The Surface Ocean-Lower Atmosphere Study

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Science Implementation Strategy

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Wade McGillis
Chair and Editor

US-SOLAS

Science Implementation Strategy

United States Surface Ocean Lower Atmosphere Study (US-SOLAS)

In collaboration with the US Ocean Carbon and Biogeochemistry (OCB) program and the international Integrated Marine Biogeochemistry Ecosystem Research (IMBER) and SOLAS programs

Front Cover:

(Top left) Polar regions that are sensitive to climate change and vulnerable if global warming is being anthropogenically accelerated. Air-ocean-ice exchange process studies are challenging because of the remote and extreme conditions. The ocean/atmosphere chemistry, physics, and biology have a significant role in these regions.

(Top right) Dust transport off continents carry many particles and compounds that influence surface ocean processes. For example, iron-rich dust from the Saharan Desert may seed the Atlantic Ocean and Mediterranean Sea and stimulate phytoplankton blooms.

(Bottom right) A substantial amount of cloud condensate nucleation particles emerge from the ocean surface. They transform with a wide range of chemical reactions and may influence climate, weather, health, and pollutants. Clouds also enhance the planet's albedo. This phenomenon mitigates some of the sun's energy reaching the earth's surface.

(Bottom left) The 2005 hurricane season set a record-breaking number of tropical storms and Katrina, a Category 5 hurricane. Hurricanes are an extreme air-sea interaction event that can cause significant loss of life and property. Hurricanes are important in SOLAS research because they may be partially caused by climate changes on air-sea exchange processes. Hurricanes, in turn, may affect the atmosphere-ocean exchange of climate relevant compounds. SOLAS will continue to study how hurricanes respond to climate change, as well as the fundamental processes that control their formation, evolution, intensity, and fate.

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Purpose

The Surface Ocean Lower Atmosphere Study (SOLAS) is an international science program (http://www.solas-int.org), that has as its goal:

> ***To achieve quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and the atmosphere, and of how this coupled system affects and is affected by climate and environmental change.***

On behalf of the United States Surface Ocean Lower Atmosphere Study (US-SOLAS) Scientific Community, this Science Implementation Strategy offers some recommendations for future US-SOLAS scientific research activities. The International SOLAS and the U.S. SOLAS (http://www.aoml.noaa.gov/ocd/solas/) Science Plans have defined the scientific scope of the SOLAS program. This Implementation Strategy document was written to address some of the major scientific issues faced in the ocean-atmosphere domain. With this strategy defined, scientists may begin to build on the US-SOLAS science activities outlined in this document. This Science Implementation Strategy will be continuously updated with new ideas and new projects in view of the quick developments and innovative nature of this area of research.

US-SOLAS science encompasses: ocean and atmosphere biology; chemistry and physics; ocean-atmosphere interactions; carbon dioxide (CO_2), methane (CH_4), sulfur (S), iron (Fe), halogens, and numerous other climate- and weather-related compounds; climate forcing and feedbacks between the ocean and atmosphere; process studies; modeling, remote sensing; and societal relevant environmental issues. To ensure that US-SOLAS advances in step with scientific and technological advances, implementation plans have been produced for some targeted climate and weather issues. These plans, which are often written collaboratively by oceanic and atmospheric scientists, will be updated regularly and posted on the US-SOLAS Web site.

SOLAS focuses on the ubiquitous processes in the water and air that affect local ecosystem dynamics including: heat, momentum, gas exchange, the fate and transport of elements across and at the ocean surface, and atmospheric chemistry. It is a very interdisciplinary program. SOLAS focuses on the needs and linkages of two of the major carbon cycle biospheres. Remote sensing from satellites and aircraft are ideal for scientific investigations. Satellite remote sensing is the only method to date that can capture and achieve regional and global scale ocean biogeochemical and atmospheric chemistry. US-SOLAS process-level research will also explore the feedbacks between the ocean, atmosphere, climate, and weather.

