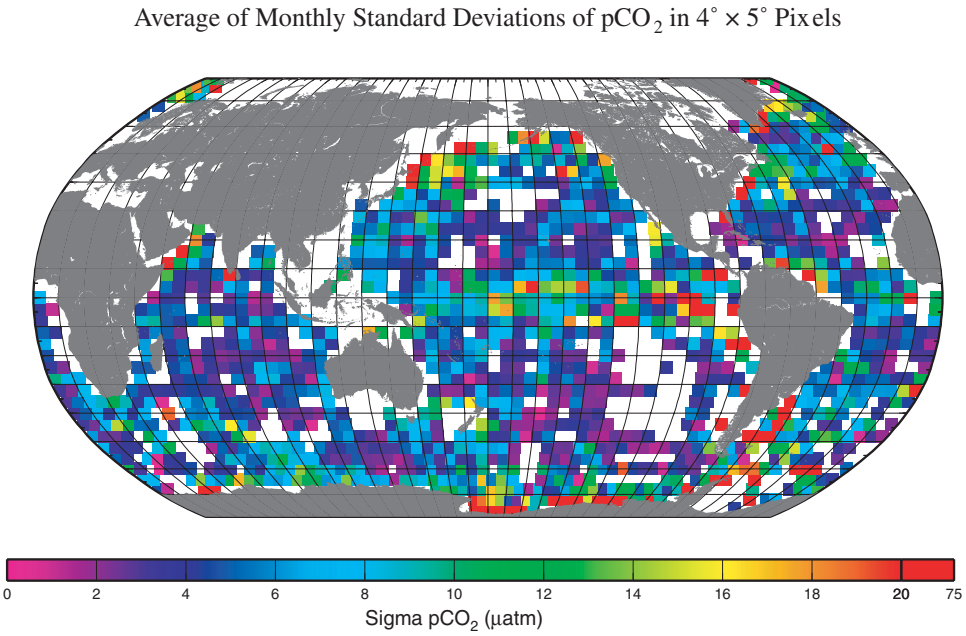


Figure D-1: Spatial variability of the surface water pCO_2 represented by the standard deviation of observed pCO_2 values in a month.

northwestern Arabian Sea, the northwestern subarctic Pacific, the subarctic North Atlantic, the eastern Sargasso Sea (Bermuda area), and the Ross and Weddell Seas, Antarctica. In subtropical gyre areas (e.g., Bermuda area), the seasonal variation in surface water pCO_2 is primarily driven by seasonal temperature changes, and hence pCO_2 is highest during summer and lowest in winter. On the other hand, in subpolar and polar oceans, the pCO_2 is highest during winter due to upwelling and is lowest during summer due to photosynthesis. Therefore, seasonal changes in high latitude areas are about 6 months out of phase from those in subtropical areas. Transition areas in between these two regimes (e.g., Weather Station "P") exhibit small seasonal amplitudes as a result of interactions of these out of phase forcings. The seasonal and temporal variability of surface water pCO_2 in specific areas will be discussed in Section 4.

D.3 Regional CO_2 Flux and Sea-Air pCO_2 Difference

The monthly distributions of the sea-air pCO_2 difference over the global oceans for a reference year 1995 have been estimated using about 700,000 pCO_2 measurements made over the past 40 years. The methods for data corrections and interpolation used have been described in Takahashi *et al.* (1997, 1999). The monthly distribution maps produced represent a climatological mean for non-El Niño conditions with $4° \times 5°$ spatial resolution. The net flux values for the global oceans and various oceanic regions have been estimated on the basis of the sea-air pCO_2 difference maps and the depen-

Table D-1: Mean annual sea-air pCO_2 difference, annual flux and the sea-air pCO_2 required for 0.1 Pg C flux*.

Ocean Regions	Average ΔpCO_2 (μatm)	Ocean Area 10^6 km^2	ΔpCO_2 per 0.1 Pg C/yr uptake	Annual Flux Pg C/yr
Northern North Atlantic	−47.4	7.45	10.8	−0.39
Temperate North Atlantic	−9.3	23.95	5.6	−0.27
Equatorial Atlantic	+19.9	15.43	14.0	+0.13
Temperate South Atlantic	−3.1	26.08	4.4	−0.24
Polar South Atlantic	−26.4	7.10	11.3	−0.22
Northern North Pacific	−8.8	4.45	20.1	−0.02
Temperate North Pacific	−10.0	43.04	2.9	−0.47
Equatorial Pacific	+29.6	50.19	4.4	+0.64
Temperate South Pacific	−7.4	53.05	2.6	−0.36
Polar South Pacific	−9.0	17.44	4.3	−0.20
Temperate North Indian	+35.9	2.12	13.6	+0.03
Equatorial Indian	+14.0	21.05	3.7	+0.10
Temperate South Indian	−20.0	30.49	10.1	−0.57
Polar South Indian	−10.1	7.16	10.8	−0.10
Global Oceans		308.99		−1.94

*All the values are for the reference year 1995. The wind speed data of Esbensen and Kushnir (1981) and the wind speed dependence of gas transfer coefficient of Wanninkhof (1992) have been used.

dence of the CO_2 gas transfer coefficient across the sea surface on long-term wind speed, that has been formulated by Wanninkhof (1992). If the monthly mean climatological wind speeds of Esbensen and Kushnir (1981) is used, the pCO_2 data yield a global oceanic uptake of 1.94 Pg C/yr. If the 40-year mean NCEP/NCAR wind speed data are used, a global ocean uptake of 2.45 Pg C/yr is obtained. Table D-1 shows the annual mean sea-air pCO_2 difference and the net CO_2 uptake flux in various oceanographic regions, that was estimated using the wind speed data of Esbensen and Kushnir (1981).

Table D-1 shows that, in order to estimate a regional CO_2 flux within $\pm$0.1 Pg C/yr for the major oceanic regions, the sea-air pCO_2 difference should be determined within 3 to 15 μatm. Figure D-2 shows the geographical distribution of the sea-air pCO_2 differences required for constraining flux estimates within $\pm$0.1 Pg C/yr. Small oceanic regions such as northern North Pacific and temperate North Indian Oceans (area $<4 \times 10^6$ km^2) are exceptions, since the net flux for these areas is much smaller than 0.1 Pg C/yr.

In order to estimate the terrestrial ecosystem uptake flux of CO_2 reliably on the basis of an inversion of atmospheric CO_2 concentration data, it has been suggested that the net CO_2 flux over each oceanic region be known within $\pm$0.1 Pg C/yr. For this reason, the analysis presented below is focused on evaluating the error in air-sea pCO_2 difference, that corresponds to a flux error of $\pm$0.1 Pg C/yr.

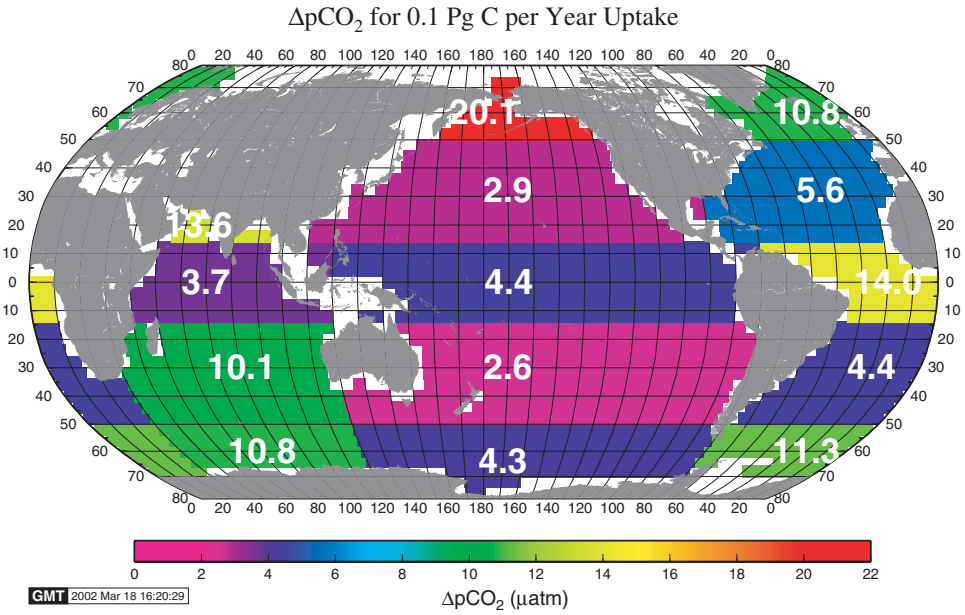


Figure D-2: Target pCO_2 to estimate a regional CO_2 flux within ± 0.1 Pg C/yr for the major oceanic regions from Table D-1. Polar regions cover areas between 50° and 90° (North and South), temperate regions cover areas between 14° and 50° (North and South) and equatorial regions are between 14°N and 14°S.

D.4 Temporal Variability of pCO_2 and Sampling Frequency

There are only a few locations where seasonal changes in surface water pCO_2 have been determined throughout a year. The data obtained at three locations (i.e., in the vicinity of Bermuda, Equatorial Pacific, and Weather Station "P") will be presented and analyzed. These three locales represent the temperate gyre regime (Bermuda), the high seasonal upwelling regime (equatorial Pacific and a subarctic area north of Iceland), and the transition zone between the temperate and subarctic regimes (Weather Station "P"), respectively.

D.4.1 Temperate Gyre Regime

The temporal (seasonal) variability of pCO_2 and SST observed in the vicinity of the BATS Site (31°N, 64°W) are shown in Fig. D-3. Seasonal amplitude of about 100 μatm for pCO_2 and that of 8°C for SST are observed. The seasonal changes for pCO_2 appear to be in phase with those for SST. However, the observed pCO_2 amplitude is much smaller than that anticipated from a temperature change of 8°C, which should cause a pCO_2 change of about 150 μatm. This difference has been attributed to the effect of biological drawdown of pCO_2 (about 50 μatm), which is about 6 months out of phase from the effect of temperature changes (Takahashi *et al.*, submitted).

Using these data, we have computed the following two quantities. (1) Errors anticipated from measurements made at random sampling intervals,

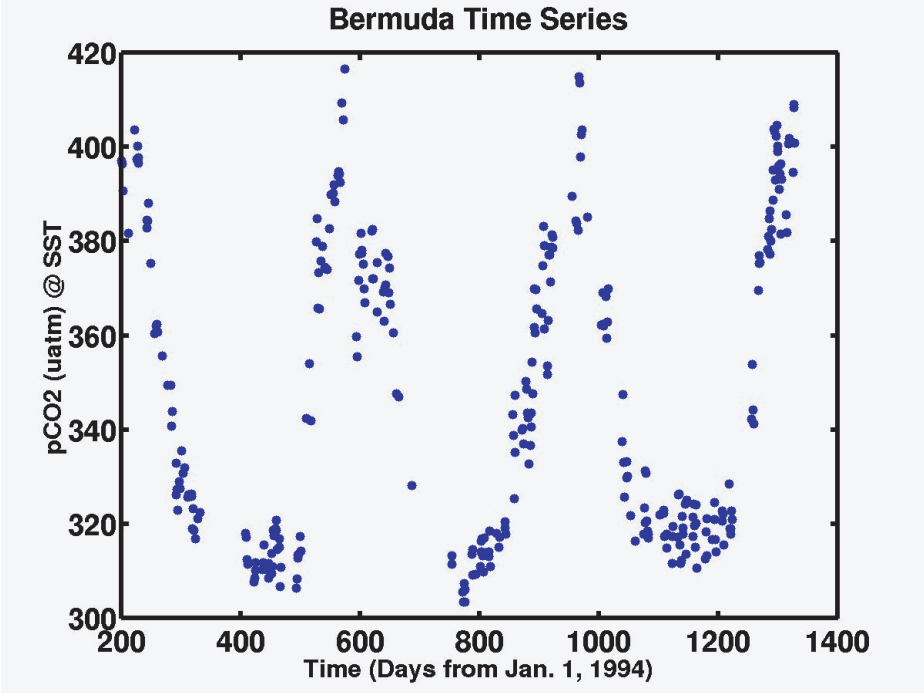


Figure D-3: Temporal variation of surface water pCO_2 observed in the vicinity of the BATS site (31°N, 64°W) observed in mid-1994 through early 1998 by N. Bates (BBRS).

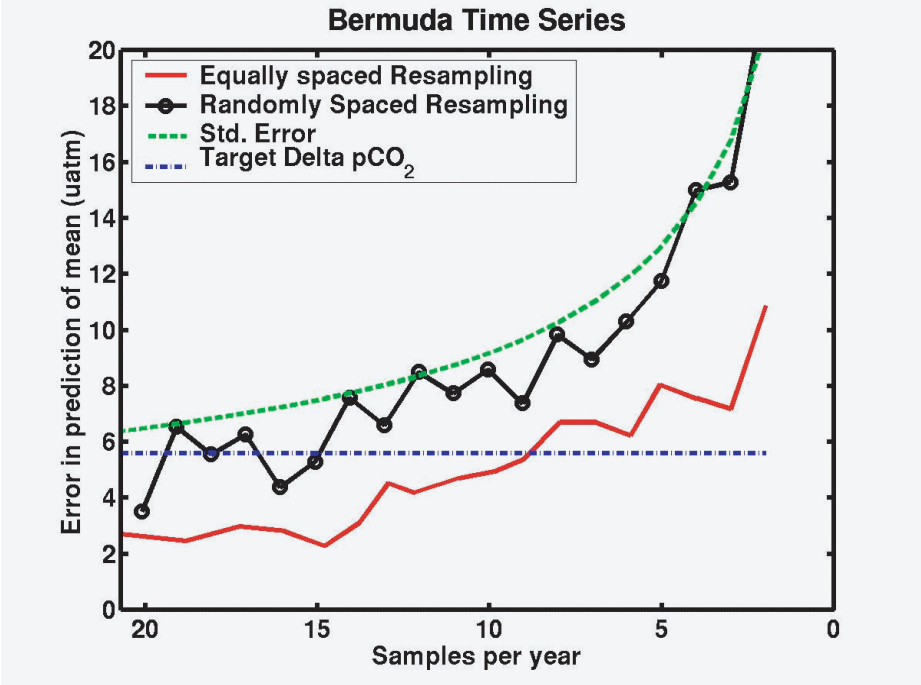


Figure D-4: Error for the annual mean value as a function of sampling frequency per year in the temperate North Atlantic in the vicinity of the BATS site. The standard error of the mean (dashed curve). Sampling with equal time intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The horizontal dashed-dotted line refers to the error in ΔpCO_2 needed for the estimated flux of CO_2 to the nearest 0.1 Pg C in the temperate North Atlantic.

where errors are represented by the standard error of the mean ($\sigma/\sqrt{n}$). The dashed curve in Fig. D-4 shows the anticipated error in annual mean as a function of the number of measurements made in a year. For a calendar year of 1997, 104 measurements were made in the area yielding a mean pCO_2 of 347.9 μatm with a one-sigma of 33 μatm. This curve represents simply this standard deviation (σ) value divided by the square root of the number of observations, n, per year. In order to obtain an error in the mean of 6 μatm or better (see Table D-1), measurements must be made as frequently as 30 times a year. (2) The solid curve shows errors anticipated in the mean value calculated at equally spaced sampling distances. The mean at each sampling interval was calculated by subsampling the originally oversampled time series and using a piece-wise linear interpolation to interpolate the subsampled time series back to the original sampling interval of the time series. Thus, the mean of the subsampled time series is calculated using the same number of observations as the mean calculated from the original time series. The mean for each sampling interval was calculated a number of times by subsampling different parts of the original time series. The error in the predicted mean was computed by calculating the difference between the mean value of the linearly interpolated sub-sampled time series and the mean obtained for the entire data set. To achieve a level ± 6 μatm of precision in the prediction of the mean using equal sampling intervals in time nine observations are needed a year. (3) The solid line open with circles shows errors in the calculated mean if samples are taken at randomly spaced intervals in time and interpolated with a piece-wise linear fit to the original sampling intervals. As above, the error in the prediction of the mean is calculated as the difference between the mean value of the linearly interpolated sub-sampled time series and the mean obtained for the entire data set. Figure D-3 indicates that if the time series is sampled at randomly spaced intervals in time it will require at least 15 samples a year to predict the mean annual pCO_2 to within ± 6 μatm.

