Final Report
DOE Ocean Carbon Sequestration Research Workshop 2005

Held at: Belmont Manor House and Conference Center
Thursday-Friday, May 26 to 27, 2005

Follow-up meeting held at: MBARI and UCLA, September 11-15, 2006

The purpose of this proposal was to fund a workshop to bring together the principal investigators of all the projects that were being funded under the DOE ocean carbon sequestration research program. The primary goal of the workshop was to interchange research results, to discuss ongoing research, and to identify future research priorities. In addition, we hoped to encourage the development of synergies and collaborations between the projects and to write an EOS article summarizing the results of the meeting.

Appendix A summarizes the plan of the workshop as originally proposed, Appendix B lists all the principal investigators who were able to attend the workshop, Appendix C shows the meeting agenda, and Appendix D lists all the abstracts that were provided prior to the meeting.

The primary outcome of the meeting was a decision to write two papers for the reviewed literature on carbon sequestration by iron fertilization, and on carbon sequestration by deep sea injection and to examine the possibility of an overview article in EOS on the topic of ocean carbon sequestration. There has been significant progress on several of these goals since the meeting:

(1) Review of carbon sequestration by iron fertilization:

One of the most interesting results of the meeting was a presentation by John Marshall of iron fertilization simulations carried out at MIT that suggested a much higher efficiency of CO_2 uptake from the atmosphere with a newer generation model (since published by *Dutkiewicz, et al.*, 2006]) than earlier studies had found with an older generation model (cf., *Gnanadesikan, et al.*, 2003). The decision was made that this finding should be investigated with a new set of simulations using other newer generation models with realistic parameterization of biological processes. This research has progressed considerably, with the modeling groups of MIT, Princeton University, UCLA, Stanford University, and Los Alamos National Laboratory participating. A follow up meeting of the principal participants was held on September 11-15, 2006, using remaining funds from the original grant, and three manuscripts are now in an advanced state of preparation:

Chavez, F., et al., in preparation. A review of iron fertilization

Jin, X., N. Gruber, and H. Frenzel, in preparation. Factors impacting the atmospheric uptake efficiency of iron fertilization.

Sarmiento, J. L., R. D. Slater, M. E. Maltrud, and J. Dunne, in preparation. Iron fertilization models revisited.

The new iron fertilization simulation results confirm some of the MIT results of higher efficiency, while also drawing attention to several additional processes not considered in previous studies such as the effect of eddies in an eddy resolving model (Jin et al., in preparation), and the effect of including a realistic atmospheric reservoir in the models as in *Gnanadesikan, et al.* [2003], which leads to a significant reduction in the overall efficiency (cf., Sarmiento et al., in preparation).

(2) Review of carbon sequestration by deep sea injection:

An outline of paper was completed by J. Barry, but this project has not progressed beyond this point.

(3) Overview article for EOS on ocean carbon sequestration.

This idea was put on hold until the issues raised by the MIT study of iron fertilization had been resolved. After the three papers on this topic are completed, we will decide if an overview article is still merited.

References

Dutkiewicz, S., et al. (2006), Controls on ocean productivity and air-sea carbon flux: An adjoint model sensitivity study, *Geophysical Research Letters, 33, L02603*, doi:10.1029/2005GL024987.

Gnanadesikan, A., et al. (2003), Effects of patchy ocean fertilization on atmospheric carbon dioxide and biological production, *Global Biogeochem. Cycles, 17,* doi: 10.1029/2002GB001940.

Appendix A
Proposed plan of the workshop

- The workshop will run for a day and a half.
- During the first day, each PI will summarize their project goals, accomplishments, and plans for future research. The presentations will be organized into two groups on sequestration by (a) iron fertilization and (b) CO_2 injection.
- The project summaries will be followed by paired "pro" and "con" presentations focusing on the following three questions:
  1. Can the sequestration method under consideration contribute toward slowing future growth of CO_2 in the atmosphere?
  2. Can the CO_2 sequestration be verified?
  3. What are the possible side-effects?
- In the evening, after a break and casual dinner, the PI's will meet again either in plenary or in smaller working groups to discuss the "pro" and "con" presentations, identify the major scientific issues hindering our understanding of ocean carbon sequestration, and begin to think about how to write the EOS article.
- The next morning we will meet as a group to review the conclusions of the previous evening and plan the EOS article. We will then break up into groups for discussion and to carry out writing assignments.
- A final session of the group will be convened to summarize the results of the group discussions and come up with a final set of overall conclusions and recommendations.

Appendix B
Meeting Attendees

Name	Institution
Adams, Eric	Massachusetts Institute of Technology
Amthor, Jeff	Department of Energy
Barry, James	Monterey Bay Aquarium Research Institute
Bleck, Rainer	Los Alamos National Laboratory
Bishop, James	Lawrence Berkeley National Laboratory
Carmen, Kevin	Louisiana State University
Chavez, Francisco	Monterey Bay Aquarium Research Institute
Erickson, David	Oak Ridge National Laboratory
Gnanadesikan, Anand	Geophysical Fluid Dynamics Laboratory
Kennett, James	University of California, Santa Barbara
Maltrud, Matthew	Los Alamos National Laboratory
Marshall, John	Massachusetts Institute of Technology
Paytan, Adina	Stanford University
Repeta, Daniel	Woods Hole Oceanographic Institution
Sarmiento, Jorge	Princeton University
Tagliabue, Alessandro	Now at Laboratoire des Sciences du Climat et de l'Environnement
Tsouris, Costas	Oak Ridge National Laboratory
Yager, Patricia	University of Georgia

Appendix C
Meeting agenda

Thursday, May 26
Kickoff Session

8:30 Jorge Sarmiento (Princeton University) Introductions and welcome. Discussion of three questions to be addressed during "debates" and idea of writing an EOS article.

8:40 Jeff Amthor DOE perspective

<u>First Day, Project Reports</u>

FERTILIZATION

Surface Processes

8:50 – 9:05	*Yager, P. L.* – The impact of enhanced nitrogen fixation on carbon sequestration: A reassessment of the inorganic carbon system in Low Nutrient Low Chlorophyll regions
9:05 – 9:20	*Tabliague, A.* – Arrigo grants on (1) Photosynthetic characteristics, carbon metabolism, and nutrient requirements of *P. Antarctica* and diatoms from the Ross Sea, Antarctica and (2) Iron fertilization of the Southern Ocean
9:20 – 9:45	*Paytan, A.* – Organic matter composition, recycling susceptibility, and the effectiveness of the biological pump – An evaluation using NMR spectra of marine plankton

Water Column Processes

9:45 – 10:00	*Bishop, J.* – Autonomous strategies for measurements of global ocean particulate carbon flux
10:00 – 10:15	*Repeta, D.* – Sequestration of dissolved organic carbon in the deep sea
10:15 – 10:45	COFFEE BREAK

Modeling

10:45 – 11:00	*Sarmiento, J. L.* – Carbon sequestration by patch fertilization: A comprehensive assessment using coupled physical-ecological-biogeochemical models
11:00 – 11:15	*Marshall, J.* – Pathways and mechanisms of ocean tracer transport: Implications for carbon sequestration

Debate on Fertilization

11:15 – 12:30 Pro and con 15 minute presentations by *F. Chavez* and *A. Gnanadesikan*, respectively, followed by discussion. The focus of the debate will be on the three questions:

1. Can the fertilization method for sequestration contribute toward slowing future growth of CO_2 in the atmosphere?
2. Can the CO_2 sequestration be verified?
3. What are the possible side-effects?

12:30 – 1:30 LUNCH

INJECTION (Moderated by F. Chavez)

Plume dynamics

1:30 – 1:45 *Tsouris, C.* – Sinking CO_2 particle plumes

Modeling

1:45 – 2:00 *Bleck, R.* – Comparison of Cartesian and isopycnal simulations of oceanic carbon sequestration via iron fertilization and deep injection

Biological Impacts

2:00 – 2:15 *Barry, J.* – Direct experiments on the ocean disposal of fossil fuel CO_2

2:15 – 2:30 *Carman, K. R.* – The influence of deep-sea CO_2 sequestration on small metazoan (meiofaunal) viability and community structure

2:30 – 2:45 *Kennett, J.*, Potential effects of CO_2 hydrates on benthic foraminifera

2:45 – 3:15 COFFEE BREAK

Debate on Injection

3:15 – 4:30 Pro and con 15 minute presentations by Jim Kennett and Jim Barry, respectively, followed by discussion. The focus of the debate will be on the three questions:

1. Can the injection method for sequestration contribute toward slowing future growth of CO_2 in the atmosphere?
2. Can the CO_2 sequestration be verified?
3. What are the possible side-effects?

4:30 – 5:00 Open discussion

Evening: Identification of major scientific issues

8:00 – 9:30 *Small working groups*: Discussion of ongoing research and identification of major scientific issues hindering our understanding of carbon in the ocean.