US-SOLAS requires interagency involvement because the climate and weather relevant compounds are crosscutting with diverse science missions and geographic domains. It is necessary to have a dedicated program to study this integrated research domain.

In summary, SOLAS strives to solve many of the complexities of trying to control the transport and transformation of climate-relevant compounds near the ocean and atmospheric surface. Due to the physical and temporal domains of the research, multidisciplinary approaches are necessary. Carrying out such high quality research will require focused attention, collaborations, innovative scientific investigations, specialized tools, and refined resources.

Acknowledgments

The US-SOLAS Scientific Steering Committee wishes to thank many people and organizations for contributing to the implementation of US-SOLAS, and to the writing of the 2001 US-SOLAS Bolger Center Workshop Report and the US-SOLAS Science Plan. Components of the International SOLAS Science Plan and the US-SOLAS Science Plan were used to write this US-SOLAS Science Implementation Strategy document. We appreciate and recognize that these contributions helped in the development of this US-SOLAS Science Implementation Strategy.

The first United States Surface Ocean Lower Atmosphere Study (US-SOLAS) workshop and report production was made possible through financial contributions from the National Science Foundation (NSF), the Office of Naval Research (ONR), the National Oceanic and Atmospheric Administration (NOAA), and the National Aeronautics and Space Administration (NASA). In particular, we wish to acknowledge the encouragement and support of the following program managers: Dr. Don Rice, NSF; Dr. Ron Ferek, ONR; Dr. Lisa Dilling, NOAA; and Dr. John Marra, NASA. Monika Gurnee of AOML/NOAA has allowed working group members, workshop participants, and the community at large to maintain updated communications.

The SOLAS Science Steering Committee members that organized and led the USA Bolger Science Plan included the following *Ad Hoc* Planning Team Members: Richard Barber; Doug Capone; Russ Dickerson, co-Chair; Robert Duce; David Erickson; Paul Falkowski; Kenneth Johnson; William Keene; Don Lenschow; Patricia Matrai; Dennis McGillicuddy; Wade McGillis; Joyce Penner; Alex Pszenny; and Rik Wanninkhof, co-Chair.

Since 2001, US-SOLAS graciously acknowledges the support of workshops and scientific research grants from: NASA (Paula Bontempi), NOAA (Kathy Tedesco), NSF Atmospheric Chemistry (Anne-Marie Schmoltner), NSF Chemical Oceanography (Don Rice), NSF Physical Oceanography (Eric Itsweire), and ONR (Ron Ferek).

Special acknowledgment goes to Beth Ann Bartel, who provided major edits in both grammar and formatting that improved the scientific clarity of this document. Her distinguished professionalism and persistence was a major asset that was invaluable in assembling disparate chapters written by many authors into a coherent document. In addition, US-SOLAS is tremendously grateful to Dr. Kathy Tedesco, Program Manager of the Global Carbon Cycle Program in the NOAA Climate Program Office. Dr. Tedesco recognized the asset the US-SOLAS program provides to scientific progress and provided both financial support and strong encouragement for this document.

Executive Summary

Achieving the goals of SOLAS is important to quantify and understand the role that ocean-atmosphere interactions play in the regulation of climate and global change. The domain of SOLAS is focused on processes at the air-sea interface. Therefore, SOLAS has a natural emphasis on the atmospheric and ocean boundary layers, although some of the processes to be studied will need to be linked to significantly greater heights and depths. SOLAS research will cover all ocean areas including coastal seas and ice-covered regions. One fundamental characteristic of SOLAS is that the research is interdisciplinary in that it involves biology, geochemistry, physics, and mathematical modeling. It also involves another layer of interdependence because each of these disciplines has a marine side and an atmospheric side. The two sides of each discipline will need to work together so the SOLAS research can be meaningful and successful. This multi-layered dependence will require a paradigm shift in the arenas of academia and funding, which is more likely to separate disciplines than to combine them.