The error for annual mean pCO_2 value depends not only on the total number of measurements made in a year, but also on time intervals for measurements. Considering that the temporal pattern of seasonal pCO_2 changes might be somewhat different from year to year, measurements should be made more often than nine times a year. Therefore, we estimate that *one set of measurements for every 1 to 1.3 months annually should yield an annual mean value within the desired ± 6 μatm (needed for ± 0.1 Pg C/yr, see Table D-1) over the temperate North Atlantic region.*

D.4.2 Equatorial Pacific regime

The temporal variability of the sea-air pCO_2 difference (ΔpCO_2) at the Equatorial Pacific is shown from mooring data taken at 2°S and 170°W from 22 June 1998, to 3 May 2000 (Gernot Friederich and Francisco Chavez, MBARI, see Fig. D-5). The variability of surface water pCO_2 in this region is very closely associated with sea surface temperature values indicating upwelling events due to a combination of local wind events, the remnants of tropical instability waves and Kelvin waves propagated by Madden and Ju-

lian Oscillation in the atmosphere (Chavez *et al.*, 1999). The increase in ΔpCO_2 over the measurement period is most likely due to the increase in upwelling as the Eastern Equatorial Pacific recovers from El-Niño conditions. Figure D-6 shows the error in the estimate of the mean from the standard error (dashed curve), randomly spaced sampling (open circles and solid line), and evenly spaced sampling (solid curve) over an annual cycle. This data set would need to be sampled ∼30 times a year randomly or ∼15 times a year at equal intervals to achieve an average annual ΔpCO_2 of 4.4 μatm (the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the North Pacific, Table D-1).

D.4.3 Subarctic regime

The temporal (seasonal) variability of the surface water pCO_2 in an approximately $4^\circ \times 5^\circ$ area located north of Iceland is shown in Fig. D-7. The pCO_2 values were obtained by Jon Olafsson of MRI, Rekjavik, and the LDEO staff over the 14-year period, 1983–1997. Since no obvious interannual changes can be identified, the data in this period are plotted against a time span of 1 year, and thus the plot includes the interannual variability as well as the spatial variability within this area box. The data associated with salinity values less than 34.0 have been removed in order to eliminate the effects of low salinity arctic waters. An abrupt drawdown of surface water pCO_2 amounting to about 250 μatm is observed about Julian day 150, and this coincides with the formation of a well-stratified mixed layer and a rapid increase in the temperature of the mixed layer. The sudden decrease in pCO_2 is attributed primarily to the biological utilization of CO_2, but is partially compensated by the concurrent increase in temperature (Takahashi *et al.*, 1993). The mean annual pCO_2 in surface waters is 311.3 μatm with a standard deviation of 41 μatm and a standard error in the mean of $\pm$2.4 μatm (with a total of 284 measurements).

The error for the annual mean pCO_2 calculated by randomly and evenly time-spaced sampling of the observation is shown in Fig. D-8 as a function of the number of sampling events per year. Based on this plot, we estimate that 5 to 8 evenly spaced observations or 8 to 15 randomly spaced observations annually should yield an annual mean value within the desired $\pm$11 μatm (needed for $\pm$0.1 Pg C/yr, see Table D-1) over the subarctic North Atlantic region.

D.4.4 Transition zone between the temperate and subarctic regimes

The temporal (seasonal) variability of the surface water pCO_2 in an approximately $4^\circ \times 5^\circ$ area that includes the Weather Station "P" in the northeastern North Pacific (50°N, 145°W) is shown in Fig. D-9. The observations were made in the 3-year period, 1972–1975, and are plotted against Julian day as though all measurements were made in one year. Therefore, the plot includes the interannual variability. Figure D-9 shows relatively small seasonal peak-to-peak amplitude of about 50 μatm (compared with

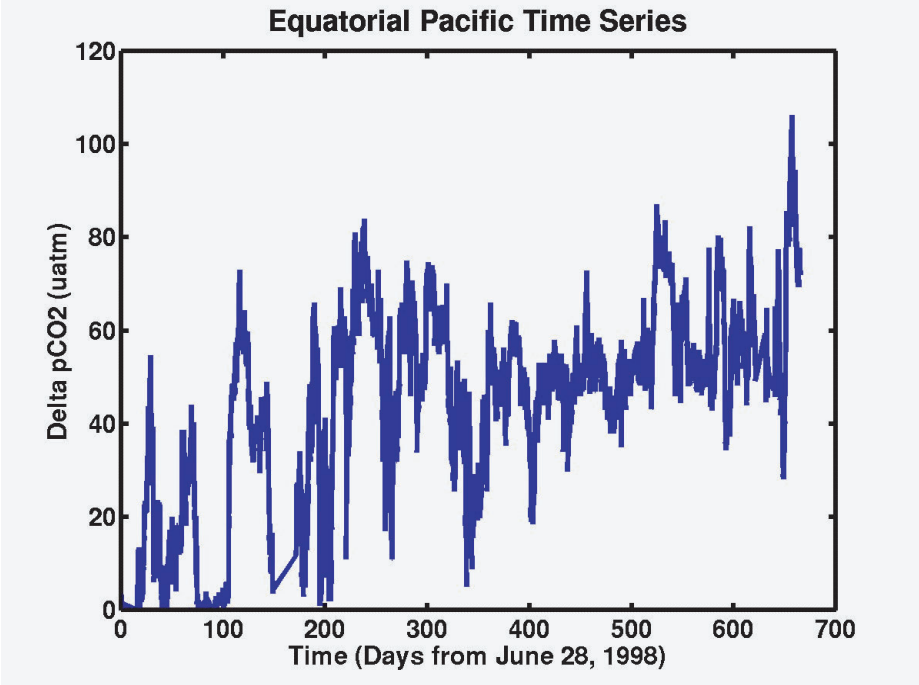


Figure D-5: Equatorial Pacific mooring measurements of ΔpCO_2 taken at 2°S and 170°W from 22 June 1998, to 3 May 2000. This data was collected by Gernot Friederich and Francisco Chavez (MBARI).

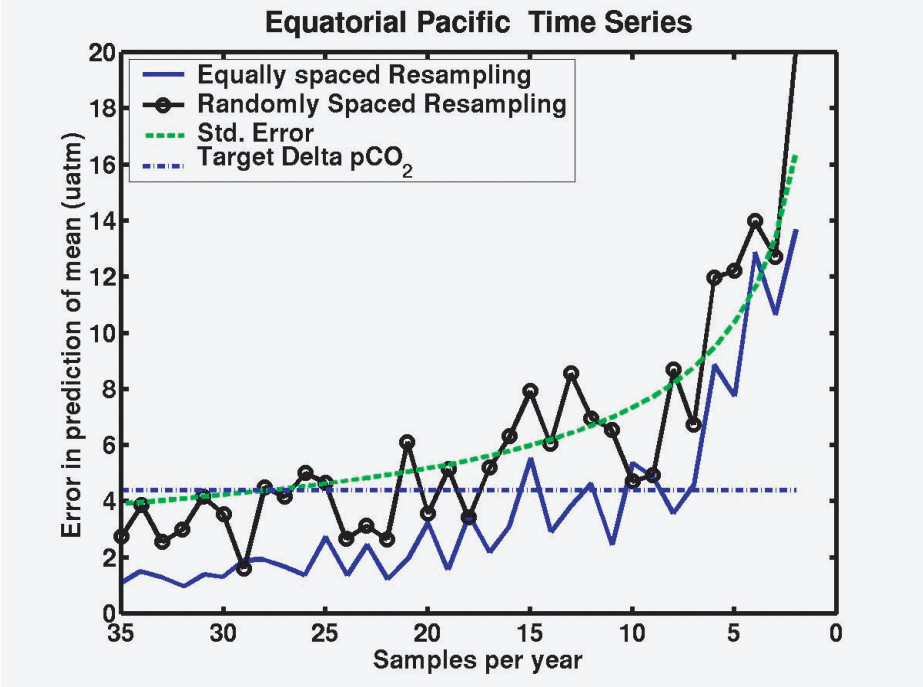


Figure D-6: Error for the annual mean value as a function of sampling frequency per year in the Equatorial Pacific at 2°S and 170°W. The standard error in the mean (dashed curve). Sampling with equal time intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted-dashed line refers to the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the Equatorial Pacific.

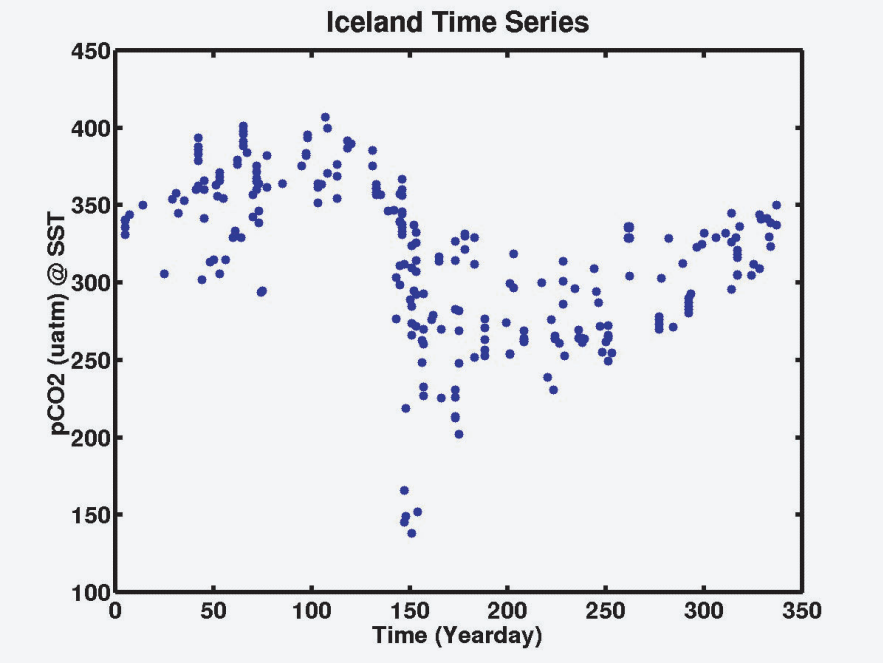


Figure D-7: The temporal (seasonal) variation of surface water pCO_2 in a 4° × 5° area located north of Iceland. The data were obtained by Jon Olafsson (MRI, Reykjavik) and the LDEO staff over the 14-year period, 1983–1997.

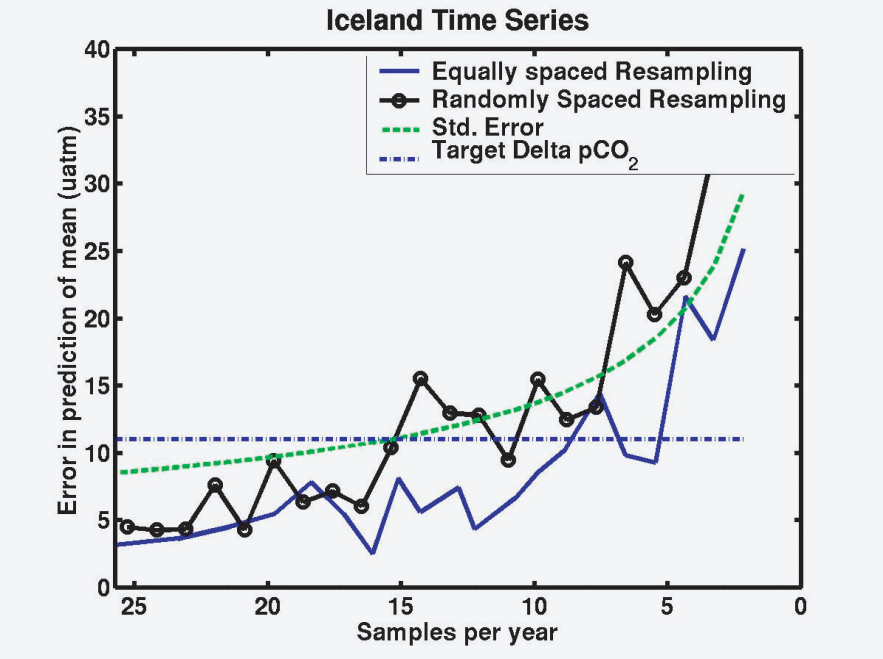


Figure D-8: Error for the annual mean value of surface pCO_2 as a function of sampling frequency per year in a 4° × 5° area located north of Iceland. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the subarctic North Atlantic region.

100 μatm near Bermuda (Fig. D-3) and 250 μatm near Iceland (Fig. D-7)), and shows no simple sinusoidal seasonal patterns (like that observed near Bermuda (Fig. D-3)). This may be attributed to the fact that the seasonal temperature effect on pCO_2 is similar in amplitude but about 6 months out of phase from the biological effect (Takahashi *et al.*, 1993). While the effect of summer warming of water increases surface water pCO_2, the biological CO_2 utilization that increases toward a summer maximum reduces pCO_2, thus partially or entirely canceling each other. Large oceanic areas located along the boundary between the temperate and subpolar regimes, especially in the southern hemisphere oceans between 40°S and 60°S, also exhibit a zone of small seasonal amplitude in surface water pCO_2 (Takahashi *et al.*, submitted).