Friday, May 27

Second Morning: Future directions for research (and possible collaborations)

Plenary sessions to be moderated by J. Sarmiento

8:30 – 9:00	*Plenary session*: report on evening working groups, set topics for discussion during the remainder of the morning, and set writing assignments for EOS article.
9:00 – 10:30	*Working groups*: discussions and writing
10:30 – 11:00	COFFEE BREAK
11:00 – 12:30	*Plenary session*: report on group discussions and decide on a set of conclusions and recommendations for future research needs and for EOS article summary
12:30	LUNCH and adjournment

Appendix D
Abstracts
(All abstracts included even those who did not attend)

Kevin R. Arrigo
Department of Geophysics, Stanford University

Iron fertilization of the Southern Ocean:
Regional Simulation and Analysis of C-sequestration in the Ross Sea

A modified version of the dynamic 3-dimensional mesoscale Coupled Ice, Atmosphere, and Ocean model (CIAO) of the Ross Sea ecosystem has been used to simulate the impact of environmental perturbations upon primary production and biogenic CO_2 uptake. The Ross Sea supports two taxonomically, and spatially distinct phytoplankton populations; the haptophyte *Phaeocystis antarctica* and diatoms. Nutrient utilization ratios predict that *P. antarctica* and diatoms will be driven to nitrate and phosphate limitation, respectively. Model and field data have confirmed that the Ross Sea is iron limited with only two-thirds of the macronutrients consumed by the phytoplankton by the end of the growing season.

In this study, the CIAO model was improved to simulate a third macronutrient (phosphate), dissolved organic carbon, air-sea gas exchange, and the carbonate system. This enabled us to effectively model pCO_2 and subsequently oceanic CO_2 uptake via gas exchange, allowing investigations into the affect of alleviating iron limitation on both pCO_2 and nutrient drawdown.

New Additions

First, cycling of Fe is treated very simply in the current version of CIAO, with a single bio available Fe pool that is augmented from melting sea ice and mixing of Fe-rich deep waters to the surface. Therefore, we will implement a more complex Fe cycle in CIAO by adding state variables for ligand bound and unbound Fe(II) and Fe(III), as well as the processes of photoreduction, scavenging, and redox reactions (described more thoroughly below).

Second, the effectiveness of a Fe-fertilization strategy to sequester carbon depends upon the degree and depth of remineralization within the water column. We will test a number of models of particle flux and remineralization in the Ross Sea and implement these within the framework of CIAO. Models will be tested/developed using high temporal resolution estimates of surface primary production, weekly to monthly resolution sediment trap data from surface (<200 m), intermediate (500 m), and deep waters (1000 m), and vertical profiles of POC, TDIC, DOC, and O_2 collected over a number of annual cycles.

Finally, large-scale biogeochemical GCMs suggest that nitrification (oxidation of ammonium to nitrate) and denitrification in waters where sinking organic carbon from Fe-stimulated phytoplankton blooms is decomposed can be a significant source of N_2O to the atmosphere. In some cases, the radiative heating resulting from the liberation of this potent greenhouse gas can more than offset the impact of a decrease in atmospheric CO_2 resulting from Fe-fertilization. More importantly, model results suggest that the impact of Fe-fertilization on N_2O emissions is greater when the fertilization is carried over small temporal and spatial scales [*Jin and Gruber* 2003]. Unfortunately, the resolution of these models precluded evaluation of this effect for fertilized patches smaller than 1×10^6 km^2, much larger than any in situ fertilization experiment carried out to date. We propose to use a higher resolution regional model (625 km^2) to evaluate N_2O production and its potential impact at the smaller patch sizes likely to be employed in the field.

Hypotheses to be tested

Three major hypotheses will be tested during the course of the proposed study. Hypothesis 1 deals with the degree of Fe-cycle complexity required to simulate the dynamics of added Fe in surface waters; Hypothesis 2 addresses the most effective Fe fertilization strategy given differences in particle flux and export for blooms dominated by different phytoplankton taxa (e.g. diatoms and *P. antarctica*); Hypothesis 3 is concerned with assessing the degree of feedback between CO_2 sequestration and N_2O liberation as a result of Fe additions.

Kevin R. Arrigo
Department of Geophysics, Stanford University

Dale H. Robinson
Romberg Tiburon Center, San Francisco State University

Photosynthetic characteristics, carbon metabolism, and nutrient requirements of Phaeocystis antarctica and diatoms from the Ross, Sea, Antarctica

This is an intensive laboratory study to quantitatively characterize the photophysiology, carbon uptake and metabolism, and nutrient requirements of *P. antarctica* and the major diatom species that dominate the phytoplankton community of the Ross Sea (e.g. *Nitzschia curta*, *Fragilariopsis cylindrus*, and *N. subcurvata*). Previous field studies have not provided definitive answers about the taxon-specific physiological characteristics that determine algal community composition or that can be used to predict the outcome of a Fe-fertilization strategy. In order to understand observed distributions of diatoms and *P. antarctica*, we believe that it is imperative to obtain laboratory data for these taxa under realistic, yet controlled, environmental conditions. In particular, the relative roles of light and Fe in controlling primary production, and particularly in defining phytoplankton species composition, are not well understood in these waters because Fe uptake kinetics and cellular requirements for the relevant phytoplankton taxa have not been measured. Addressing these issues is focus of this proposal.

We propose to use recent isolates of ecologically important species of diatoms and of *P. antarctica* collected from Southern Ocean waters rather than algal clones that are ecologically irrelevant or that have been cultured for many years under unnatural temperature, nutrient, and irradiance conditions and thus may not accurately reflect responses of algae to *in situ* conditions. While we have chosen to focus on taxa that dominate the Ross Sea because this is the system we are most familiar with, we believe that the lessons learned from that system will be applicable to other productive areas of the Southern ocean as well. It is our hope that the knowledge gained during this project will lead to an improved understanding of 1), the relative roles that light and Fe play in controlling phytoplankton community composition in the Southern Ocean, 2) the reason for the vastly different N/P and C/P ratios expressed by diatoms and *P. antarctica* and how important these differences will be to the magnitude of CO_2 removal from surface waters, and 3) how an Fe-fertilization strategy is likely to alter phytoplankton community composition and carbon sequestration under a variety of conditions (e.g. deep versus shallow mixed layers, fertilizing early versus late in the bloom). In addition, the results obtained during this study will be critical for the development of improved taxon-specific parameterizations to be used within the 3-dimensional Coupled Atmosphere, Ice, and Ocean (CIAO) model of the Ross Sea. The added information provided by this proposed study should markedly improve the ability of CIAO to predict with accuracy the ecological consequences of changes in nutrient supply as well as to shifts in climate in productive waters of the Southern Ocean.

Objectives

The main research questions and the specific hypotheses that will be tested during this study are described below in the general framework of two overlying objectives. The first objective is to quantify characteristics of the photophysiology, C metabolism, and nutrient acquisition that determine whether diatoms or *P. antarctica* will dominate the phytoplankton population under varying simulated mixing conditions. The second objective is to determine the role that Fe availability plays in structuring phytoplankton community composition and controlling phytoplankton C-fixation.

Kathy Barbeau
Scripps Institution of Oceanography
University of California, San Diego

Project Summary: Characterizing the production and retention of dissolved iron as Fe(II) across a natural gradient in chlorophyll concentrations in the Southern Drake Passage

Recent mesoscale iron fertilization studies in the Southern Ocean (e.g. SOIREE, EisenEx, SOFeX) have demonstrated the importance of iron as a limiting factor for phytoplankton growth in these high nutrient, low-chlorophyll (HNLC) waters. The unexpected longevity of soluble reduced iron, Fe(II), as documented within iron-enriched waters during these experiments has important implications for the future development of iron fertilization protocols to enhance carbon sequestration in high-latitude oceans. Creation of effective fertilization schemes will require more information about extended lifetimes of Fe(II) in Southern Ocean waters as a means to retain new iron within the euphotic zone. To contribute to our knowledge base, this project involves the study of Fe(II) dynamics across a significant natural gradient in chlorophyll concentrations in the Southern Drake Passage. This area was the focus of a multidisciplinary NSF/OPP-funded investigation in February and March 2004 to determine the influence of mesoscale circulation and iron transport with regard to satellite-observed patterns in sea surface chlorophyll in the region near the Shackleton Fracture Zone. A number of parameters were assessed across this gradient in order to reveal interactions between plankton community structure and iron distributions.

During the Feb/March 2004 cruise, we employed the FeLume chemiluminescence system (Waterville Analytical) to study gradients in Fe(II) in our study area. We found detectable levels of Fe(II) only in the most near-surface samples (upper 10 m) taken during daylight hours, with no apparent strong correlation between Fe(II) concentrations and total Fe concentration or chlorophyll fluorescence. Shipboard studies conducted to determine Fe(II) lifetime in low chlorophyll Drake Passage waters indicated a lifetime of about 46 minutes, in good agreement with previous studies in Southern Ocean waters. Photolysis experiments conducted in natural sunlight on board ship indicated the potential for a diurnal cycle in Fe(II) photoproduction, with maximal Fe(II) photoproduction occuring in low-chlorophyll Drake Passage waters, relative to higher chlorophyll waters sampled east of the Shackleton Fracture Zone.

We are currently pursuing follow-up laboratory studies of Fe(II) photoproduction and ligand binding, using frozen water samples brought back from the Feb/March 2004 cruise. Initial studies of Fe(II) binding by tetrapyrrole-type model ligands (eg. coproporphyrin) have been carried out in UV-irradiated seawater at pH 6 (reduced pH was used to extend the lifetime of Fe(II)). We have observed no Fe(II) binding by porphyrins under these conditions (as analyzed via HPLC separation and UV-Vis spectroscopy). We intend to repeat these experiments at pH 8, keeping temperatures $< 3°$ C to mimic Southern Ocean conditions and to extend the lifetime of Fe(II). We are also pursuing additional photoreduction studies using waters from different endmember stations sampled during the Feb/March 2004 cruise. Currently, we are using a competitive ligand exchange – adsorptive cathodic stripping voltammetry technique to characterize these different water masses with respect to the presence of Fe(III)-binding ligands, and have found that while vertical profiles of ligand concentrations generally show surface depletion throughout our study area, the surface concentrations of ligands in the low-chlorophyll Drake Passage are extremely low relative to the higher chloropyll surface waters east of the Shackleton Fracture Zone. We interpret these patterns as likely being due to the influences of biological ligand production and photochemical ligand destruction. We will be conducting Fe(II) photoproduction studies in these different water masses to determine the influence of Fe(III) ligand concentration on Fe(II) photoproduction. Preliminary results from shipboard studies indicate that higher chlorophyll surface waters containing more Fe(III) ligands may have a less-pronounced diurnal cycle of Fe(II). A high priority of the laboratory studies will be to confirm these interesting preliminary results, which have direct relevance to the evolution of Fe(II) dynamics in Fe-fertilized HNLC Southern Ocean waters.

Jim Barry & Peter Brewer
Monterey Bay Aquarium Research Institute (MBARI)

Direct Experiments on the ocean disposal of fossil fuel CO^2

A major goal of our DoE-funded project, *Direct Experiments on the Ocean Disposal of Fossil Fuel CO_2*, is to evaluate the potential biological consequences of large-scale carbon dioxide sequestration in the deep-sea, particularly near the seabed. Marine animals exposed to elevated CO_2 and reduced pH are faced with several physiological challenges, including reduced oxygen-binding capacity of respiratory proteins, acidosis of animal tissues, metabolic depression, arising from the combined effects of elevated CO_2 and acidosis. Some impacts may be sublethal for individuals, but may reduce rates of activity, growth, and reproduction, thereby affecting population dynamics.

We performed several deep-sea CO2 release experiments to evaluate the survival of infaunal and epibenthic animals exposed during month-long periods to hypercapnic, acidic CO2 dissolution plumes emanating from pools of liquid CO2 released on the seafloor. Results from these experiments indicate that 1) the pH-field in experimental areas is highly variable due to the effects of tidal motions on near-bottom currents, leading to episodic hypercapnia and normocapnia at the experimental site, and 2) infaunal organisms suffer high mortality within ~5 m of CO2 pools, where pH changes were on average quite small (pH reduction of less than 0.1 units). Meiofaunal and macrofauna suffered highest mortalities, determined from changes in abundance or the percentage killed among treatments. The common deep-sea eelpout fish (Pachycara sp.) survived even when positioned near pools of liquid CO2. Although the average pH reductions in CO2 treatments was small, these plots experienced episodes of low pH (changes of -0.2 units or greater) during a small percentage of each experiment. It remains unclear whether the effects of acute, short term hypercapnia or chronic mild hypercapnia had the greatest impact on infaunal survival.

Our focus has shifted to the development of instruments for detailed studies of the effects of hypercapnia in the field and laboratory. We have developed 3 new systems for CO2 studies, including 1) a deep-sea hyperbaric fish trap / respirometer, 2) a benthic respiration system with pH, O2 sensors, and syringe samplers / injectors, and 3) a gas-concentration control system for flow through seawater system. The fish trap respirometer is a free vehicle for the capture of deep-sea fishes (particularly macrourids) and their return to the surface under deep-sea pressures, for physiological studies of hypercapnia. The benthic respiration system can be configured to inject acid into respiration chambers to measure rates of carbon remineralization by the seafloor community under simulated acidic conditions by acid injection. The seawater system will be used for long term studies of deep-sea animals tolerant of surface pressures.

Drazen, J.C., Bird, L.E., Barry, J.P. 2005. Development of a hyperbaric trap-respirometer for the capture and maintenance of live deep-sea organisms. Limnology and Oceanography Methods (submitted).

Barry, J.P, Buck, K.R., Lovera, C., Kuhnz, L, Whaling, P.J. Utility of deep-sea CO_2 release experiments in understanding the biology of a high CO_2 ocean: Effects of hypercapnia on deep-sea meiofauna. Journal of Geophysical Research, Oceans (in press)

Thistle, D., Carman, K.R., Sedlacek, L., Brewer, P.G., Fleeger, J.W., Barry, J.P. Deep-ocean experimental tests of the sensitivity of sediment-dwelling animals to imposed CO_2 gradients. Marine Ecology Progress Series, 289: 1-4

Barry, J.P., Kurt R. Buck, Chris F. Lovera, Linda Kuhnz, Patrick J. Whaling, Edward T. Peltzer, Peter Walz, and Peter G. Brewer (2004) Effects of Direct Ocean CO2 Injection on Deep-Sea Meiofauna. Journal of Oceanography, 60: 759-766

Carman, K.R., Thistle, D., Fleeger, J., Barry, J.P. (2004) The influence of introduced CO2 on Deep-Sea metazoan meiofaunal, Journal of Oceanography, 60(4): 767-772

Jim Bishop
Lawrence Berkeley National Laboratory

Most of our work aims at understanding carbon system processes and how they will change in the future. See www-ocean.lbl.gov for more background. Look forward to seeing every one again in May.

here are my current project descriptions:

1) Autonomous strategies for measurement of global ocean carbon flux

Understanding the biological/physical mechanisms of carbon sedimentation in the oceanic water column is of fundamental importance to the prediction of future levels of atmospheric CO2. Very little is known about the vertical transports and fate of organic and inorganic carbon in the water column at depths between 100 and 1,000 m (also known as the forbidden or Twilight Zone). The scant information obtained to date has been largely limited to short-term-duration ship studies. To overcome this problem, LBNL is developing a prototype optical sediment trap system designed to record the high frequency (hours to days) variations of organic and inorganic carbon sedimentation within the upper one to two kilometers of the ocean over seasonal time scales. This three-year effort aims to realize a fully autonomous imaging optical sediment trap system on a profiling float (Carbon Flux Explorer). Our work will step-wise prove the device at sea in the North Pacific ocean as part of the VERTIGO (expeditions near Hawaii, March and July 2004; near Japan, July-August 2005). In FY06 we aim to realize a fully autonomous Carbon Flux Explorer. The benefit of this work will be technical means to achieve a much improved predictability of how carbon will be sequestered in the ocean in a changing world.

2) Ocean Carbon Dynamics and Transfer Processes: SOFEX and Beyond

Fossil fuel use is enriching the atmosphere in CO2, and there is a high likelihood there will be measurable changes to the earth's climate. How ocean biological systems that are important to atmospheric CO2 will respond to climate-induced physical and chemical changes to the ocean is an open question. Under this project LBNL has investigated ocean carbon dynamics in high-nutrient low-chlorophyll ecosystems of the subarctic North Pacific and Southern Ocean (PJ Lam, PhD thesis; Bishop et al., 2004, Science). The current field work, is a process-oriented study of particulate carbon dynamics and sedimentation as part of the international experiment, VERTIGO. LBNL's Multiple Unit Large Volume in-situ Filtration System and optical biomass concentration sensors were deployed in oligotrophic waters near Hawaii in June and July 2004. Productive waters near Japan will be studied in late summer of 2005. In FY06 we propose to complete sample and data analyses from the 2005 field campaign. We will synthesize all project results with those from the Optical sediment trap project, and with those of other VERTIGO investigators. The benefit will be a much improved and integrated understanding of particulate carbon sedimentation.

Rainer Bleck
Los Alamos National Laboratory

Comparison of Cartesian and Isopycnal Simulations of Oceanic Carbon Sequestration via Iron Fertilization and Deep Injection

This project, which draws on the expertise of 4 LANL and 3 outside investigators, uses numerical models of the global ocean circulation and ocean biogeochemistry to explore the feasibility and long-term consequences of oceanic carbon dioxide sequestration. Two sequestration techniques -- direct injection of liquefied CO_2 in the deep ocean and enhancement of biomass production (photosynthesis) through iron seeding -- are being investigated. The specific goal of this project is to assess the uncertainty of computer projections with emphasis on those related to the modeling of long-term 3-dimensional transport and ventilation processes in the ocean. This is done by conducting parallel simulations in two models that treat ocean circulation numerics in substantially different ways. The two models are the z-coordinate Parallel Ocean Program (POP) and the density coordinate-based Hybrid Coordinate Ocean Model (HYCOM).