The error for the annual mean pCO_2 anticipated for measurements with evenly time-spaced sampling, is shown in Fig. D-10 as a function of the number of sampling events per year. Based on this plot, we estimate that ∼9 evenly spaced observations or ∼15 randomly spaced observations a year should yield an annual mean value within the desired ±3 μatm (needed for ±0.1 Pg C/yr, see Table D-1) over the temperate/subarctic North Pacific region.

D.5 Spatial Variability of CO_2 and Sampling Intervals

We have also analyzed scales of variability in the surface water pCO_2 values measured along ship's tracks using semicontinuous equilibrator-IR systems. To represent different oceanographic regimes, we have chosen (1) an E-W traverse across the temperate North Atlantic, (2) a N-S traverse across the central Pacific including the high pCO_2 equatorial zone, and (3) a pair of N-S traverses during summer and winter across the subpolar and polar regimes in the Pacific sector of the Southern Ocean. The analysis of these data sets, which cover major oceanographic regimes, should yield the basis for designing sound strategies for mapping of the surface ocean pCO_2 over the global oceans.

D.5.1 E-W traverse across the temperate North Atlantic Ocean

The spatial variability in pCO_2 for the temperate North Atlantic is illustrated using a transect from Punta Del Gado, Azores to Miami, FL (Fig. D-11A) during the GASEX 98 cruise using measurements made on the NOAA research vessel R/V *Ron Brown.* The measurements of pCO_2 were made over a 10-day period extending from 28 June 1998, to 7 July 1998, and show a steady increase in pCO_2 over the westward transect to Miami, with a peak in the Gulf Stream (∼5000 km from the Azores, Fig. D-11B). These data were provided by the joint collaboration of AOML and PMEL (`http://www.aoml.noaa.gov/ocd/oaces/mastermap.html`).

The large-scale change in surface water pCO_2 over the course of the

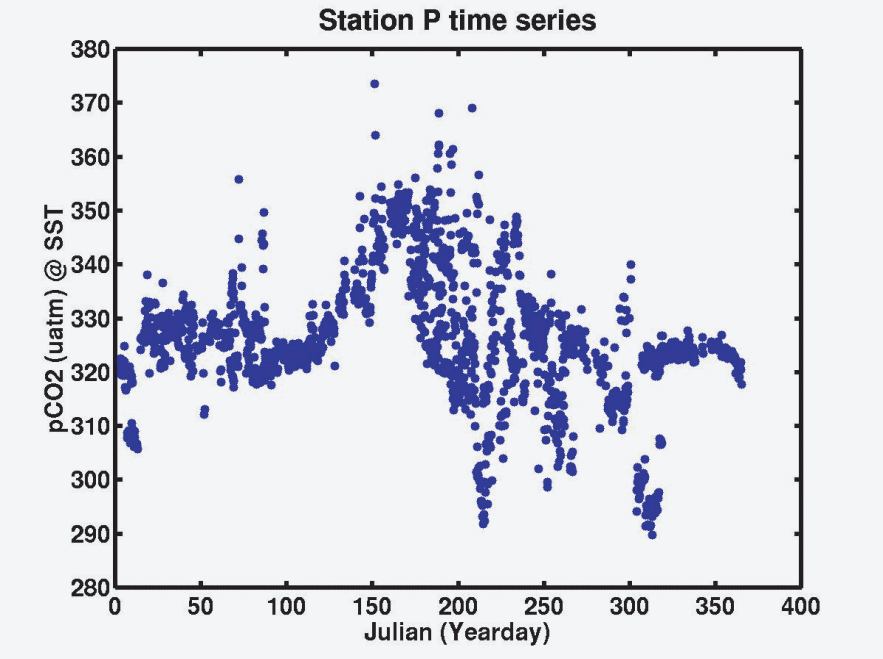


Figure D-9: Seasonal variation of surface water pCO_2 and SST observed at the Weather Station "P" (50°N and 145°W) by Wong and Chan (1991) in 1972–1975. Note that the SST changes more or less sinusoidal with a seasonal amplitude of 8°C, and that the surface water pCO_2 does not exhibit a simple sinusoidal pattern and changes only by 50 μatm (compared to 130 μatm expected from a 8°C temperature change).

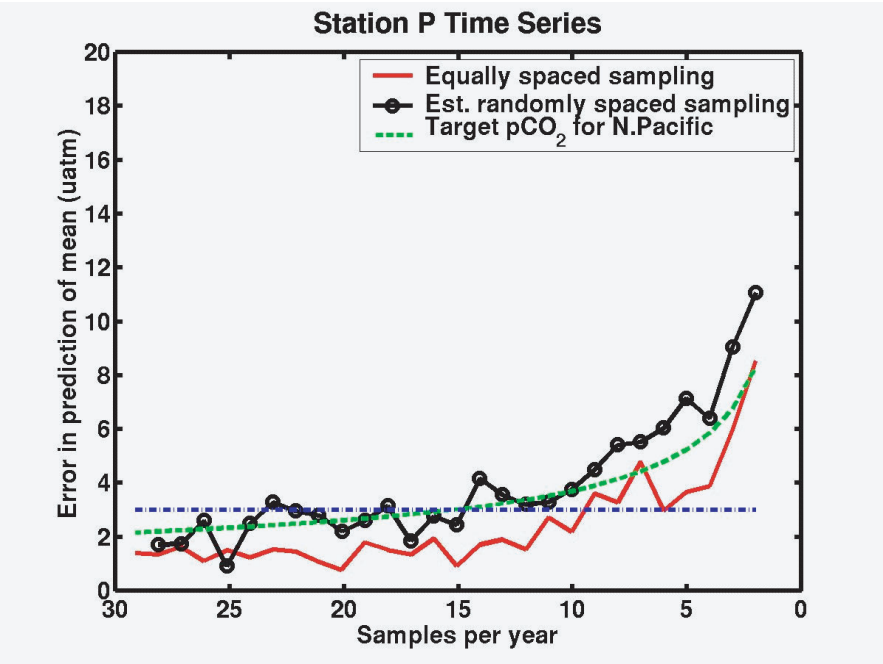


Figure D-10: Error for the annual mean value at Weather Station "P". The standard error in the mean (dashed curve). Sampling with equal time intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted-dashed line refers to the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the temperate North Pacific.

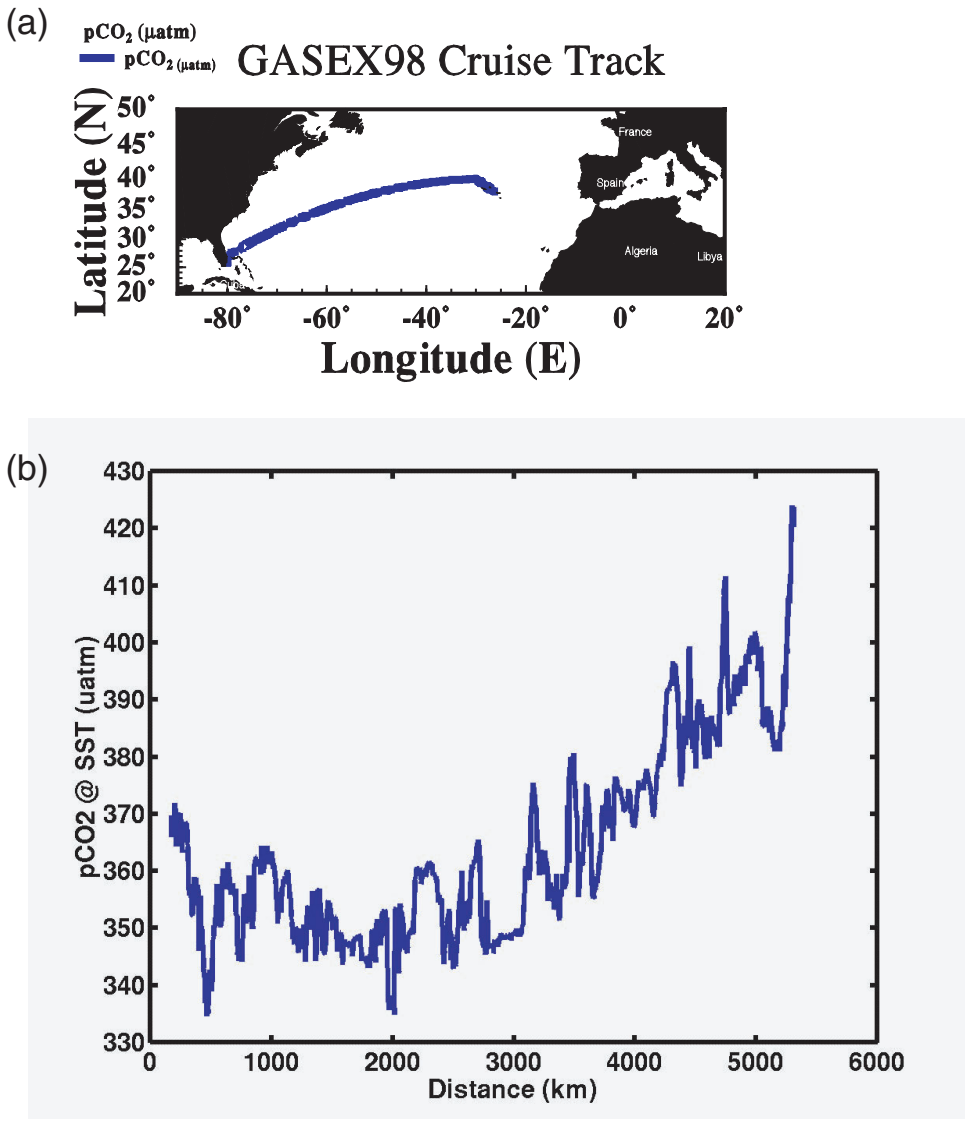


Figure D-11: (a) Cruise track of the NOAA R/V *Ron Brown* from Punta Del Gado, Azores, to Miami, FL, from 28 June 1998, to 7 July 1998, during GASEX 98. (b) Surface water pCO_2 as a function of the distance from Azores. These data were provided by the joint collaboration of AOML and PMEL (`http://www.aoml.noaa.gov/ocd/oaces/mastermap.html`).

transect clearly dominates the variance about the mean. When the error in the estimates of the transect mean is computed for equally spaced samples (Fig. D-12), we observe that randomly spaced samples taken every ∼750 km and evenly spaced samples taken every 1500 km should yield an annual mean value within the desired ±5.6 μatm (needed for ±0.1 Pg C/yr, see Table D-1).

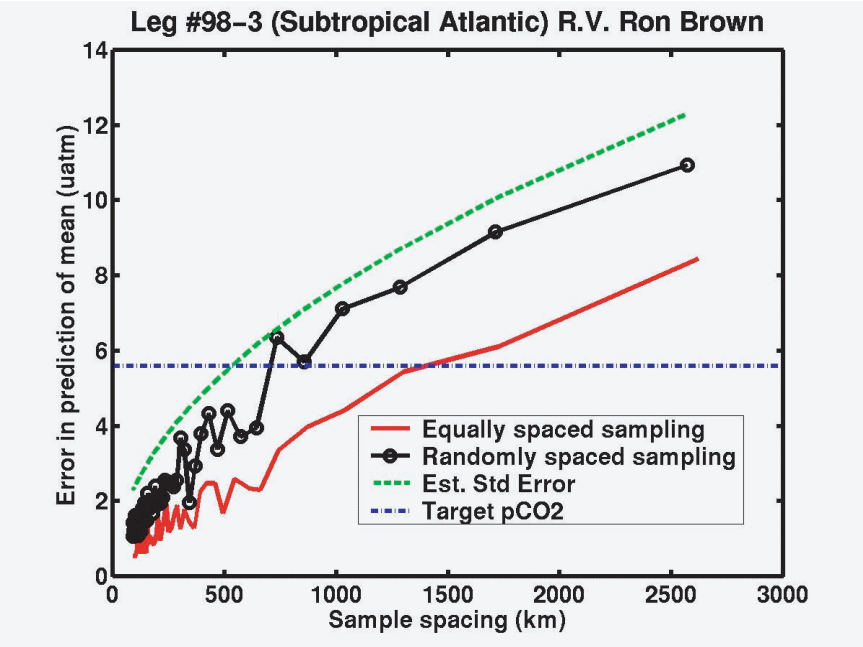


Figure D-12: Error estimate of mean surface pCO_2 during transect of the NOAA R/V *Ron Brown* from Punta Del Gado, Azores, to Miami, FL. The standard error in the mean (dashed curve). Sampling with equal time-intervals (solid curve). Sampling with randomly spaced time intervals (open circles and solid line). The dotted dashed line refers to the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the temperate North Atlantic.

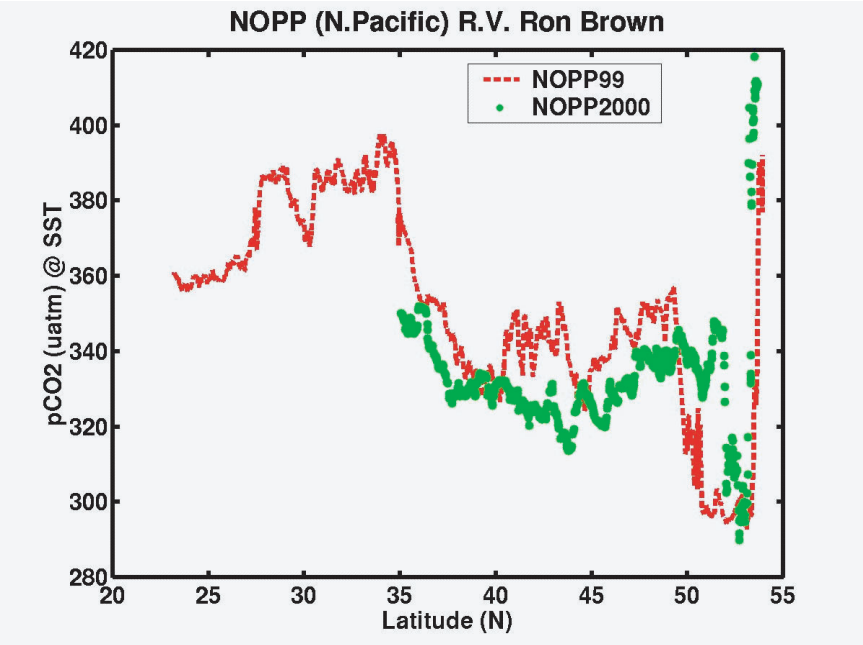


Figure D-13: Surface pCO_2 at sea surface temperature measured on the NOAA R/V *Ron Brown* from Honolulu, HI, to Dutch Harbor, AK, along the ∼170°W meridian between 26 September and 3 October 1999 (NOPP99). Surface pCO_2 at sea surface temperature measured on the R/V *Ron Brown* from Dutch Harbor, AK, to San Diego, CA, during a 12-day period between 27 September and 9 October 2000 (NOPP2000). These data were provided by the joint collaboration of AOML and PMEL (`http://www.aoml.noaa.gov/ocd/oaces/mastermap.html`).