These two models obey the same physical laws but use a different mix of dependent and independent physical variables. Solving equations for depth as a function of density rather than density as a function of depth -- which is the principal difference between z coordinate and isopycnic modeling -- results in major differences in model behavior, which in turn causes discernible differences in the projected residence time of sequestered CO_2 in the world occean. This difference provides at least a qualitative measure of uncertainty.

Explicit modeling of stirring processes by ocean eddies is considered important in this context but requires a computational mesh consisting of 10^5 or more grid points. To conduct multi-century simulations on such a fine "eddy-permitting" mesh, a technique has been developed to decouple the simulation of the oceanic circulation from the simulation of tracer transport and stirring. In short, archived flow fields from decadal fine-mesh simulations are used in cyclic fashion over several centuries for long-term CO_2 transport. Computational economy is achieved in this "offline" approach through the use of a much longer model time step than
is required in the original ocean model simulations.

To simulate the effect of iron fertilization on phytoplankton growth, the 20-variable LANL biogeochemistry model originally developed in the POP framework has been successfully ported to HYCOM. Significant progress has been made in improving the realism of the biogeochemical model as far as global nutrient and biomass distribution is concerned. Simulations in HYCOM paralleling those done in POP are about to commence. Up to this point, these simulations have been carried out online (i.e., with the biological model embedded in the physical model) on a coarse mesh over less than a decade. Fine-mesh simulations as well as long-term offline simulations to follow the fate of biologically sequestered CO_2 are planned.

500-year simulations of CO_2 dispersion from a continuous source at 4000 m depth near the Atlantic and Pacific continental margins have been conducted at two spatial resolutions in both POP and HYCOM. The feasibility of the offline transport method is being assessed by comparing it to online coarse-mesh tracer transport simulations with both physical models. Limited-duration (i.e., decadal) fine-mesh online tracer simulations are in progress as well.

Kevin R. Carman[1], David Thistle[2], & John Fleeger[1]
[1]Louisiana State University
[2]Florida State University

The influence of deep-sea bed CO_2 sequestration on small metazoan (meiofaunal) viability and community structure

We are examining the influence of deep-sea CO_2 sequestration on the meiofaunal (metazoans < 1.0 mm in body length) component of deep-sea benthic communities. Our research is integrated with the DOE project of Drs. Jim Barry and Peter Brewer (MBARI), which involves the application of liquid CO_2 to the seabed in experimental corrals at depths ranging from 3100-3600 m in the Monterey Canyon.

We have participated in 3 experiments to determine the effects of injected CO_2 on the meiofaunal community in the Monterey Canyon. The basic design of experiments involves filling cylindrical corrals with approximately 20 L of liquid CO_2. After 30 days cores are collected from within corrals, within 2 m of corrals, and 40-50 m away (controls).

On board ship, vertical profiles of pH were measured in overlying water and in the top 8 mm of sediment. Cores were then vertically sectioned down to 30 mm and preserved in buffered formaldehyde. Abundances of major taxa were determined for each layer. Harpacticoid copepods were identified to species. The condition of harpacticoid copepods was determined by microscopic examination of internal tissues, and by analysis of lipid-storage material. The condition of nematodes was examined by measuring biovolume of individual animals.

In experiment 1 (2002), pH values in sediments from the CO_2 treatment area were 0.4-1.0 pH units lower than in the control area, providing compelling evidence that the experiment successfully exposed the treatment area to elevated CO_2 concentrations. However, CO_2 exposure did not significantly influence the abundances or vertical distributions of any of the major taxa. The lack of influence on vertical distribution suggests that meiofauna do not respond behaviorally to CO_2 or associated changes in pH; that is, they do not appear to move deeper into sediment or exit the sea bed in response to CO_2 exposure. Intriguingly, meiofaunal abundances in cores collected from within CO_2 corrals were equal to or greater than abundances in the treatment area or the control area. Closer examination of meiofaunal condition revealed that exposure to CO_2 does have adverse effects. Specifically, 70-100% of harpacticoid copepods from the CO_2-treatment were partially decomposed, but only 0-40% of harpacticoids from control sediments were partially decomposed. Similarly, the biovolume of nematodes in the CO_2-treatment area was significantly increased relative to those from control sediments (longitudinal muscles of nematodes relax upon death allowing nematodes to expand). Thus analysis of abundance alone did not provide an accurate assessment of the effect of CO_2 on meiofauna. Slow *in situ* decomposition rates of meiofaunal carcasses can mask adverse effects of CO_2 and longer experiments and/or careful examination of meiofaunal condition is needed to accurately evaluate CO_2 effects. Species level-analysis of harpacticoid copepods indicates that some species are resistant to the adverse effects of elevated CO_2 concentration, while most are not. Variable influences among species may have important implications for potential impacts on biodiversity.

In our most recent experiment we deployed our recently acquired *in situ* profiler that employs microsensors to measure vertical gradients of pH and O_2 in deep-sea sediments. Thirty days after release of CO_2, sediment pH near a CO_2 corral was lower than in control sediments by approximately 0.3-0.4 pH units. Sediment inside of CO_2 corrals had pH and O_2 profiles that differed dramatically from ambient sediments. pH was approximately 5.7 at the sediment surface and increased gradually with depth into the sediment. O_2 readings were anomalous and indicated supersaturated concentrations. Further investigation will be required to properly interpret the O_2 data. It is clear, however, that pH and O_2 conditions in sediments under CO_2 corrals differs dramatically from surrounding sediments.

Francisco Chavez
Monterey Bay Aquarium Research Institute (MBARI)

In the early 1990s scientists debated whether iron limitation was responsible for the high nutrient low chlorophyll areas found in the subarctic Pacific, equatorial Pacific and Southern Ocean. After 10 or more mesoscale iron fertilization experiments the answer is rather clear: iron does limit biological production in these areas. Today we are in a position similar to that we were over a decade ago but in this case the debate centers over the biogeochemical effects of iron fertilization. Does iron fertilization actually sequester carbon and are there potential side effects to large scale fertilization efforts? The scientific community has been conservative in their approach to the issue, much as they were with iron limitation when it was first suggested, and argue that carbon sequestration by iron fertilization is not significant, and further that side-effects can be considerable. A review shows that the data in support of this argument are weak. In addition simulations with rather primitive models are being used to support the same arguments. Simple back of the envelope calculations show that iron fertilization must sequester carbon. The potential side effects also seem to have little observational evidence and may lack merit. Should John Martin still be alive he would most certainly be arguing for a large scale fertilization experiment, perhaps over the entire equatorial Pacific, so that the debate over the biogeochemical effects of iron fertilization could be settled. The validation for such an experiment would be if atmospheric carbon dioxide levels are affected.

James Kennett

Department of Geological Sciences
University of California, Santa Barbara

This study, conducted with the Monterey Bay Aquarium Research Institute (MBARI), is the first to investigate potential effects of carbon dioxide (CO_2) hydrates on benthic microfossils, specifically foraminifera. The experiment was conducted in September 2003 aboard the *R/V Western Flyer* using the *ROV Tiburon*. Experimental (CO_2 exposed) and control cores were collected at 3600m and stained to distinguish live (stained) from dead (unstained) individuals. Foraminifera are ideal for these investigations because of differing test composition (calcareous and agglutinated) and thickness, and diverse epifaunal and infaunal depth preferences, The effects of the CO_2 on assemblages have been tracked both vertically (10cm depth) and horizontally, and between live and dead individuals. Increased mortality and dissolution of calcareous forms resulted from exposure to CO_2 hydrate. Preliminary results suggest several major effects on surface sediment assemblages: 1) total number of foraminifera in a sample decreases; 2) foraminiferal diversity decreases in both stained and unstained specimens. The number of planktonic and hyaline calcareous tests declines greatly, with milliolids being more resistant to dissolution when stained; and 3) percentage of stained (live) forms is higher. Down-core trends (up to 10cm) indicate: 1) percent agglutinated forms decline and calcareous forms increasingly dominate; 2) agglutinated diversity decreases with depth; and 3) assemblages become increasingly similar with depth to those in control cores not subjected to CO_2 hydrate. These results imply almost complete initial mortality and dissolution upon CO_2 hydrate emplacement in the corrals.

John Marshall and Mick Follows
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Progress summary for: Pathways and Mechanisms of Ocean Tracer Transport: Implications for Carbon Sequestration

We are using ocean models to study mechanisms and pathways of ocean tracer transport with particular emphasis on impacts of ocean dynamics and biogeochemistry on, and optimal strategies for, direct ocean carbon sequestration.

In particular our study focusses on the development of adjoint formulations that include active biogeochemistry.

Building on our earlier work developing and applying an adjoint of the MIT ocean circulation model, we have developed a global adjoint mode that includes dissolved inorganic carbon (DIC), alkalinity, phosphate, dissolved organic phosphorous and oxygen. The adjoint model has been evaluated by using it to develop spatial maps of the sensitivity to biogeochemical export production parameters of the misfit between simulated and observed phosphate distributions. Our results show that realistic, physically sensible adjoint sensitivities can be obtained for our biogeochemical parameterizations.

The adjoint approach can be used to identify regions in the ocean where export production plays a significant role in determining biogeochemical tracer concentrations. In such regions (for example the strong upwelling regions in the equatorial Pacific), biogeochemical parameters such as the maximum rate of export can potentially play a rate limiting role in regulating ocean biogeochemistry. In the same way a biogeochemical adjoint allows us to determine regions of the ocean that are strongly dominated by dynamics. These regions appear as areas of low sensitivity to biogeochemical parameters. In these regions, the leading order effects governing biogeochemistry are likely to be related to ocean transport mechanisms and water mass pathways.

We are beginning to apply our biogeochemical adjoint to the task of solving for uncertain biogeochemical parameters. This should ultimately lead to more precise biogeochemical models that can more accurately capture the ocean carbon cycle. We are also planning to build on our adjoint work to develop the technology to estimate CO2 outgassing sensitivities in the presence of active biology. This will complement our prior work estimating sensitivities of air-sea exchange of passive tracers to injection location. Together the dynamical and biogeochemical adjoint results can be used to further understand the combined impact of circulation and biology on deep ocean CO2 reservoirs.

Publications emanating from the study include:

Hill, C., V. Bugnion, M. Follows and J. Marshall (2004) Evaluating carbon sequestration efficiency in an ocean circulation model by adjoint sensitivity analysis. JGR Oceans, vol 109, C11005, doi:10.1029/2002JC001598

Comparison of passive tracer evolution between offline and online models of the North Atlantic: Helen Jones, Chris Hill, Mick Follows and Stephanie Dutkiewicz. Paper in preparation.

New estimates of near surface eddy diffusivity in the Southern ocean and implications for the dynamics of the Antartic Circumpolar Current: John Marshall, Emily Shuckburgh, Helen Jones, Chris Hill. submitted to J.Phys. Oceanogr.

Toward next-generation eddy-premitting reanalyses of the global ocean circulation: Dimitris Menemenlis, Chris Hill, Ichiro Fukumori, Benny Cheng, Alistair Adcroft, John Marshall. Paper in preparation.

Adina Paytan

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Organic Matter Composition, Recycling Susceptibility and the Effectiveness of the Biological Pump – An Evaluation using NMR Spectra of Marine Plankton

The degree of organic matter biodegradation and recycling depends on the "reactivity" of compounds synthesized by the biota, which in turn is controlled by the structural characteristics of these compounds. Thus, abundance of a wide-range of organic compounds in seawater would lend itself to different susceptibility for biodegradation, which in turn is important for estimating the potential for rapid regeneration in the euphotic zone and thus the effectiveness of the biological pump.

We employed ^{13}C and ^{31}P NMR spectroscopy on cultures of phytoplankton dominating blooms in the Southern Ocean grown under five light levels at $3^{o}C$. We found differences in both C and P compounds synthesized by the different taxa as well as for each species at various light levels. Results suggest variability in synthesized organic compounds by different taxa and by a single species grown in different environmental conditions. understanding of the oceanic C cycle in general and C sequestration effectiveness in particular.

Dan Repeta

Woods Hole Oceanographic Institution

Sequestration of Dissolved Organic Carbon in the Deep Sea

There are approximately 680 GT of dissolved organic carbon (DOC) sequestered in seawater. The marine inventory of DOC is set by its concentration in the deep sea, which is nearly constant at 40±2µM C, irrespective of sample location or depth. Isotopic measurements show deep sea DOC to be depleted in radiocarbon, with an apparent radiocarbon age of between -4000yr (Atlantic) and -6000yr (Pacific). From the radiocarbon data, we can infer that deep sea DOC is inert and does not cycle on less than millennial time scales. However, DOC concentrations rise to 60-80µM in the upper ocean (0-200m), nearly double their deep-water value. This excess or "new" DOC is a by-product of algal production in the euphotic zone. Upper ocean DOC is enriched in radiocarbon, and can be modeled as a two end member mixing between newly synthesized DOC (with a high radiocarbon value), and old DOC from the deep ocean.

DO^{14}C measurements average a number of different carbon reservoirs that cycle at different rates. In order to identify which components of DOC are labile and which are recalcitrant, we developed protocols for compound specific radiocarbon analyses of neutral sugars and amino acids isolated from DOC. Chemical analyses show that carbohydrates, (including neutral sugars) contribute > 50% of the carbon in high molecular weight DOC. Likewise, amino acids contribute a major fraction of the total dissolved organic nitrogen. We therefore targeted these two compound classes for radiocarbon analyses. We find that neutral sugars isolated from the surface ocean are enriched in radiocarbon and have Δ^{14}C values equal to DIC. Our data show that DOC neutral sugars have a residence time of < 3 yr in the upper ocean. In the mesopelagic ocean (600 –1800m) we also find some enrichment in neutral sugar ^{14}C values relative to DI^{14}C values, suggesting active transport of dissolved sugars to these depths. Amino acids show a much broader range of ^{14}C values, from modern (>60 ‰) to values equal to deep sea DOC (-480‰). Amino acids are therefore partitioned into a number of different DOC reservoirs with a range of residence times. Finally, we have also been able to isolate the recalcitrant component of DOC from surface water samples, demonstrating that DOC in the upper ocean is indeed a mixture of upwelled recalcitrant and newly produced DOC.

J. L. Sarmiento[1] & N. Gruber[2]
R. Armstrong[3], J. Dunne[4] & A. Gnanadesikan[4]

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Carbon Sequestration by Fertilization: A Comprehensive Assessment Using Coupled Physical-Ecological Biogeochemical Models

The goal of our project is a comprehensive assessment of the proposal to fertilize the ocean with nutrients (such as iron) in order to increase the export of organic matter from the ocean's near surface waters and consequently increase the uptake of CO_2 from the atmosphere. There are several critical questions that need to be addressed before carbon sequestration by fertilization can be deemed viable. (1) If iron is added to the ocean, will export of organic carbon from the surface actually occur? (2) If the export of organic carbon from the surface of the ocean were increased, how much CO_2 would actually be removed from the atmosphere? (3) What is the time scale of any sequestration that occurs? (4) Can the magnitude of sequestration be verified? (5) What unintended consequences might there be from fertilizing the ocean with iron? We have addressed various aspects of all these questions in our research.

Despite the completion of ten iron enrichment experiments of various sizes and durations, the degree to which iron addition will draw down nutrients and export carbon below the mixed layer is poorly understood. This question will likely be difficult to fully resolve in the field due in part to the exponential expansion and dilution of an iron-enriched patch. For example, in the Southern Ocean Iron Experiments (SOFeX) of 2002, the two iron enriched patches increased in area by an order of magnitude in twenty days. Such a ten-fold dilution increases the macronutrients available to the patch while decreasing the concentration of iron and biomass within the patch and is not reflective of the potential drawdown and bloom of a basin scale Southern Ocean iron enrichment.

We have taken two approaches to bridging the gap between *in situ* and global scale model studies. In one of these, we use an eddy-permitting high resolution Pacific Ocean model based on ROMS (the Regional Oceanic Modeling System). By coupling an ecosystem model to this circulation model and performing nutrient depletion simulations in scale ranging from the same patch size of the in situ experiments to the several 100 km size of the coarse resolution model, we can establish a connection between these model studies and the many insights emerging from the small-scale patch fertilization studies. (*Jin et al.,* 2005). Our second approach is to combine climatological observations on such properties as the light supply and mixed layer depth with information on the biological response from *in situ* iron-enrichment measurements to develop a simple empirical model of an iron-replete Southern Ocean in an attempt to determine if it is possible to draw down the vast supplies of nutrients in the various physical zones of the Southern Ocean. Preliminary results suggest that substantial regions of the Southern Ocean are light limited (*Hiscock et al.*, in preparation). The response to iron fertilization in these regions is thus likely to be substantially less than might be otherwise predicted.