D.5.2 N-S traverse across the central north and equatorial Pacific Ocean

As in the temperate North Atlantic, the required sampling intervals to make flux estimates with errors less than 0.1 Pg C/yr requires less sampling because of a reduced level of mesoscale variability in surface pCO_2 in these areas. This is demonstrated by a transect from Honolulu, HI, to Dutch Harbor, AK, along the ∼170°W meridian during an 8-day period between 26 September and 3 October 1999 (NOPP99, Fig. D-13). A similar transect is also shown from a transect that took place a year later from Dutch Harbor, AK, to San Diego, CA, during a 12-day period between 27 September and 9 October 2000 (NOPP2000, Fig. D-13). These data were provided by the joint collaboration of AOML and PMEL (`http://www.aoml.noaa.gov/ocd/oaces/mastermap.html`). Both surface pCO_2 profiles indicate strong fronts at ∼34°N, ∼50°N, and ∼54°N where surface pCO_2 varies by as much as 60 μatm. However, between fronts the mesoscale (∼100 km) variability is small. Subsampling the original datasets (Fig. D-14) indicates that evenly spaced sampling intervals of 300–700 km should yield an annual mean value within the desired ±2.9 μatm (needed for ±0.1 Pg C/yr, see Table D-1).

The spatial variability in surface pCO_2 in the temperate and northern Pacific appears to be small compared to those found in the equatorial zone (Fig. D-1). Two transects across the equator along the 95°W (eastern Pacific, the data obtained by the LDEO staff) and 170°W (central Pacific, the data provided by R.A. Feely, PMEL/NOAA) meridians show closely spaced fronts less than 200 km apart which exhibit changes in surface pCO_2 of greater than 100 μatm (Fig. D-15). A subsampling in the central and eastern Equatorial Pacific (Fig. D-16) indicates that evenly spaced sampling of 200–500 km intervals should yield an annual mean value within the desired ±4.4 μatm (needed for ±0.1 Pg C/yr, see Table D-1).

D.5.3 N-S traverses across the high-latitude Southern Ocean

The Southern Ocean exhibits the same degree of variability seen in the Pacific equatorial zone, through a combination of the ACC, strong Coriolis forcing and a large biological drawdown of CO_2, which act together to increase the mesoscale variability in this region. The effect of biology on mesoscale variability in the Southern Ocean is demonstrated by Fig. D-17, which shows two transects, one prior to the phytoplankton bloom (winter-NBP9708) and one following the phytoplankton bloom (summer-KIWI8), along ∼170°W from 45°S to 63°S. It is important to note the variability north of 50°S in both transects. Variability in pCO_2 due to primary productivity during the summer months in the lower latitudes significantly affects our ability to estimate the mean by subsampling the original data set. Figure D-18 suggests that during the summer samples need to be taken every 400–800 km to get a robust estimate of the basin-scale mean value within the desired ±4.3 μatm (needed for ±0.1 Pg C/yr, see Table D-1).

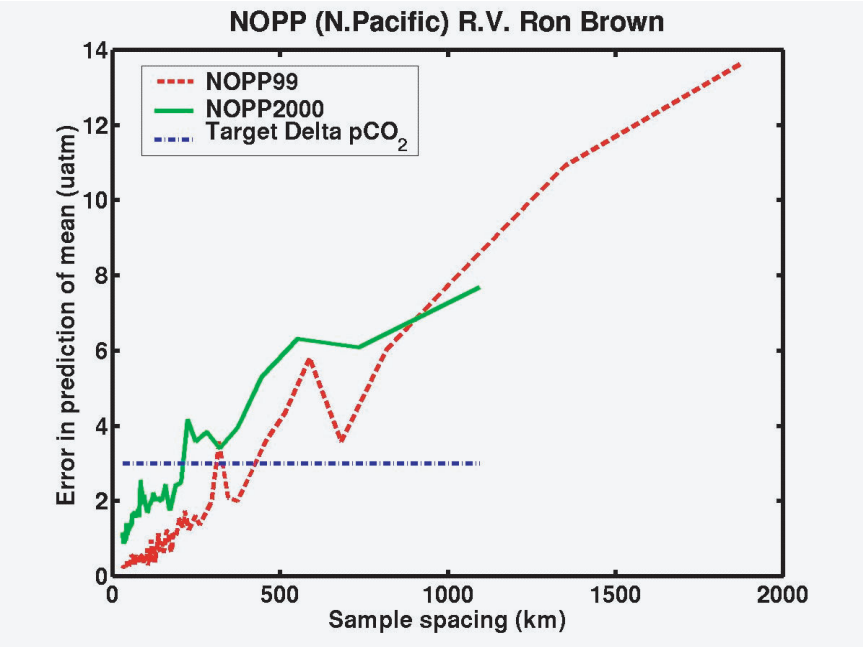


Figure D-14: Error estimate of mean surface pCO_2 using evenly spaced sampling intervals during the transect of the NOAA R/V *Ron Brown* from Honolulu, HI, to Dutch Harbor, AK, along the ∼170°W meridian between 26 September and 3 October 1999 (NOPP99). Error estimate of mean surface pCO_2 using evenly spaced sampling intervals during the transect of the NOAA R/V *Ron Brown* from Dutch Harbor, AK, to San Diego, CA, during a 12-day period between 27 September and 9 October 2000 (NOPP2000). The dotted dashed line refers to the ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the temperate North Pacific.

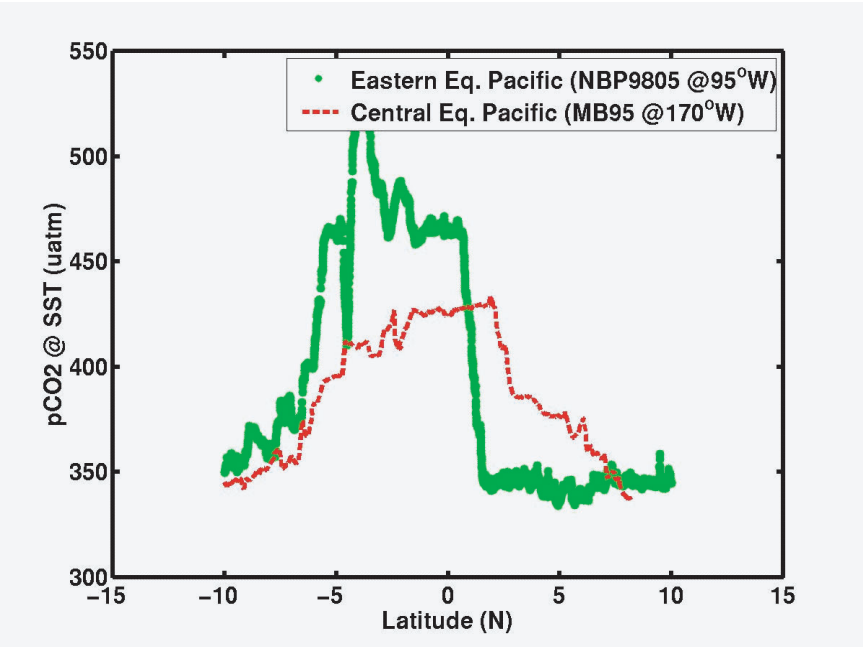


Figure D-15: Surface pCO_2 at sea surface temperature measured on the R/V I/B *Nathaniel B. Palmer* from Punta Arenas, Chile, to Seattle, WA, along the ∼95°W meridian between 26 July and 12 August 1998 (NBP9805). Surface pCO_2 at sea surface temperature measured on the NOAA R/V *M. Baldrige* from Darwin, Australia to Rodman, Panama between 21 November 1995, and 17 January 1996 (MB95).

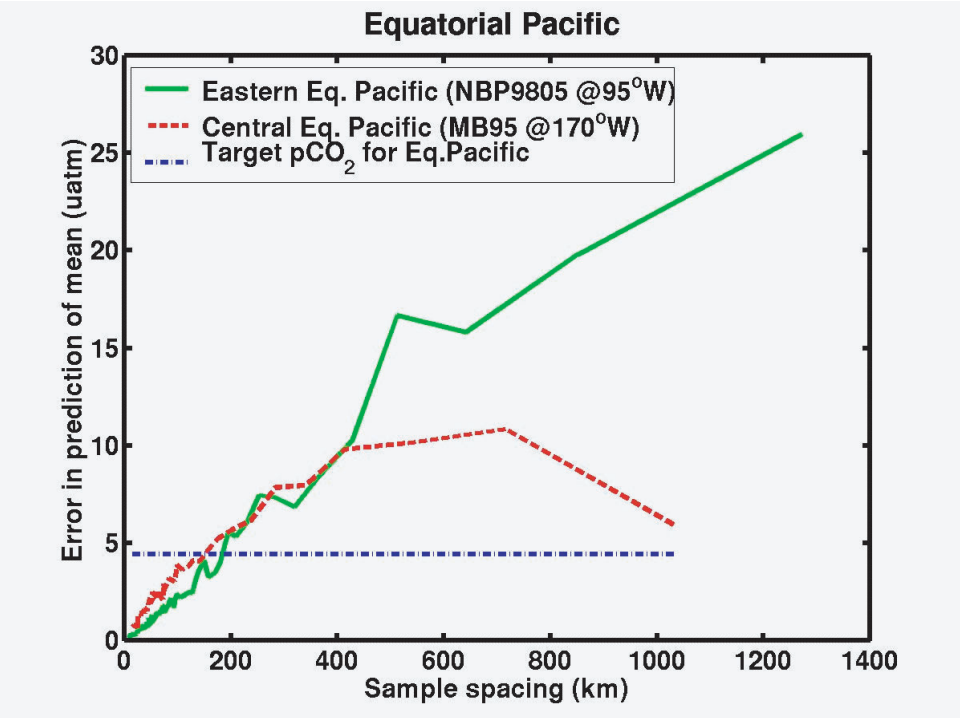


Figure D-16: Error estimate of mean surface pCO_2 using evenly spaced sampling intervals during the transect on the R/V I/B *Nathaniel B. Palmer* from Punta Arenas, Chile, to Seattle, WA, along the ∼95°W meridian between 26 July and 12 August 1998 (NBP9805). Error estimate of mean surface pCO_2 using evenly spaced sampling intervals during the transect on the NOAA R/V *M. Baldrige* from Darwin, Australia, to Rodman, Panama, between 21 November 1995, and 17 January 1996 (MB95). The dotted-dashed line refers to the ΔpCO_2 uncertainty needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the Equatorial Pacific region.

D.6 Conclusion

D.6.1 Temporal and spatial sampling requirements

In the above analysis we have shown how often the sea-air pCO_2 difference in the temperate regions of North Pacific and North Atlantic need to be sampled using evenly spaced sampling to estimate regional fluxes to better than 0.1 Pg C/yr (Table D-2). In addition, we have also included the Equatorial Pacific and Southern Pacific Polar Ocean because of the high mesoscale variability in these areas. The results presented assume that the uncertainty in the estimated fluxes are due entirely to the precision of the sea-air pCO_2 difference and do not include the errors from the sea-air gas transfer coefficient. Our analysis points out that a desired uncertainty of ±0.1 Pg C/yr in the basin-scale mean annual estimates for net sea-air CO_2 flux may be achieved by evenly time-spaced measurements of pCO_2 **6–15 times a year** throughout the regions of the world ocean with evenly spaced sampling **200–1500 km apart** (or 2–20 degrees longitude, depending on region and latitude). This analysis also points out the advantage of evenly spaced sampling in time and space over randomly spaced sampling.

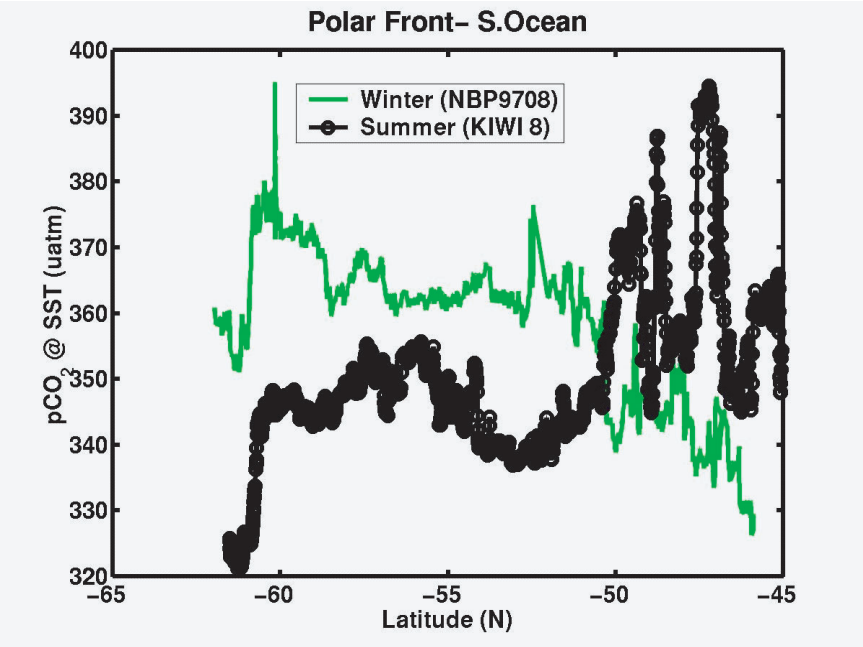


Figure D-17: Surface pCO_2 at sea surface temperature measured on the R/V I/B *Nathaniel B. Palmer* along ∼170°W meridian between 7 and 11 November 1997 (Winter-NBP9708). Surface pCO_2 at sea surface temperature measured on the R/V *Revelle* along ∼170°W meridian between 2 and 11 February 1998 (Summer-KIWI 8).