If we nevertheless take as a starting point that iron fertilization will lead to a total drawdown of nutrients along with the associated carbon, we can use model simulations to examine the other critical questions raised above about the viability of fertilization as a carbon sequestration option. Our studies primarily of the patch fertilization option have thus far led us to the following conclusions: (i) the efficiency of fertilization is low, i.e. only a small fraction of the exported carbon comes actually from the atmosphere (*Gnanadesikan et al.,* 2003). (ii) Unless fertilization is done continuously, most of the sequestered carbon goes back to the atmosphere within a few years to decades after the fertilization is stopped, most often far away from where it was originally taken up (*Gnanadesikan et al.,* 2003**)**. (iii) This leads to substantial problems with verification, as the air-sea CO_2 balance would need to be monitored globally in order to account for this efflux (*Gnanadesikan et al.,* 2003). (iv) Finally, our model simulations coupled with detailed studies of the global distribution of nutrients indicate substantial unintended consequences of iron fertilization, ranging from massive alterations of biological productivity in regions thousands of miles away from where the fertilization took place (*Gnanadesikan et al.,* 2003; *Marinov et al*., in prep; *Sarmiento et al.,* 2004) to the release of large amounts of nitrous oxide from the ocean (*Jin and Gruber*, 2003), which being a greenhouse gas that is 200 times more potent than CO_2 itself, can significantly offset the radiative benefit of iron fertilization.

In terms of biogeochemical model development, our focus has been on developing a new model of biological processes in the surface of the ocean including a particular focus on a diagnostic assessment of the contribution of various functional groups to the production and export of organic matter. In *Dunne et al.* (submitted), we synthesized a broad range of field observations on upper ocean biogeochemical cycling to develop new empirical and mechanistic models for predicting the export of organic carbon out of the surface ocean by sinking particles. We found that representing grazing dynamics by power laws in the closure terms for small and large phytoplankton reproduces observed patterns of phytoplankton community composition, where large forms augment small ones as production increases. This novel yet simple approach, in which zooplankton grazing pressure is implicit, proved extremely powerful in representing bulk ecosystem variability. In *Dunne et al.,* (in preparation), we incorporated our new models into an ocean biogeochemical general circulation model (OBGCM). Our new model is able to diagnose primary production, phytoplankton size structure and dissolved organic matter cycling by restoring model nutrient fields to surface observations. As an encouraging validation of this OBGCM, we are able to reproduce the major patterns in marine primary production as interpreted from satellite observations of ocean color. However, important differences exist, pointing primarily to deficiencies in the ocean circulation model, but also to deficiencies in the chosen biological representation of ocean ecosystems and the satellite-based chlorophyll and primary productivity algorithms.

In *Jin et al.* (submitted) we have diagnosed the export of $CaCO_3$ and opal and phytoplankton functional groups on the basis of global nutrient and alkalinity distributions. Net primary production (NPP) is modeled by restoring model concentrations of nitrate and ammonia toward observed concentrations and zero, respectively, and is then allocated to small and large phytoplankton following the mechanistic model developed by *Dunne et al.* (submitted). $CaCO_3$ and opal export are diagnosed by restoring model concentrations of silicic acid, and potential alkalinity toward observed concentrations. In our standard model, global $CaCO_3$ and opal export are diagnosed as 1.1 Pg C/yr and 180 T mol Si /yr, respectively. Large phytoplankton dominate the export of particulate organic Carbon (POC), accounting for 73% of global export. About half this export can be attributed to diatoms, while the contribution of coccolithophorids is only 11%. Small phytoplankton dominate NPP with a fraction of 70%. Diatoms and coccolithophorids account for 14% and 1.4% of NPP, respectively, with a very distinct spatial distribution. Correlation and regression analyses show that NPP and $Si(OH)_4$ are the two main control factors for the $CaCO_3$ and opal export, respectively. $CaCO_3$ and opal export, the fraction of large phytoplankton allocated to diatoms, and the fraction of small phytoplankton allocated to coccolithophorids can be predicted by using a set of the empirical equations derived by our analysis.

In *Deutsch et al.* (in preparation) we investigate a new geochemical approach for estimating N_2 fixation that combines an Ocean Biogeochemistry/General Circulation Model with observed global nutrient distributions in the upper water column. By assimilating climatological surface concentrations of both nitrate and phosphate, we obtain an estimate of the net biological phosphate uptake that cannot be explained by a Redfield stoichiometric uptake of nitrate. When we interpret this excess phosphate uptake as a signal of N_2 fixation, spatial patterns and rates of global marine N_2 fixation can be computed. We calculate a global N_2 fixation rate of ~130 Tg N/yr. The sensitivity of this result to key model parameters suggests that the uncertainty obtained with this approach is better than +/- 30%. The geographical pattern of inferred N_2 fixation, which is predominantly subtropical and has highest rates in the Pacific Ocean, is remarkably insensitive to parameters of the model and has important implications for the understanding of environmental controls on marine N_2 fixation.

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David Siegel
University of California

The overall goal of the VERTIGO project (Buesseler, lead-PI, WHOI) is to address the formation and fate of sinking particles to assess their fate in the mesopelagic. My DOE supported component of VERTIGO is to conduct and analyze physical oceanographic observations and to collect and to assess satellite data and to analyze them to assess how physical oceanographic factors and the natural spatial scales of the productivity in the euphotic zone affect the magnitude and sampling of export flux in the mesopelagic.

Specifically, my research objectives are to:

- Characterize how different sediment trap designs (fixed, surface tethered, neutrally buoyant, etc.) collect sinking particles,
- Examine the links between spatial scales of export and individual trap collections, and
- Explore how convergences and divergences of surface currents may have a role in changing export fluxes due to changing aggregation probabilities.

This past summer we made physical oceanographic measurements from R/V Kilo Moana in support of VERTIGO. At sea participants from our group were David Siegel and Erik Fields. In support of the overall VERTIGO project, we led the grid surveys of CTD/hydrographic variables with simultaneous determination of horizontal velocity from the ship's ADCP system. We provided the waypoints for conducting the grid, stood CTD watches and performed all processing of the data sets. A total of 103 CTD stations were taken over a 2^o by 2^o box centered at the Hawaii Ocean Time Series site (HOT). This will enable us to assess horizontal gradients in biological and chemical properties to compare with available satellite ocean color imagery. Subsequent to the cruise, we reprocessed all of the CTD data and made them available to all participants in the VERTIGO project (www.icess.ucsb.edu/~damk2000/). The reprocessing of CTD variables at UCSB was done by an undergraduate work study student, Damien Kunz.

The focus of our group was the determination and analysis of the horizontal velocity field for modeling activities to follow. We sampled horizontal currents using three basic methods; satellite altimetry, which provides large spatial coverage of surface currents, the Kilo Moana's acoustic Doppler current profiler (ADCP) system, which provides vertical profiles of currents to 1000 m at the ship's locations and 10 surface drifters (supported by DOE), which provide a Lagrangian measure of the surface current field and some aspects of its spatial variability. An example of an objectively analyzed map of sea level and surface currents is shown in Figure 1 made towards the end of the VERTIGO field season. Gridded fields of absolute sea level and associated geostrophic velocity were provided from the Ssalto/Duacs project (see http://www-aviso.cls.fr/html/donnees/produits/madt_uk.html). These data show the region is affected by a series of eddy-like features with sea level amplitudes of +/- 20 cm and velocity fluctuations of 20 or so km per day. In particular, notice the anticyclonic (high sea level) feature at the HOT location. This feature dominated the movement of traps and surface drifters and presumbably sinking particles. Similar data were also collected in real-time from Bob Leben (Univ. Colorado) and used for positioning the ship tracks and make predictions of where traps will drift and where collected particles have come from.

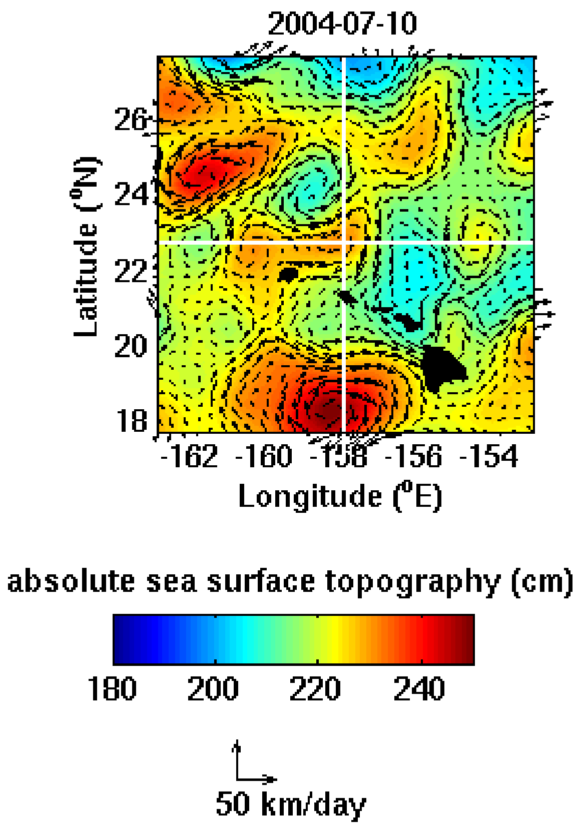

Figure 1: Absolute sea surface topography and surface currents during the end of the VERTIGO cruise. Note the anticyclonic (high sea level) feature at the HOT location (white crosshairs) which creates a clockwise circulation around the HOT site. This circulation dominated the drift of all traps (and particles!!) during VERTIGO.