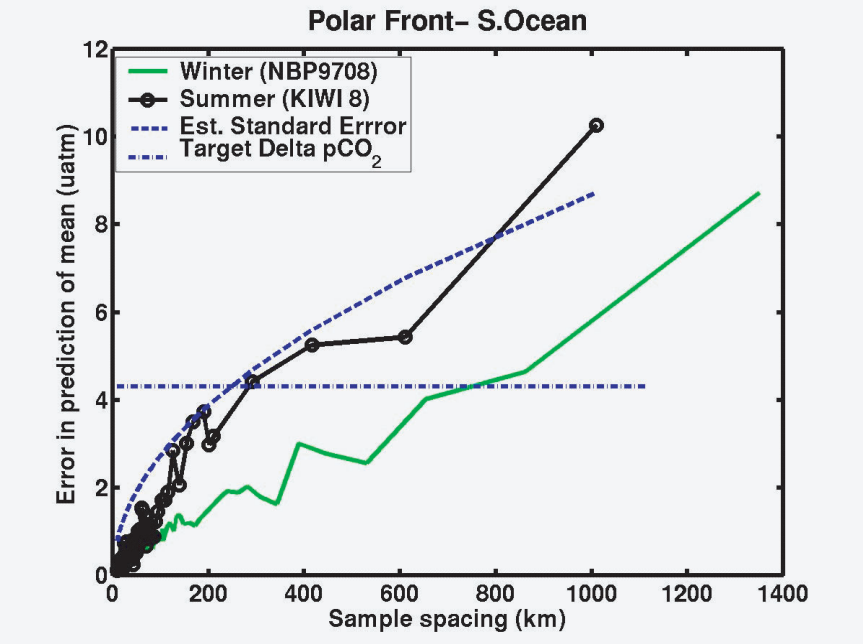


Figure D-18: Error estimate of mean surface pCO_2 using evenly spaced sampling intervals on the R/V I/B *Nathaniel B. Palmer* along ∼170°W meridian between 7 and 11 November 1997 (Winter-NBP9708). Error estimate of mean surface pCO_2 using evenly spaced sampling intervals during transect on the R/V *Revelle* along ∼170°W meridian between 2 and 11 February 1998 (Summer-KIWI 8). The dotted dashed line refers to the uncertainty of ΔpCO_2 needed to estimate the flux of CO_2 to the nearest 0.1 Pg of C in the Polar South Pacific. The smooth dashed curve indicates the estimated standard error.

Table D-2: Mean annual sea-air pCO_2 difference, the sea-air pCO_2 required for 0.1 Pg C flux, the required evenly spaced spatial and temporal sampling needed to achieve the sea-air pCO_2*.

Region	Average ΔpCO_2 (μatm)	ΔpCO_2 Flux = 0.1 Pg C/yr (μatm)	Samples Spacing (km)	Samples per year
Northern North Atlantic	−47.4	10.8		∼5–9
Temperate North Atlantic	−9.3	5.6	∼1500	∼6
Temperate North Pacific	−10.0	2.9	200–600	∼9
Equatorial Pacific	29.6	4.4	200	∼15
Polar South Pacific	−9.0	4.3	300–800	

*All the values are for the reference year 1995. The wind speed data of Esbensen and Kushnir (1981) and the wind speed dependence of gas transfer coefficient of Wanninkhof (1992) have been used.

In real ocean environments, wind speeds change with short timescales, and hence the sea-air CO_2 flux as the gas transfer piston velocity is affected sensitively with wind speed. Using the wind speed and pCO_2 data observed by the AOML and PMEL staff during the NOAA *Ron Brown* cruise (98-3) over the subtropical North Atlantic, we have computed the sea-air CO_2 flux using the shipboard wind speed data, and the flux data have been analyzed similarly as done for the pCO_2 data shown in Fig. D-12. While we have found on the basis of the pCO_2 data analysis that a sampling spacing of 750 km should give a precision of 0.1 Pg C in the temperate North Atlantic, an analysis of the flux data shows that about 250 km sampling spacing is needed to obtain the same precision. This suggests that the sampling spacing values evaluated in Table D-2 above represent a maximum spacing applicable to wind speeds averaged over a month rather than those averaged over a shorter time (hourly) period. We therefore recommend that surface water pCO_2 measurements be made with greater frequencies (or shorter spatial intervals) comparable to wind speed variability, so that the magnitude of the cross-correlation term for pCO_2 and wind speed variations can be evaluated.

D.6.2 Ways to lower sampling requirements

The above sampling recommendations assume that we have no prior knowledge about the spatial and temporal variability and no other proxies estimating the surface concentration of pCO_2.

Subjective sampling

Given some knowledge of the known spread of variance throughout time and space, it may be possible to improve our estimate of the mean by sampling at high resolution in spatial or temporal gradients and lower resolution in areas where the known gradients are not as steep. This subjective approach may serve to reduce the required number of samples in a given area. In order

to insure that no bias results from this approach to sampling, each region will need to be oversampled initially.

Use of proxies

The fact that we are able to predict the mean value of the sea-air pCO_2 difference with evenly spaced sampling so much better than randomly spaced sampling is directly related to the fact that the sea-air pCO_2 difference is autocorrelated. Simply stated, sequential measurements of surface pCO_2 in time and space are correlated with each other over some distance that is related to the sampling frequency that we have specified in Table D-2. Without prior knowledge of the field, it is more efficient to sample at evenly spaced intervals than randomly spaced intervals.

In addition to being autocorrelated, surface pCO_2 is also correlated with other parameters such as temperature (Stephens *et al.*, 1995) and chlorophyll concentrations, which can be observed remotely using instruments like the Pathfinder AVHRR for sea surface temperature and SeaWiFS for ocean color and biological productivity estimates. By building regionally specific algorithms to take advantage of these correlations we should be able to further decrease samples needed to predict the mean surface water pCO_2 for both regional and annual estimates.

While it is clear from this analysis that the mean surface water pCO_2 is driven primarily by large-scale variability in the ocean (>300 km), it is important that mesoscale processes not be disregarded. Multiparameter observations of mesoscale processes using moorings and high-resolution underway sampling techniques will be essential to understanding the processes that are responsible for the statistical covariance observed. It is therefore important to design a sea-air CO_2 flux program that combines the regional scale surface ocean pCO_2 observations with an ample dose of relevant process studies.

D.7 References

Chavez, F.P., P.G. Strutton, G.E. Friederich, R.A. Feely, G.A. Feldman, D. Foley, and M.J. McPhaden (1999): Biological and chemical response of the equatorial Pacific Ocean to the 1997 and 1998 El Niño. *Science, 286,* 2126–2131.

Esbensen, S.K., and Y. Kushnir (1981): The heat budget of the global ocean: An atlas based on estimates from the surface marine observations. *Climatic Research Institute Report #29*, Oregon State University, Corvalis, OR.

Stephens, M.P., G. Samuels, D.B. Olson, R.A. Fine, and T. Takahashi (1995): Sea-air flux of CO_2 in the North Pacific using shipboard and satellite data. *J. Geophys. Res, 100,* 13,571–13,583.

Takahashi, T., J. Olafsson, J. Goddard, D.W. Chipman, and S.C. Sutherland (1993): Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. *Global Biogeochem. Cycles, 7*, 843–878.

Takahashi, T., R.A. Feely, R. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi (1997): Global air-sea flux of CO_2: an estimate based on measurements of sea-air pCO_2 difference. *Proc. Natl. Acad. Sci., 94*, 8292–8299.

Takahashi, T., R.H. Wanninkhof, R.A. Feely, R.F. Weiss, D.W. Chipman, N. Bates, J. Olafsson, C. Sabine, and S.C. Sutherland (1999): Net sea-air CO_2 flux over

the global oceans: An improved estimate based on the sea-air pCO_2 difference. In *Proceedings of the 2nd International Symposium, CO_2 in the Oceans* (ISSN 1341-4356), Yukihiro Nojiri (ed.), Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Japan, 9–14.

Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R.A. Feely, C. Sabine, and J. Olafsson, Biological and temperature effects on seasonal changes of pCO_2 in global ocean surface waters, submitted to *Deep-Sea Research*.

Wanninkhof, R. (1992): Relationship between wind speed and gas exchange. *J. Geophys. Res., 97*, 7373–7382.

Wanninkhof, R., and W.R. McGillis (1999): A cubic relationship between air-sea CO_2 exchange and wind speed. *Geophys. Res. Lett., 26(13)*, 1889–1892.

Wong, C.S., and Y.-H. Chan (1991): Temporal variations in the partial pressure and flux of CO_2 at ocean station P in the subarctic northeast Pacific Ocean. *Tellus, 43B*, 206–223.

Appendix E

Errors in the Sea-Air CO_2 Flux Due to Time-Space Ocean Sampling Strategies for Sea-Air pCO_2 Difference

Taro Takahashi and Colm Sweeney

E.1 Objective

One of the means for estimating CO_2 flux across the sea surface is to measure the sea-air pCO_2 difference (ΔpCO_2) and multiply this quantity with the CO_2 gas transfer coefficient that may be estimated using a measurable parameter such as wind speed and surface roughness. Therefore, it is important to understand how the estimated CO_2 flux across the sea surface may be affected by time-space sampling frequencies of surface water pCO_2 measurements over the global oceans. In our previous report presented at the Boulder Workshop (Sweeney *et al.*, 2002), we analyzed the time-space variability of several surface water pCO_2 data sets (which contain high-frequency variability components) obtained at fixed stations as well as along long transects over various oceanic regimes. The results of the analysis have led to the conclusion that, to obtain a precision of ± 0.1 Pg C/yr over the temperate regions of the North Pacific and North Atlantic, the surface water pCO_2 over these areas must be sampled 7 to 10 times a year with evenly spaced measurements ranging from 200 km to 2,000 km apart (or 2° to 20° apart). Further, for a given number of measurements, sampling schedules with equally spaced time and space intervals are more effective than randomly spaced schedules. To test the validity of the analysis, we have assumed a known distribution of ΔpCO_2 over the global oceans and sampled it with various space-time intervals. The global and regional CO_2 flux values have been computed under different sampling schedules and compared with the original values. The results should represent a more realistic test for various sampling strategies. In this report, we summarize the findings of our study.

E.2 Method

For this purpose, the climatological mean monthly distributions of sea-air pCO_2 difference (ΔpCO_2) that have been obtained by the interpolation method of Takahashi *et al.* (1997) for the global oceans with $4° \times 5°$ resolution have been used as an *ocean* to be sampled. These monthly maps have been constructed using about 700,000 measurements for surface water pCO_2 for non-El Niño conditions. In constructing these monthly distributions, measurements were binned into $4° \times 5°$ pixels and averaged over a month. Hence, our ocean smoothes out any high-frequency variation of ΔpCO_2 in

time and space, and accordingly our tests apply primarily to the sampling schedule for large-scale features (greater than 4° in the meridian, greater than 5° in the zonal direction, and greater than 1 month in time).

We sampled this ocean along meridional and zonal transects with varying spacing and with different time intervals. This simulates surface water pCO2 measurements made aboard transoceanic ships of opportunity. The sea-air CO_2 flux values have been computed for the global and regional oceanic areas using ΔpCO_2 values obtained under various time-space sampling schemes. Throughout this study, the effect of wind speed on the sea-air CO_2 gas transfer coefficient formulated by Wanninkhof (Eq. 1, 1992) and the NCEP 40-year mean monthly wind field have been used for the calculation of the net CO_2 flux. Table E-1 shows the CO_2 flux values computed when the ocean was sampled along N-S transects that are 5°, 10°, and 25° apart in the E-W direction. Since the data pixels are 5° wide in the E-W direction, this is the finest resolution that can be obtained for the data set. ΔpCO_2 values were read for each pixel along all N-S transects during a given month as though all measurements were made in a single month. The number of evenly spaced sampling periods in a year (i.e., 12, 6, and 3) is shown in the third column from the left, indicating that the samples were collected once every month, once every other month, and once every 4 months. A set of ΔpCO_2 values collected for the respective sampling schedule was interpolated in space and time using the 2-dimensional diffusion-advection transport equation according to the procedures described by Takahashi *et al.* (1995) and Takahashi *et al.* (1997). A monthly distribution of ΔpCO_2 in each of 12 months representing a sampling scheme has been computed and the corresponding net CO_2 flux distribution has been obtained. These flux values have been summed to a year for each oceanic region and are listed in Table D-1.

E.3 Results

E.3.1 Meridional transects

The first three rows in Table E-1 show the results of sampling along N-S transects every 5° apart, that is, all pixels have been sampled at evenly spaced time intervals. The first row shows a special case, in which daily ΔpCO_2 values in each 4° × 5° (400 km × 500–200 km) pixel using an objective interpolation based changes in mean monthly flow fields as specified in the Princeton GCM (Toggweiler *et al.*, 1989). This interpolation scheme preserves some high-frequency time variability, which would not be present in the monthly mean values. The daily flux values have been computed using the daily samples, and compared with the results (listed in row 2) obtained using monthly mean values for each pixel. They are found to be consistent within 0.01 Pg C/yr, indicating that the daily ΔpCO_2 variability does not significantly change the mean flux estimates in any ocean basin. For the subsequent calculations of the CO_2 flux, we use monthly mean ΔpCO_2 values. The flux values obtained for monthly sampling are found to be similar to those obtained for six samplings a year (i.e., every other month). The

Table E-1: Global and regional sea-air CO_2 fluxes computed on the basis of sampling along evenly spaced meridional transects.

Transects/Time	Transect Spacing (degrees)	Temporal Spacing (No./yr even space)	Global Ocean Flux (Pg C/yr)	Temperate N. Pacific >14°N (Pg C/yr)	Eq. Pacific 14°N–14°S (Pg C/yr)	Northern N. Atlantic >50°N (Pg C/yr)	Temperate N. Atlantic 14°N–50°N (Pg C/yr)	Eq. Atlantic 14°N–14°S (Pg C/yr)
Meridional*	5	365	−2.45	−0.65	+0.73	−0.50	−0.32	+0.19
Meridional*	5	12	−2.44	−0.64	+0.73	−0.51	−0.32	+0.19
Meridional	5	6	−2.37	−0.60	+0.71	−0.51	−0.30	+0.17
Meridional	10	12	−2.09	−0.51	+0.58	−0.44	−0.26	+0.15
Meridional	10	6	−1.95	−0.47	+0.54	−0.43	−0.23	+0.13
Meridional	10	3	−1.72	−0.37	+0.52	−0.43	−0.19	+0.12
(Jan/May/Sept)								
(Feb/June/Oct)	10	3	−1.81	−0.42	+0.50	−0.40	−0.21	+0.13
(March/July/Nov)	10	3	−1.81	−0.42	+0.45	−0.37	−0.20	+0.12
(Apr/Aug/Dec)	10	3	−1.84	−0.40	+0.47	−0.43	−0.20	+0.13
Meridional	25	12	−1.19	−0.26	+0.36	−0.27	−0.14	+0.11

*All pixels are sampled throughout the year.

latter are smaller than the former by no more than 0.04 Pg C/yr in regional fluxes (temperate North Pacific). A reduction of the sampling frequency from monthly to every other month does not significantly alter the annual flux in the regional and global scales.

An increase of spacing between N-S transects to 10° (or 1,000 km near the equator) causes some reductions in the CO_2 flux. Compared to the global flux of –2.45 Pg C/yr for the full-sample case, the global flux computed for 10° intervals is reduced by about 0.35 Pg C/yr when each transect is sampled 12 times a year, and by 0.5 Pg C/yr when each transect is sampled 6 times a year. The fluxes for the northern and temperate North Atlantic regions obtained for the 10° spacing with 12 monthly sampling are within 0.1 Pg C/yr, and those for the North Pacific region are within 0.15 Pg C/yr of the full sampling flux. If these regions are sampled 3 times a year at evenly spaced intervals (i.e., January/May/September, February/June/October, March/July/November or April/August/December), the data yield fluxes within 0.1 Pg C/yr of the flux values by full sampling. This suggests that, for the North Atlantic Ocean (including high-latitude, temperate, and equatorial areas), a precision of 0.1 Pg C/yr may be attainable with N-S transects 10° apart (1,000 km near the equator and 400 km at high latitudes) with a repeat frequency of 3 or 4 times a year. On the other hand, the North Pacific requires N-S transects more closely spaced than 10°, also with a repeat frequency of 3 or 4 times. This may be due to the fact that the fronts running E-W in the Pacific exhibit more pronounced changes in ΔpCO_2. The timing of the sampling does not appear to be critical as long as they are more or less evenly spaced. Further, the flux values are relatively insensitive to temporal frequency of sampling, whereas they are more sensitive to spatial intervals. This suggests that transect sampling aboard transoceanic ships may yield more effective data sets than those obtainable via time-continuous observations made at fixed locations using moored buoys.

The last row of Table E-1 shows the flux values obtained for N-S transects 25° apart (2,500 km near the equator). This spacing yields flux values nearly 50% of the reference values, and hence is not acceptable. With this coarse spacing, major oceanographic features are missed.

E.3.2 Zonal Transects

The flux values are computed using ΔpCO_2 values read along various E-W zonal transects for each month and are summarized in Table E-2. The first row lists the full-sampling reference values, to which other values are to be compared. Zonal transects 8° (800 km) apart yield smaller uptake fluxes by 0.1 Pg C/yr in the Atlantic and 0.17 Pg C/yr in the Pacific. The flux values obtained for transects 12° (1,200 km) and 16° (1,600 km) apart drop off significantly. For a given transect spacing, N-S transects appear to yield better flux values than E-W transects. This may be due to the fact that meridional gradients of surface water pCO_2 are generally much steeper than zonal gradients. Hence, N-S transects tend to cut across major steep gradients and thus are able to document the major oceanic features.

Table E-2: Global and regional sea-air CO_2 fluxes computed on the basis of sampling along evenly spaced zonal transects and along a grid of evenly spaced meridional and zonal transects.

Transects/Time	Transect Spacing (degrees)	Temporal Spacing (No./yr even space)	Global Ocean Flux (Pg C/yr)	Temperate N. Pacific >14°N (Pg C/yr)	Eq. Pacific 14°N–14°S (Pg C/yr)	Northern N. Atlantic >50°N (Pg C/yr)	Temperate N. Atlantic 14°N–50°N (Pg C/yr)	Eq. Atlantic 14°N–14°S (Pg C/yr)
Meridional*	5	12	−2.44	−0.64	+0.73	−0.51	−0.32	+0.19
Zonal only	8	12	−1.83	−0.47	+0.56	−0.40	−0.24	+0.15
Zonal only	12	12	−1.69	−0.42	+0.48	−0.28	−0.23	+0.12
Zonal only	16	12	−1.07	−0.27	+0.35	−0.21	−0.13	+0.10
Meridional + Zonal	10 × 12	12	−2.29	−0.57	+0.66	−0.47	−0.30	+0.17
Meridional + Zonal Feb/June/Oct	10 × 12	3	−2.10	−0.50	+0.59	−0.45	−0.25	+0.16

*All pixels are sampled throughout the year.

Listed in Table E-2 are the flux values obtained by a combination of E-W and N-S transects for two sampling intervals, 12 times and 3 times a year, respectively. As expected, these grid sampling schemes yield flux values significantly better than the meridional or zonal transects alone.

E.4 Conclusion

Various surface water pCO_2 sampling strategies have been tested using the climatological mean monthly distributions of ΔpCO_2. To simulate transoceanic observations of surface water pCO_2, the climatological ΔpCO_2 field was sampled along evenly spaced N-S or E-W transects at various time intervals. Global and regional CO_2 flux values have been computed using the numerical scheme of Takahashi *et al.* (1995, 1997) for space-time interpolation of ΔpCO_2, the Wanninkhof (1992) formulation of wind speed dependence of gas transfer coefficient, and the NCEP 40-year mean monthly wind speed. We have found that, for the North Atlantic Ocean (including high-latitude, temperate, and equatorial areas), a precision of 0.1 Pg C/yr may be attainable with N-S transects 10° (1,000–400 km) apart with a repeat frequency of 3 or 4 times a year. On the other hand, the North Pacific requires N-S transects more closely spaced than 10°, also with a repeat frequency of 3 or 4 times annually. Greater spacing causes significantly smaller ocean CO_2 flux. For a given number of ocean transects, N-S transects appear to yield better flux values than E-W transects. Decreasing the sampling from 12 to 3 months of the year at equal intervals does not seem to have an effect on CO_2 flux estimates. This would suggest that, given the spatial distribution needed, ocean transect sampling aboard transoceanic ships may be a more effective means than the time-continuous observations that can be made at fixed locations using moored buoys.

While it is clear that taking data that has been binned into $4° \times 5°$ areas and 1-month time blocks over the last 30 years adds considerable smoothing to the data, the results of this study support those using actual transects and time series that used measurements taken at much higher resolution (1–2 orders of magnitude) (Sweeney *et al.*, 2000). For the North Pacific, Sweeney *et al.* (2000) suggest that samples should be taken every 200–600 km while in the North Atlantic samples could be taken as little as every 2,000 km. Time-series stations analyzed by Sweeney *et al.* (2002) suggest a slight increase in sampling frequency that may be due to scarcity of data in some seasons in parts of the North Pacific and North Atlantic. Despite this discrepancy it is clear that short-term variability ($<$ monthly) has little effect on the annual averages.

E.5 References

Sweeney, C., T. Takahashi, and A. Gnanadesikan (2002): Spatial and temporal variability of surface water pCO_2 and sampling strategies. Appendix D in this report.

Takahashi, T., T.T. Takahashi, and S.C. Sutherland (1995): An assessment of the

role of the North Atlantic as a CO_2 sink. *Philos. Trans. R. Soc. Lond., Series B, 348*, 143–152.

Takahashi, T., R.A. Feely, R. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi (1997): Global air-sea flux of CO_2: an estimate based on measurements of sea-air pCO_2 difference. *Proc. Natl. Acad. Sci., 94*, 8292–8299.

Toggweiler, J.R., K. Dixon, and K. Bryan (1989): Simulations of radiocarbon in a coarse resolution world ocean model I: Steady state pre-bomb distributions. *J. Geophys. Res., 94*, 8217–8242.

Wanninkhof, R. (1992): Relationship between wind speed and gas exchange. *J. Geophys. Res., 97*, 7373–7382.

Appendix F

The Role of Remote Sensing in an Ocean CO_2 Observing Plan

Mary-Elena Carr, Charles R. McClain, and J. Keith Moore

F.1 Introduction

Remote sensing of the world ocean presently provides measurements of sea-surface temperature (SST), sea surface height, wind speed and direction, and ocean color, from which chlorophyll concentration and aerosol optical thickness are obtained. It is well known that satellites enable excellent spatiotemporal coverage and consistency of methodology, but they are limited by what they can measure, their resolution, and depth of penetration. Conversely, the sampling coverage that is only possible from satellite-borne sensors provides a powerful capability for extrapolating, integrating, and constraining other observations and model results.

Although the need to lobby for and defend the continuation of satellite-borne ocean-observing systems may not be as pressing as for in situ observations, it would be a mistake to take the present capabilities for granted. It is important that we acknowledge and highlight advances in the development of algorithms to improve estimation of biogeochemical variables, and that we encourage and request the development of new sensor suites. There are proposed missions (such as the Ocean Salinity Mission) that are critical to carbon observations and that would benefit from outspoken support from the carbon community.

F.2 General Background

F.2.1 Biogeochemical variables that can be measured or inferred from satellite-borne sensors

The following components of the carbon cycle and accompanying oceanographic processes can be addressed with remote-sensing observations.

Air-sea exchange of CO_2

Estimates of two major components relating to the exchange of CO_2 between ocean and atmosphere can be improved upon by using remote sensing: the air-sea gas exchange coefficient, and oceanic pCO_2. The air-sea exchange coefficient is usually parameterized using wind speed. Scatterometers provide global observations of wind speed and direction on a daily basis. Likewise improved parameterizations that use measurements of surface roughness (from which capillary wave height is estimated) from the TOPEX/Poseidon altimeter (Frew *et al.*, 1999) or from scatterometers (such as QuikSCAT or

SeaWinds) may give a more direct value of the exchange rate than wind-based parameterizations.

Much research has gone into parameterizing the partial pressure of CO_2 in ocean water (pCO_2) with SST or salinity (Boutin *et al.*, 1999; Loukos *et al.*, 2000). The general consensus is that the relationships between SST and pCO_2 are not globally applicable and that they change in space and time (Lee *et al.*, 1998). The use of salinity, which is proposed to be measured remotely on European and U.S. satellite missions would enable the application of local relationships obtained from shipboard and moored or drifting platforms. Although chlorophyll concentration (obtained from ocean color) is often invoked as a factor determining pCO_2, the algorithms that would incorporate it are still under development.

In addition to the development of empirical relationships between pCO_2 and remotely measured oceanographic variables, the latter also provide information on oceanographic processes that control patterns and variability of carbon fluxes, such as water masses, upwelling, subduction, or biological productivity.

Primary production

The rate of carbon uptake or photosynthesis is a process of major importance as it draws down carbon in surface waters. The advent of ocean color measurements, from which chlorophyll concentration can be derived, has fueled the development of a suite of primary production (PP) models that use chlorophyll concentration, irradiance, and SST (all measured remotely). There are several types of PP models with varying degrees of complexity (Behrenfeld and Falkowski, 1997). At present, they provide estimates within a factor of two when compared with in situ rates of carbon uptake determined with ^{14}C uptake measurements (Campbell *et al.*, submitted). Research is ongoing to improve their performance. All PP algorithms require a measure of irradiance at the ocean surface (photosynthetically available radiation from 400–700 nm or PAR) and its decrease with depth (which can be estimated with PAR and the light attenuation coefficient, k), both of which are also accessible from ocean color.

New or export production

Although models exist to estimate primary production, our estimations of new or export production carry an additional level of uncertainty. The methods used address various aspects of the export process. Most estimates utilize a relationship between f-ratio and SST or primary production, nitrate or chlorophyll concentration (Sathyendranath *et al.*, 1991; Laws *et al.*, 2001). These approaches can be used with satellite-derived measurements, but will only be as good as the primary production estimate and the inferred f-ratio, which may vary regionally and with time. Other potential approaches directly address the supply of nitrate via heat fluxes (and the relationship with nitrate) or precipitation. Other estimates are based on nutrient uptake as

derived from changes in SST (Goes *et al.*, 2000) or heat content (Carr *et al.*, 1999).

Community structure

Information on the role of community structure and export fluxes can be employed for those situations in which one or more functional groups can be identified with space-based observations. A few organisms have been identified from space, namely, coccolithophorids (Brown and Yoder, 1994) and the diazotroph *Trichodesmium* (Subramaniam *et al.*, 1999). The concentration of calcium carbonate ($CaCO_3$) is derived routinely from ocean color and work is ongoing to improve algorithm implementation for both SeaWiFS and MODIS (Gordon *et al.*, in preparation). Other efforts are underway to distinguish *Phaeocystis* and diatoms, usually with the help of one or more sensors and ancillary in situ information. The differences in pigmentation are not readily distinguishable remotely, as they require fourth-order differentiation of the absorption spectra of cultures in laboratory flasks. The groups that have been distinguished so far are characterized by their unique "packaging" characteristics, such asthe coccoliths of *Emiliana* and the gas vesicles of *Trichodesmium*.

Partitioning of carbon species

It is important that we distinguish the partitioning of carbon species (POC, DOC). A recent study has provided an estimate of POC using reflectance measurements (Stramski *et al.*, 1999). Although applied to the Southern Ocean, this method may be extended, with proper in situ validation, to the global ocean. DOC is a much trickier problem. Although there are algorithms to quantify colored dissolved organic matter (CDOM) (e.g., Hoge and Lyon, 1999), the relationship between CDOM and DOC is not straightforward (Nelson *et al.*, 1998).

Photochemistry

Dissolved organic carbon undergoes transformation due to the effect of visible and ultraviolet light, generating dissolved inorganic carbon, DIC (Blough, 1992). This photochemical conversion of dissolved organic matter can also be addressed with remote sensing information (Cullen *et al.*, 1997, 1999; Johanssen *et al.*, 2000). Models with an experimental basis, comparable to those of primary production, utilize measurements of reflectance (which provide concentrations of CDOM) and of irradiance to derive the rate of destruction of DOC and production of DIC. Laboratory-derived action spectra, modeled irradiance, and estimated CDOM vs. total absorption can be used to quantify rates of photochemical transformation (Cullen *et al.*, 1999).

Aerosol concentrations

Aerosol concentrations can be measured using reflectance sensors designed for other applications, such as AVHRR, SeaWiFS, or MODIS, or those de-

signed specifically for aerosols such as TOMS or MISR. Atmospheric aerosols are diverse, including smoke and dust, and methods are being developed to distinguish between the various absorbing components. A special issue of the *Journal of Geophysical Research* on the Asian Dust Outbreak of February 2000 was published in August 2001 (e.g., Husar *et al.*, 2001). Tracking dust deposition patterns can provide an estimate of the supply of terrestrial iron to the ocean surface, with consequences for biological carbon uptake.

Small-scale variability

Satellites also provide an unprecedented opportunity to quantify variability and processes that are unresolved by coarse models and necessarily inadequate sampling campaigns. The quasi-synoptic coverage is an amazing benefit, even considering the loss of data due to cloud coverage in sensors that measure light. The TOPEX/Poseidon altimeter enables improved quantification of eddies for biogeochemical applications (Siegel *et al.*, 1999) and for ocean circulation models. Coastal processes, which require higher spatial and temporal resolution than is usually possible from sun-synchronous sensors, can benefit from geo-stationary platforms and multispectral reflectance measurements. The proposed NASA-NOAA Special Events Imager (SEI) would fly on a GOES satellite in the early 2000s; the spatial resolution would be 300 m and repeat sampling would occur within minutes.

F.2.2 Relevant Existing Remote-Sensing Missions

Table F-1 reviews the major satellite sensors currently in orbit, the variables they are designed to measure, their sampling resolution, and the accuracy of their measurement.