We also collected and analyzed velocity profile information over the upper 700 m from the Kilo Moana's ADCP system. The ADCP data is the central data set used in calculating the origin locations of collected particles which have entered the drifting and neutrally buoyant sediment traps. ADCP were provided with help from Jules Hummon and Eric Firing of Univ. Hawaii. At sea, we did preliminary processing of ADCP data to predict where the various traps were going. This was especially important for the neutrally buoyant sediment traps (NBSTs) which provide no information of their location when they are deployed at depth collecting particles.

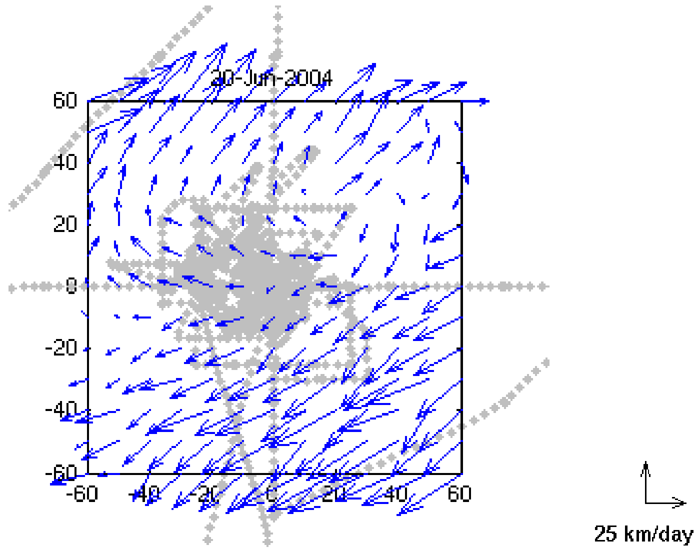

Figure 2: Objectively mapped sub-inertial currents at 50 m depth for June 20, 2004 from VERTIGO. Distances are from the nominal HOT location (22.75°N 158°W) and the ship track is superimposed.

To do this (and to do our processing on land), we removed super-inertial frequencies of motion (tides, diurnal, inertial) and produced objective maps of sub-inertial current fields on a daily basis. The super-inertial currents are assumed to be spatially independent and just time dependent and the amplitudes of the fits are allowed to vary over the experiment (following Firing, 1997; DSR2). An example of an objective map of surface current for June 20, 2004 is shown in Figure 2. Again, the anticyclonic circulation dominates the low frequency current field and we assessed its change over time and for different depth horizons. These data are used to predict where the NBST traps have drifted and the relative location of where collected particles have come from.

During the cruise, we also helped the VERTIGO project by providing real time assessments of where the different traps were spatially. In essence we developed a sediment trap "geographic information system" using data feeds from the ARGOS GPS transmissions, the ship's GPS and ADCP systems. This was developed in MATLAB for the VERTIGO project. A screen grab of this system is shown in figure 3. Each line in the printout shows the location of each trap (or surface drifter) and its distance and bearing relative to the ship. This shows where locations of traps are as a function of time and could provide rough assessments of where the traps would go in time using the ADCP data described above. This predictive capability proved critical for the successful recovery of the NBST traps. During VERTIGO, we had perfect success in predicting where the NBST traps would surface and none of the traps were lost. Graphical output was broadcast over the Kilo Moana's network and was used by the bridge crew in setting way points for collecting traps. The development of this "sediment trap GIS" was essential as the bridge crew had a hard time keeping track of the 17 objects we needed to deploy simultaneously and recover during VERTIGO.

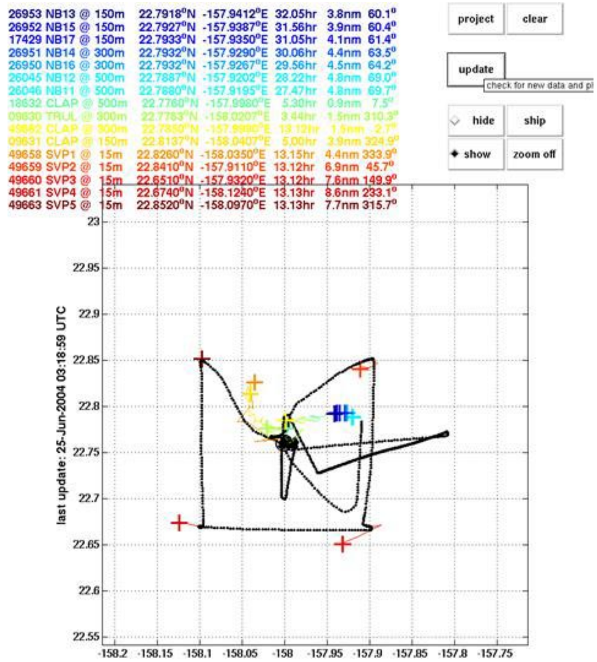

Figure 3: Screen grab from the real-time trap and drifter location plotting and analysis system developed for VERTIGO. Each line of text and mapped symbol shows the location of each trap or drifter and its distance and bearing relative to the ship. The black dots are the ship's location over time.

We have started a manuscript describing the collection of particles by the different sediment trap types during VERTIGO. The goal here is to document our first research objective; how do different sediment trap designs (bottom moored, surface tethered, neutrally buoyant, etc.) collect sinking particles. To do this we have extended our previous theory of sediment trap collection funnels to allow the traps to move in time. An example of expected collection funnels for a NBST trap deployment at 300 m is shown in figure 4. Here the filled circles show the 95% collection envelopes of where particles that were actually collected by the trap are likely to have come from (knowing the sinking speed we know at which depth these have come); whereas, the open circles show the probable location of formation within the euphotic zone. Three different sinking speeds are shown and the color coding denotes when during the deployment is each spot "sampled" (blue early – red late). From this we can get an idea of where collected particles have come from. This analysis has been conduced for each trap deployed during VERTIGO. This work is well underway and we expect to have a manuscript submitted to *Deep-Sea Research, Part I* on this by early summer. Some of this work will be presented in Siegel's plenary talk at the upcoming ASLO aquatic sciences conference in Salt Lake City.

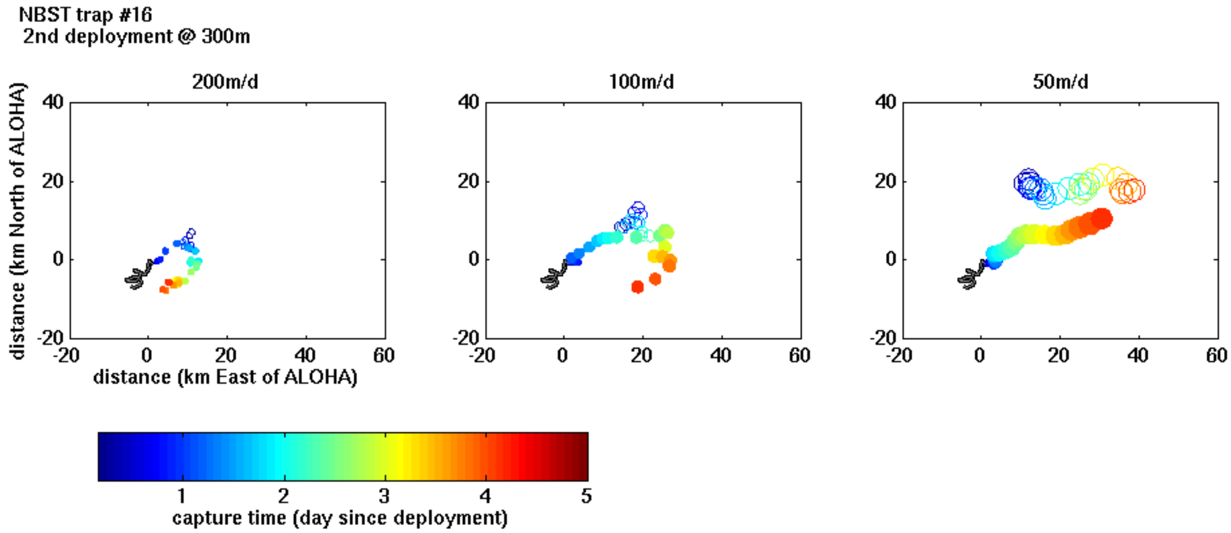

Figure 4: Example of the collection funnels for NBST-16 (300 m depth) on its second deployment during VERTIGO-Hawaii. The black symbols is the trajectory of the NBST trap during its deployment (starting at the lower left in time). The closed circles show the 95% collection envelopes of where particles that were actually collected by the trap are likely to have come from whereas the open circles show the locations of where these particles had come from in the euphotic zone. Three different sinking speeds are shown and the color coding denotes when during the deployment is each spot “sampled” (blue early – red late). From this we can get an idea of where collected particles have come from. This analysis has been conducted for each trap deployed during VERTIGO.