F.3 New Developments

F.3.1 Sensors

Multiple sensors that measure the same variable are presently space-borne, or will be shortly. Combining data from multiple sensors (specifically ocean color, SST, and scatterometers) will lead to enhanced spatiotemporal coverage. Likewise, newly measured properties, such as natural fluorescence, will contribute to our understanding of the carbon system. Microwave data to infer SST are not impeded by cloud cover and will increase coverage, especially when merged with existing infrared measurements (Wentz *et al.*, 2000).

F.3.2 Programs

The International Ocean-Colour Coordinating Group (IOCCG) has a mandate to act as liaison and communication channel between users, managers, and agencies in the ocean color arena (`http://www.ioccg.org/about.html`). Primary objectives include training, advocating the importance of ocean color data, and facilitating the merging and access to ocean color data.

Table F-1: Major satellite sensors in orbit and their characteristics.

Sensor[1]	Variable	Resolution[2]	Accuracy[2]
AVISO merged TOPEX/Poseidon and ERS1/2	SSH	0.25 deg, 10 day	5 cm
QSCAT	Wind vector	0.5 deg, 12 hour	0.5 m/s
SSM/I	Wind speed	0.5 deg, 12 hour	1.3 m/s
AVHRR	SST	9 km (Pathfinder), 12 hour	0.5C
TMI	SST	0.5 deg, 3 day	0.6C
SeaWiFS	Chlorophyll PAR $CaCO_3$ CDOM Aerosols	9 km, 8 day	10%
MODIS	SST Chlorophyll $CaCO_3$ CDOM Primary production Aerosols Fluorescence	4.6 km, daily–weekly	
MISR	Aerosols	17 km, 9 days	

[1]Acronyms: AVISO—Archiving, validation and interpretation of satellites oceanographic data; AVHRR—Advanced very high resolution radiometer; ERS—European remote sensing satellite; MISR—Multi-angle imaging spectro-radiometer; MODIS—Moderate-resolution imaging spectroradiometer; QSCAT (or QuickScat)—Quick scatterometer; SeaWiFS—Sea-viewing wide field-of-view sensor; SSM/I—Special sensor microwave imager; TMI—Tropical microwave imager.

[2]The resolution and accuracy requirements are for merged and standard mapped data products. Actual spatial resolution of the instrument is higher along track and less between tracks. The temporal resolution provided is approximately that necessary to cover the world ocean. The resolution also corresponds to data points acquired. Actual observations are much less in the case of infrared and visible observations such as ocean color or radiometer because of cloud cover. It takes at least three ocean-color sensors (with different mission coverage characteristics) to cover 60% of the world ocean in 4 days given climatological cloud cover (Gregg and Woodward, 1998).

These goals are relevant to experienced users and to a community that does not wish to specialize in remote sensing.

NASA's program for Sensor Intercomparison and Merger for Biological and Interdisciplinary Oceanic Studies (SIMBIOS) has four primary activities: (1) data product validation, (2) sensor calibration, (3) data merger algorithm evaluation, and (4) satellite data processing. More information can be found at `http://simbios.gsfc.nasa.gov/` and in McClain and Fargion (1999).

F.4 What Is Missing?

Programs for technology development (such as SBIRs), especially for field instrumentation, are not as well managed within NASA (and perhaps other agencies) as they should be. It is important that this key aspect of observa-

tional science not be neglected. A concerted and collaborative effort of all agencies could provide major breakthroughs in our measuring capabilities.

F.5 Conclusions

Satellite data are neither perfect nor complete. Though the standard products of most sensors are of high quality (in most places), compound products (such as PP, new production, functional type, etc.) should not be taken at face value.

It is extraordinarily important that emphasis be placed on satellite observations concurrently with field programs. Satellites can provide:

- The best possible coverage in space and time, thus enabling extrapolation of point or line measurements. Satellites provide, in fact, the only possibility for global ocean measurements.
- A context for oceanographic processes both in space and time (e.g., presence of eddies or plumes, shifts in wind direction) that can lead to improved understanding of the underlying oceanography.
- Data to force, assimilate into, or constrain models.
- An estimate of scales of variability that are not accessible except via process studies (e.g., eddies, wind events, bloom dynamics).

It is important that the seagoing community request new and improved sensors. For example, the salinity mission will lead to better determinations of global sea surface pCO_2 patterns and variability.

Satellite data cannot replace field observations, but they play a vital complementary role. Both field and remote-sensing approaches are necessary to tackle the goals of understanding and quantifying global patterns in carbon dynamics.

F.6 References

Antoine, D., and A. Morel (1995a): Modeling the seasonal course of the upper ocean pCO_2. 1. Development of a one-dimensional model. *Tellus, B47*(1–2), 103–121.

Antoine, D., and A. Morel (1995b): Modeling the seasonal course of the upper ocean pCO_2. 2. Validation of the model and sensitivity studies. *Tellus, B47*(1–2), 122–144.

Bailey, S.W., C.R. McClain, P.J. Wendell, and B.D. Scheiber (2000): Normalized water-leaving radiance and chlorophyll-a match-up analyses. In *SeaWiFS Postlaunch Calibration and Validation Analyses, Part 2*, C.R. McClain *et al.* NASA Tech. Memo 2000-206892, vol. 10, S.B. Hooker and E.R. Firestone (eds.), NASA Goddard Space Flight Center, Greenbelt, MD, 45–52.

Behrenfeld, M.J., and P.G. Falkowski (1997): A consumer's guide to phytoplankton primary productivity model. *Limnol. Oceanogr., 42*(7), 1479–1491.

Blough, N.V. (1992): Photochemistry in the oceans. *Oceanus, 35*(1), 36–37.

Boutin, J., J. Etcheto, Y. Dandonneau, D.C.E. Bakker, R.A. Feely, H.Y. Inoue, M. Ishii, R.D. Ling, P.D. Nightingale, N. Metzl, and R. Wanninkhof (1999): Satellite sea surface temperature: a powerful tool for interpreting in situ pCO_2 measurements in the equatorial Pacific Ocean. *Tellus, B51*(2), 490–508.

Brown, C.W., and J.A. Yoder (1994): Coccolithophorid blooms in the global ocean. *J. Geophys. Res., 99*(C4), 7467–7482.

Campbell, J., D. Antoine, R. Armstrong, W. Balch, R. Barber, M. Beherenfeld, R. Bidigare, J. Bishop, M.-E. Carr, W. Esaias, P. Falkowski, N. Hoepffner, R. Iverson, D. Kiefer, S. Lohrenz, J. Marra, A. Morel, J. Ryan, V. Vedernikov, K. Waters, C. Yentsch, and J. Yoder (2001): Comparison of algorithms for estimating ocean primary production from surface chlorophyll, temperature, and irradiance. *Global Biogeochem. Cycles*, submitted.

Carr, M.-E., O. Sato, and P. Polito (1999): A new value for oceanic new production from heat storage measured by satellite. *Eos Trans., AGU, 80*(49), 27.

Cullen, J.J., R.F. Davis, J.S. Bartlett, and W.L. Miller (1997): Toward remote sensing of UV attenuation, photochemical fluxes and biological effects of UV in surface waters. 1997 ASLO Winter Meeting, Santa Fe, NM.

Cullen, J.J., R.F. Davis, B. Nieke, S. Johannessen, and W.L. Miller (1999): Estimating UV attenuation and photochemical reaction rates from remote sensing of ocean color. XXII General Assembly, IUGG; IAPSO Symposium, Birmingham, UK, July 1999.

Frew, N.G., D.M. Glover, E.J. Bock, S.J. McCue, and W.R. McGillis (1999): Improved estimates of air-sea CO_2 exchange rates from dual frequency altimeter backscatter. *Eos Trans., AGU, 80*(49), 153.

Goes, J.I., T. Saino, H. Oaku, J. Ishizaka, C.S. Wong, and Y. Nojiri (2000): Basin scale estimates of sea surface nitrate and new production from remotely sensed sea surface temperature and chlorophyll. *Geophys. Res. Lett., 27*(9), 1263–1266.

Gordon, H.R., Retrieval of coccolithophore calcite concentration from SeaWiFS imagery, manuscript in preparation.

Gregg, W.W., and R.H. Woodward (1998): Improvements in coverage frequency of ocean color: combining data from SeaWiFS annd MODIS. *IEEE Trans. Geosci. Remote Sens., 36*, 1350–1353.

Hoge, F.E., and P.E. Lyon (1999): Spectral parameters of inherent optical property models: Method for satellite retrieval by matrix inversion of an oceanic radiance model. *Appl. Opt., 38*(9), 1657–1662.

Husar, R.B., D.M. Tratt, B.A. Schichtel, S.R. Falke, F. Li, D. Jaffe, S. Gasso, T. Gill, N.S. Laulainen, and F. Lu (2001): Asian dust events of April 1998. *J. Geophys. Res., 106*(16), 18,317–18,330.

Johanssen, S.C., W. Miller, and J.J. Cullen (2000): An estimate of the marine photochemical source of dissolved inorganic carbon from SeaWiFS ocean color. *Eos Trans., AGU, 80*(49), 62.

Laws, E.A., P.G. Falkowski, W.O. Smith, H. Ducklow, and J.J. McCarthy (2001): Temperature effects on export production in the open ocean. *Global Biogeochem. Cycles, 14*(4), 1231–1246.

Lee, K., R. Wanninkhof, T. Takahashi, S.C. Doney, and R.A. Feely (1998): Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide. *Nature, 396*(6707), 155–159.

Loukos, H., F. Vivier, P.P. Murphy, D.E. Harrison, and C. Le Quere (2000): Interannual variability of equatorial Pacific CO_2 fluxes estimated from temperature and salinity data. *Geophys. Res. Lett., 27*(12), 1735–1738.

McClain, C.R., and G.S. Fargion (1999): SIMBIOS Project 1999 Annual Report, NASA Tech. Memo. 19990209486, NASA Goddard Space Flight Center, Greenbelt, MD, 128 pp.

Nelson, N.B., D.A. Siegel, and A.F. Michaels (1998): Seasonal dynamics of coloured dissolved material in the Sargasso Sea. *Deep-Sea Res. I, 45*(6), 931–957.

Sathyendranath, S., T. Platt, E.P.W. Horne, W.G. Harrison, O. Ulloa, R. Outerbridge, and N. Hoepffner (1991): Estimation of new production in the ocean by compound remote-sensing. *Nature, 353*, 129–133.

Siegel, D.A., D.J. McGillicuddy, and E.A. Fields (1999): Mesoscale eddies, satellite altimetry, and new production in the Sargasso Sea. *J. Geophys. Res., 104*(C6), 13,359–13,379.

Stramski, D., R.A. Reynolds, M. Kahru, and B.G. Mitchell (1999): Estimation of particulate organic carbon in the ocean from satellite remote sensing. *Science, 285*(5433), 239–242.

Subramaniam, A., E.J. Carpenter, and P.G. Falkowski (1999): Bio-optical properties of the marine diazotrophic cyanobacteria Trichodesmium spp. II. A reflectance model for remote sensing. *Limnol. Oceanogr., 44*(3), 618–627.

Wentz, F.J., C. Gentemann, D. Smitt, and D. Chelton (2000): Satellite measurements of sea surface temperature through clouds. *Science, 288*(5467), 847–850.

Appendix G

Instrumentation and Platforms for Observations of Sea Surface pCO_2 and Related Properties

G.1 Introduction

Lack of data hinders progress in determining the spatial and temporal variability of surface pCO_2 and related biogeochemical tracers. Strategies are needed to increase spatial coverage and sampling frequency at reduced per datum cost. In this context, particular emphasis should be placed on the development of new sensor technology, particularly on instruments for measuring CO_2 and related quantities autonomously (Goyet *et al.*, 1992; DeGrandpre *et al.*, 1995; Friederich *et al.*, 1995; Tokar and Dickey, 2000; Varney, 2000). In particular, development should be encouraged for systems that can be interchangeably mounted on moorings and profiling floats or used as autonomous systems on volunteer observing ships (VOS). Infrastructure currently in place for other efforts such as buoys, drifters, commercial ships, and other ocean structures are prime platforms for sustained observations. Key physical parameters such as wind, salinity, and temperature are often already available from such platforms. Examples include the profiling PALACE and ARGO floats in the Atlantic and Pacific under the CLIVAR Program that currently provide T and S measurements (Davis *et al.*, 2000), the TOGA and PIRATA mooring array that provide wind, T, and current measurements, and the drifting buoy network that provides SST and sometimes pressure and wind. A combination of surface drifters, CO_2 sensors on profiling floats, and sensor arrays along mooring lines could provide a critical connection between surface and subsurface fields. In this section we describe some autonomous instruments and observing platforms that will allow us to study CO_2 and associated bioactive parameters.

G.2 Autonomous Sensors for Moorings, Drifters, Floats, and Volunteer Observing Ships

During recent years, a wide range of autonomous sensors have been developed and improved. A noninclusive list of sensors for chemical properties includes the following.

G.2.1 Sea surface pCO_2

Several autonomous and quasi-autonomous shipboard sensors have been developed by a variety of groups. One set is primarily based around LiCor infrared analyzers (Cooper *et al.*, 1998; Feely *et al.*, 1998; Wanninkhof and

Thoning, 1993). The surface water pCO_2 is determined by equilibrating surface water, pumped on board ship, with a headspace. The units commonly measure surface water and air mole fractions of CO_2. Standardization occurs by using compressed gas standards. Laboratory and shipboard intercomparison studies (Koertzinger *et al.*, 1999) have shown reasonable agreement between various units. It is thought that the major differences in results are caused by poorly calibrated thermometers, differences in compressed gas standards, and incomplete equilibration of the water flowing through the equilibrators. No commercial company currently builds a complete unit.

In situ sensors have been developed for moorings and drifters based either on an equilibrator design (Friederich *et al.*, 1995) or spectrophotometric analysis (DeGrandpre, 1995, 1999; Merlivat and Brault, 1995). In the latter design, CO_2 in seawater is equilibrated with a pH-sensitive dye across a gas-permeable membrane and the change in absorbance is measured with a small spectrophotometer. Three units, the SAMI, CARIOCA, and YSI (Yellow Springs Instruments) sensors are or will shortly be commercially available. The in situ sensors currently do not have any standards for calibration, although the IR-based unit is referenced against air.

G.2.2 pO_2

O_2 concentration measurements in the mixed layer reflect net production and gas fluxes over the O_2 residence time (typically 2 weeks). Values in the seasonal thermocline reflect net production since the onset of springtime stratification, because the thermocline is effectively capped off from the surface. O_2 can be measured continuously on moorings or along cruise tracks, thereby allowing one to collect extensive data sets that can be used to constrain biological fluxes in the upper ocean.

Several autonomous pO_2 analyzers are available for oceanographic use that can be installed on drifters, buoys, and VOS for oceanographic measurements. Rapid response units are used on CTDs. The in situ units currently available from Langdon Enterprises and YSI have an endurance of up to about 3 months without discernable drift under optimal conditions. As with the pCO_2 units, lack of calibration limits use in the fully autonomous mode. The fast response polarographic units installed on CTDs exhibit more drift on timescales of days to weeks.

G.2.3 Total dissolved gas pressure

Total dissolved gas pressure allows one to separate the contribution of physical and biological processes to dissolved O_2 supersaturation (Spitzer and Jenkins, 1989; Emerson *et al.*, 1991). The system is based on measuring the pressure under a gas-permeable membrane. An autonomous sensor is available through Pro-Oceanus Systems (McNeil *et al.*, 1995).

G.2.4 Autonomous NO_3^- and POC sensors

Euphotic zone concentrations of NO_3^- reflect seasonal net production as well as the restoration of nutrients by vertical mixing. POC concentrations give

an important constraint on the fate of organic carbon produced in the mixed layer and the relationship between net and export production. Sensors for these properties now exist and have been successfully deployed on moorings (Johnson and Coletti, in preparation).

G.2.5 Other properties

Autonomous instruments can measure other relevant biogeochemical properties, including photosynthetically active radiation (PAR), spectral properties, and fluorescence. Automated water samplers permit sampling for trace metals and other properties. There are also, of course, autonomous instruments for measuring physical properties, including Acoustic Doppler Current Profilers, current meters, and temperature/salinity measuring devices.

G.2.6 Multiparameter sensors

A high-precision in situ instrument for TCO_2, pCO_2, TA, and pH is being developed by Robert Byrne and colleagues at the University of South Florida using a compact spectrophotometric analysis system (SEAS) (Byrne *et al.*, 2001). The system is capable of spectral analysis from 400 to 750 nm in both absorbance and fluorescence modes. The sample cell is configured to use long-pathlength liquid core wave guides (10–500 cm) for pH, pCO_2, total inorganic carbon, and total alkalinity. The system is deployed with the bottom-stationed ocean profiler (BSOP) or other similar profilers, but can be modified for just about any platform. These devices have been designed to carry SEAS sensors and other instruments, and telemeter chemical and physical data after each cycle.

G.3 Conclusions

In principle, all of these instruments can be deployed on ships and moorings, although a limited subset is likely to be more practical. Moorings permit long-term, continuous observations at selected locations. VOS allow chemical and biological properties to be measured over broad reaches of the oceans, but they sample the mixed layer only. Recently developed towed systems allow almost continuous depth profiling of many dissolved properties in the upper ∼100–200 m along cruise tracks of research ships, but at reduced speed.

Sensors on drifters, floats, and moorings add considerably to our ability to sample the oceans. Fewer properties can be measured, but it is possible to measure pCO_2 and other important properties, including T, S, NO_3^-, and O_2. Calibration and long-term stability remain significant issues for the long-term deployments advocated here.

G.4 References

Byrne, R.H., E. Kaltenbacher, E.T. Steimle, and X. Liu (2001): Design of autonomous in-situ systems for measurement of nutrient and CO_2-system param-

eters. In *Proceedings of the International Workshop on Autonomous Measurements of Biogeochemical Parameters in the Ocean*, K. Harada and T. Dickey (eds.), Honolulu, HI (in press).

Cooper, D.J., A.J. Watson, and R.D. Ling (1998): Variation of pCO_2 along a North Atlantic shipping route (UK to the Caribbean): A year of automated observations. *Mar. Chem., 60*, 147–164.

Davis, R.E., W.S. Kessler, R. Lukas, R.A. Weller, D.W. Behringer, D.R. Cayan, D.B. Chelton, C. Eriksen, S. Esbensen, R.A. Fine, I. Fukumori, M.C. Gregg, E. Harrison, G.C. Johnson, T. Lee, N.J. Mantua, J.P. McCreary, M.J. McPhaden, J.C. McWilliams, A.J. Miller, H. Mitsudera, P.P. Niiler, B. Qiu, D. Raymond, D. Roemmich, D.L. Rudnick, N. Schneider, P.S. Schopf, D. Stammer, L. Thompson, and W.B. White (2000): Implementing the Pacific Basin Extended Climate Study (PBECS). U.S. CLIVAR Report, 109 pp., available from the U.S. CLIVAR Project Office.

DeGrandpre, M.D., T.R. Hammer, S.P. Smith, and F.I. Sayles (1995): In situ measurements of seawater pCO_2. *Limnol. Oceanogr., 40*, 969–975.

DeGrandpre, M.D., M.M. Baehr, and T.R. Hammar (1999): Calibration-free optical chemical sensors. *Anal. Chem., 71*, 1152–1159.

Dickey, T. (1991): The emergence of concurrent high-resolution physical and bio-optical measurements in the upper ocean and their applications. *Rev. Geophys., 29*, 383–413.

Emerson, S., P. Quay, C. Stump, D. Wilbur, and M. Knox (1991): O_2, Ar, N_2, and Rn-222 in surface waters of the subarctic ocean: Net biological production. *Global Biogeochem. Cycles, 5*, 49–69.

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. *Anal. Chim. Acta, 377*, 185–191.

Friederich, G.E., P.G. Brewer, R. Herline, and F.P. Chavez (1995): Measurements of sea surface partial pressure of CO_2 from a moored buoy. *Deep-Sea Res., 42*, 1175–1186.

Goyet, C., D.M. Walt, and P.G. Brewer (1992): Development of a fiber optic sensor for measurement of pCO_2 in sea water: Design criteria and sea trials. *Deep-Sea Res., 39*, 1015–1026.

Johnson, K.S., and L. Coletti. In situ ultraviolet spectrophotometry for high resolution and long term monitoring of nitrate, bromide and bisulfide in natural waters. *Limnol. Oceanogr.*, in preparation.

Koertzinger, A., L. Mintrop, and J. Duinker (1999): The international intercomparison exercise of underway fCO_2 systems during R/V *Meteor* cruise 36/1 in the North Atlantic Ocean. ORNL, Oak Ridge, TN.

McNeil, C.L., B.D. Johnson, and D.M. Farmer (1995): In situ measurement of dissolved nitrogen and oxygen in the ocean. *Deep-Sea Res., 42*, 819–826.

Merlivat, L., and P. Brault (1995): CARIOCA buoy: Carbon Dioxide Monitor. *Sea Technol., 10*, 23–30.

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.

Tokar, J.M., and T.D. Dickey (2000): Chemical sensor technology—Current and future applications. In *Chemical Sensors in Oceanography*, M.S. Varney (ed.), Gordon and Breach Scientific Publishers, Amsterdam, 303–329.

Varney, M.S., ed. (2000): *Chemical Sensors in Oceanography*. Gordon and Breach Scientific Publishers, Amsterdam, 333 pp.

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.

Wunsch, C. (1996): *The Ocean Circulation Inverse Problem*. Cambridge University Press, Cambridge, UK, 442 pp.

Appendix H

Efforts by the European Community

H.1 CAVASSOO

The European Community project CAVASSOO (Carbon Variability Studies by Ships of Opportunity) was approved for funding in fall 2000 and started formally in 2001. CAVASSOO is aimed at providing an improved estimate of the uptake of CO_2 by the North Atlantic, and how this varies from season to season and year to year. Results will, in turn, assist in constraining estimates of European and North American terrestrial (vegetation) sinks, using atmospheric inverse modeling techniques. To obtain whole-basin estimates, we will set up four routes (see Fig. H-1) on which automated surface pCO_2 and related measurements will be made using ships of opportunity. To interpolate between these transects, which are few in number but frequent in time, we will use the existing data on CO_2 measurements to inform the interpolation. The new data and historical data will be made rapidly available. Combined with ocean carbon models and atmospheric transport models, our data will result in improved estimates of the net CO_2 flux over the North Atlantic, Europe, and North America. The overall objective can be broken into subsidiary objectives:

1. Establish a basic North Atlantic surface pCO_2 observing system.
2. Produce and make available a North Atlantic pCO_2 database.
3. Assess errors and uncertainties in existing pCO_2 climatologies.
4. Estimate seasonal air-sea CO_2 fluxes for the North Atlantic.
5. Evaluate ocean carbon models with regard to air-sea flux variability.
6. Improve atmospheric inversion estimates of carbon sources and sinks.

The consortium includes the following groups:

- School of Environmental Sciences, University of East Anglia, Norwich, UK (A.J. Watson, N. Lefèvre).
- Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France (P. Ciais, J. Orr).
- Instituto de Investigaciones Mariñas, Vigo, Spain (A. Ríos, F.F. Pérez).
- Institute of Marine Research at the University of Kiel, Germany (D.W.R. Wallace, A. Körtzinger).
- Geophysical Institute, University of Bergen, Norway (T. Johannessen).

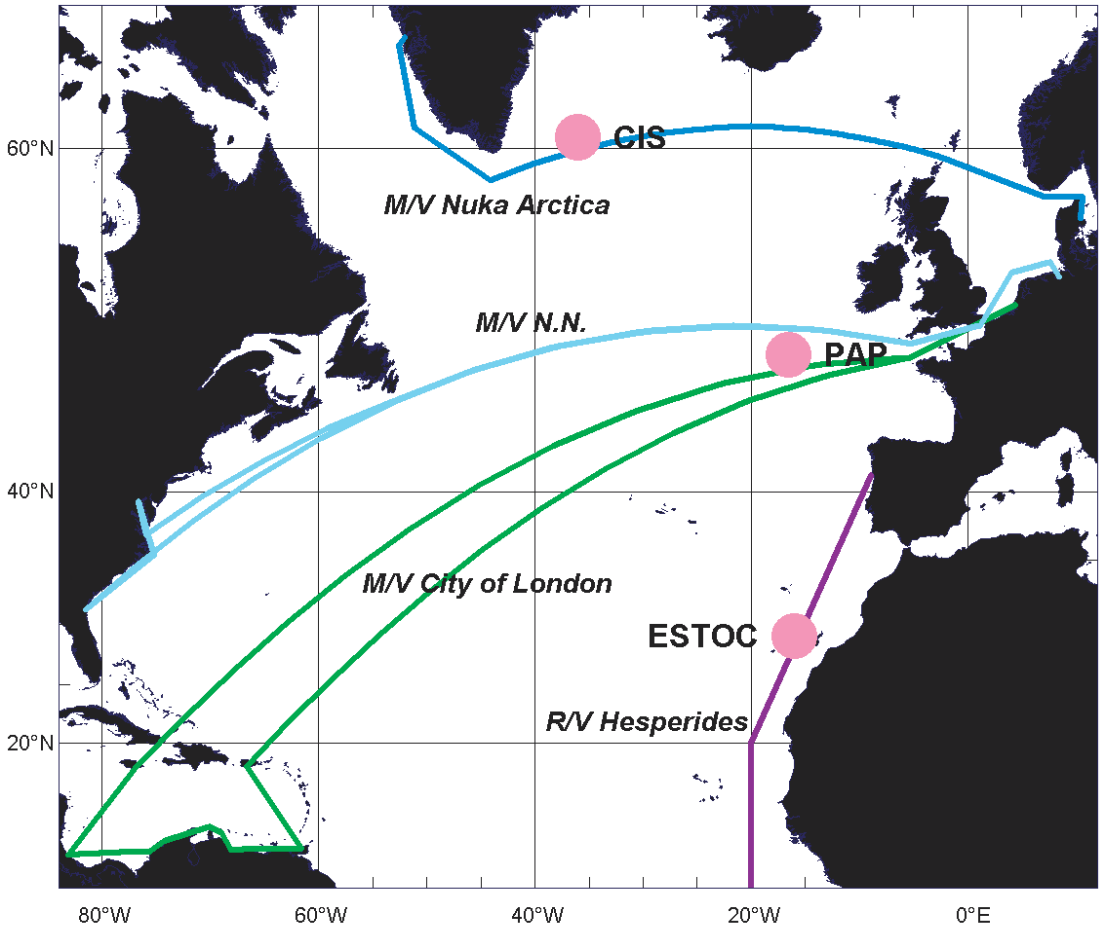


Figure H-1: Proposed ship tracks for automated pCO_2 and related measurements on ships of opportunity in the North Atlantic.

H.2 ANIMATE

The European Community project ANIMATE (Atlantic Network of Interdisciplinary Moorings and Timeseries for Europe) was approved for funding in January 2001 and the 3-year program started 1 December 2001, to continue through November 30, 2004. It will implement a moored observing infrastructure to provide regular observations of ocean carbon cycle variability and processes, from three selected sites in the northeast Atlantic. Each mooring will carry a near-surface CO_2 sensor, upper-layer temperature/salinity sensors, an upward-looking Acoustic Doppler Current Profiler (ADCP), a nutrient and fluorescence sensor, and a deeper sediment trap. Part of the data will be telemetered in real time. The specific sites were chosen to build on existing European time-series measurements and observational efforts/interests. They are representative of distinct biogeochemical regions of the northeast Atlantic, lie close to VOS lines to be implemented as part of CAVASSOO for routine surface pCO_2 measurements, and network with

non-European elements of the North Atlantic observing system. The chosen locations (see Fig. H-1) are ESTOC (European Station for Time-Series in the Ocean Canary Island) near the Canary Islands, PAP (Porcupine Abyssal Plain) west of Ireland, and CIS (Central Irminger Sea). The overall objective can be broken into subsidiary goals:

1. Assure a sustained European carbon cycle time-series infrastructure at three key sites in the northeast Atlantic that are networked within a larger-scale ocean carbon observing system.

2. Unify the present mix of uncoordinated European ship-based and moored repeat measurements in the three target areas and upgrade/replace them with identical, CO_2-relevant moored systems in all sites.

3. Make maximum use of existing infrastructure, instrumentation, hardware, and expertise from different groups; and share/transfer the existing and new elements of the system for joint implementation and operation.

4. Implement real-time telemetry of subsets of the prime data to be collected.

5. Make both the produced data and the mooring infrastructure available to the wider community.

6. Interface intimately with other programs having the same data or infrastructure requirements.

The consortium includes the following groups:

- Institute of Marine Research at the University of Kiel, Germany (U. Send [coordinator], S. Harms, D.W.R. Wallace).

- Southampton Oceanographic Centre, UK (R.S. Lampitt, D.J. Hydes, B. Dupée).

- Department of Geosciences, University of Bremen, Germany (G. Wefer, H.C. Waldmann, V. Ratmeyer).

- Instituto Canario de Ciencias Marinas, Gran Canaria, Spain (E. Pérez-Martell, O. Llinás).

- Marine Research Institute, Reykjavik, Iceland (H. Valdimarsson, O.S. Astthorsson, A. Gislason, J. Ólafsson).