Last, we are preparing to next year’s field season to the K2 site. See our preliminary analyses of surface currents at http://www.icess.ucsb.edu/~fields/Vertigo/K2/. This will be challenging…

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Sinking CO_2 Particle Plumes

Direct CO_2 injection into the ocean at depths of 0.5–3.5 km has been proposed as a cost-effective method to counteract the atmospheric CO_2 increase. To receive wide acceptance of such an approach, concerns regarding any potential negative impacts on marine biota must be addressed. This requires knowledge of the fate of injected CO_2, which directly impacts seawater pH and trace metal concentrations. The main focus of this project has been the formation of a sinking CO_2 plume at moderate ocean depths and the dissolution of CO_2 particles in seawater.

A continuous-jet hydrate reactor was developed to efficiently produce dense, negatively buoyant (i.e., sinking) CO_2 hydrate particles. The technical feasibility of the reactor was proven at Oak Ridge National Laboratory using a 72-liter seafloor process simulator and at the National Energy and Technology Laboratory using a high-pressure water tunnel facility. Field verification of laboratory results was demonstrated in Monterey Bay, California, using the facilities of Monterey Bay Aquarium Research Institute. Prior to development of the reactor, methods for direct injection of CO_2 into the deep ocean were inefficient because the injection of liquid CO_2 alone produces buoyant droplets with the risk of returning to the ocean surface and atmosphere rather than remaining in the ocean for long periods required for effective carbon sequestration. [C. Tsouris et al. (2004) *Environmental Science and Technology* 38: 2470-2475].

Plume simulations carried out at the Massachusetts Institute of Technology are being used to understand plume behavior and the effects on seawater chemistry (e.g., pH) for a range of discharge scenarios. Results suggest that a realistic injection of CO_2 from a typical powerplant would produce a sinking plume nearly 1 km deep, which is an order of magnitude further than the depth to which individual hydrate particles would sink. Current laboratory and simulation work is also focused on the scale-up of the continuous-jet hydrate reactor. The objective is to establish reliable rules for the determination of the geometry of larger injectors that could be used to form particle plumes of a realistic scale.

Future work will be focused on the effects of impurities in flue-gas CO_2, such as trace metals, on the formation and properties of hydrate particles, as well as their fate after CO_2 injection and hydrate dissolution.

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The impact of enhanced nitrogen fixation on carbon sequestration: a reassessment of the inorganic carbon system in Low Nutrient Low Chlorophyll regions
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Currently, human activities are indirectly enhancing the flux of iron to large regions of the tropical and subtropical oceans and it is thought that this iron fertilization is stimulating enhanced rates of nitrogen fixation. We intend to determine whether these enhanced rates of N_2 fixation yield enhanced carbon sequestration via the biological carbon pump. We also aim to determine how shifts in phytoplankton community structure (with fertilization) influence the export of carbon from these regions. Our project complements a major NSF-funded Biocomplexity research program (MANTRA/PIRANA, http://biology.usc.edu/bc/) investigating N_2 fixation in the Subtropical Pacific and Western Tropical Atlantic Oceans. The Biocomplexity program measures and models ecosystem processes involved with marine nitrogen fixation, focusing on the fertilization effects of wind-driven dust and riverine mineral inputs enhanced by land use changes. Our complementary measurements of the key CO_2 system parameters (total dissolved inorganic carbon, alkalinity, surface pCO_2, and isotopic composition of the inorganic carbon) will allow us to determine the rates of net air-sea CO_2 exchange, total oceanic and anthropogenic CO_2 concentrations, and carbon export in regions where these reservoirs and fluxes are poorly known. The proposed research is intended to provide direct estimates of the impact of N_2 fixation and community structure on the uptake of atmospheric CO_2 and to yield a quantitative link between anthropogenic and climate-induced changes in marine N_2 fixation and the sequestration of anthropogenic CO_2 in the ocean.

Results from the Western Tropical Atlantic (Cooley and Yager, submitted) confirm the large impact of the Amazon River on the local carbon cycle. The river plume reaches far out into the basin and significantly reduces the surface carbon dioxide concentrations below atmospheric levels. This reduction is amplified by biological activity, particularly nitrogen fixation, as the primary producers in the plume shift from typical oceanic diatoms, to diatoms containing nitrogen-fixing endosymbionts, and then to blooms of *Trichodesmium*. The greatest export occurs where the symbiotic diatoms bloom, confirming the importance of riverine iron and silica fertilization.

Preliminary results from the Pacific show significant reductions in surface DIC and pCO2 associated with mesoscale eddies and other physical oceanographic features around Hawaii. Enriched surface delta-13DIC indicates that export is significant in some of these areas. Preliminary data from our collaborators confirm this with elevated levels of N* (a calculated nitrate anomaly indicative of nitrogen fixation).

One additional outcome of this project is the development of a new method (Miller and Yager; submitted) for using a gas chromatograph and mass spectrometer (GC/MS) to analyze for delta-13DIC. We modified published methods (Miyajima et al. 1995, Salata et al. 2000) to 1) improve precision (from 0.2 to 0.14 per ml), 2) improve the length of time prepared samples can be stored (from one day to one week), and 3) allow for the possibility of re-running samples. Modifications include an improve vial and septa system and the addition of a water trap between the GC and the MS.

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Consequences of iron fertilization: factors affecting community changes and sinking

The central hypothesis guiding our work is that substantial increases in the concentrations of the stronger of two Fe(III) complexing organic ligand classes measured during the mesoscale Fe enrichment studies IronEx II and SOIREE sharply curtailed Fe availability to diatoms and thus limited the efficiency of carbon sequestration to the deep. A more detailed understanding of Fe complexing ligand effects on long-term ecosystem structure and carbon cycling was deemed essential to ascertain not only the effect of Fe enrichment on short-term carbon sequestration in the oceans, but also the potential effect of Fe enrichment in modifying ecosystem structure. The specific goals of our project were to employ novel manipulation experiments to: 1) determine how different natural and synthetic Fe chelators affect Fe availability to phytoplankton species that are representative of offshore HNLC waters, 2) elucidate how the changes in absolute concentrations of these chelators will affect the ecosystem response beyond the normal (1-4 week) period of observations, and 3) ascertain how changes in the ligand composition affect cell sinking and aggregation rates; measures of the efficiency of carbon sequestration to the deep.

Our primary emphasis has been to use, semi-continuous batch cultures to measure how a suite of natural ligand analogs as well as Fe-complexing ligands isolated from seawater affect Fe availability to phytoplankton. Growth rates, macronutrient utilization rates, and physiological parameters (variable fluorescence, cell size, Fe use efficiencies, and light dependent rates of carbon and Fe uptake) have been used to ascertain the organism-specific responses to Fe supplied in these different chemical forms with and without elevated UV treatment. The relationship between ligand types and individual cell sinking rates and the kinetics of cell aggregation was determined to better assess the linkage between Fe ligands and export of carbon and macronutrients to the deep. A “ship-of-opportunity” program to HNLC waters was undertaken to assess how ligand substrates affect the differential supply of Fe to members of the phytoplankton assemblage, and how they influence the kinetics and magnitude of carbon uptake and ultimately planktonic carbon sinking rates.

Laboratory evidence on the role of ligands illustrates several fundamental principles. First, the dichotomy of diatoms verses flagellates cannot be fully explained by the addition of commercially available ligands. Some ligands result in a preference of diatoms in the laboratory, but natural populations fail to respond similarly. Second, the use and availability of specific ligands (and the outcome of competition) appears to depend primarily on the form of available nitrogen (nitrate vs. ammonium) for assimilation. Multialgal competition cultures supplied with reduced nitrogen result in flagellate dominance if there is ligand-induced iron stress, but flagellates and diatoms co-exist if iron is replete. Thus phytoplankton blooms in HNLC regions will likely be dominated by flagellates even following iron enrichment (naturally or experimentally) if recycling by grazers is prevalent and reduced nitrogen forms are used preferentially.

These laboratory findings were tested in ship-based incubation studies and during an mesoscale Fe enrichment experiment (SEEDS-II) of the western sub-arctic Pacific Ocean, in collaboration with Japanese scientists. Iron additions did not stimulate the prevalent centric diatoms but accelerated the dominance of small flagellates (primarily Prasinophytes). Elevation of the surface waters by 1-2 nM total iron only increased the chlorophyll biomass to 2-3 ug/L, in stark contrast to the original SEEDS enrichment that elevated chlorophyll a concentrations to values greater than 25 ug/L. The difference in these two enrichments is the prevalence of remineralizers that supplied considerable ammonium to the fertilized zone. The most profound difference in these fertilization studies is the lack of any significant sedimentation in the flagellate dominated SEEDS-II. Phytoplankton biomass was consumed and remineralized rapidly in the upper waters likely resulting in minimal net sinking flux to the deep.