US-SOLAS deals with the following scientific foci. Each focus is divided into several projects.

Focus 1: Quantify the Biogeochemical Interactions and Feedbacks Between the Ocean and Atmosphere.

The objective of Focus 1 is to quantify feedback mechanisms that involve biogeochemical couplings across the air-sea interface. These couplings are the emissions of trace gases and particles and their reactions of importance in atmospheric chemistry and climate, as well as the deposition of nutrients that control marine biological activity and carbon (C) uptake. This research can be successfully achieved only by studying the ocean and atmosphere in concert.

- Project 1.1 Global Ocean Trace Gas Surveys
- Project 1.2 The North-Atlantic African Dust-Aerosol Experiment (NafDAE)
- Project 1.3 Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS)
- Project 1.4 Climate Modeling in SOLAS (CLIMAS)

Focus 2: Understand the Exchange Processes at the Air-Sea Interface and the Role of Transport and Transformation in the Atmospheric and Oceanic Boundary Layers.

The objective of Focus 2 is to develop a quantitative understanding of processes responsible for air-sea exchange of mass, momentum, and energy. Then with this understanding accurately calculate regional and global fluxes. These calculations require establishing the dependence of the interfacial transfer mechanisms on physical, biological, and chemical factors within the boundary layers. They also require understanding the horizontal and vertical transport and transformation processes that regulate these exchanges.

- Project 2.1 World Ocean Gas Exchange Process Studies
- Project 2.2 Surface Spray *In-Situ* and Modeling Studies
- Project 2.3 Halogens in the Troposphere - US-SOLAS (HiT-US)
- Project 2.4 Cape Verde Air-Sea Interaction Time-Series Station

Focus 3: Characterize Air-Sea Flux of Carbon Dioxide (CO_2) and Other Long-Lived Radiatively Active Gases.

The air-sea CO_2 flux is a key inter-reservoir exchange within the global carbon cycle. The oceans also play an important role in the global budgets of other long-lived radiatively active gases, including nitrous oxide (N_2O) and to some extent methane (CH_4). The objective of Focus 3 is to characterize the air-sea flux of these gases and the boundary layer mechanisms that drive them, in order to assess their sensitivity to variations in environmental forcing.

- Project 3.1 Air-Water Carbon and Volatile Carbon Compounds in the Coastal Margins
- Project 3.2 Southern Ocean Carbon Dioxide Studies
- Project 3.3 Global Surface Ocean Carbon Concentration Surveys
- Project 3.4 Perturbation Experiments in Ocean-Atmosphere Carbon Dioxide Studies

Focus 4: Promote Enabling Technologies, Outreach, and Data Management.

There is a fourth area of projects; this area is concerned with promoting technologies, outreach, and data management. These projects include the dissemination of the purpose and utility of the program to society, scientists, and policy makers. The projects also include special activities, such as satellite usage in SOLAS platforms.

- Project 4.1 Autonomous and Lagrangian Platforms (ALPS) for SOLAS
- Project 4.2 Diagnostic Modeling of Air-Sea Trace Gas Exchanges
- Project 4.3 US-SOLAS Linkages to the United States Ocean Carbon and Biogeochemistry (OCB) Program and the Ocean Observing Initiative (OOI)
- Project 4.4 Data Management for US-SOLAS

This document includes a description of the organization and management of US-SOLAS and an outline of how parts of it will be implemented. The Science Plan and portions of this document are largely based on the results of the International SOLAS Open Science Meeting held in Damp, Germany, in February 2000 and the United States Open Science Meeting held at the Bolger Center, in Potomac, Maryland, in May 2001. The Commission on Atmospheric Chemistry and Global Pollution (CACGP), the Inter-

national Geosphere-Biosphere Program (IGBP), the Scientific Committee on Oceanic Research (SCOR), and the World Climate Research Program (WCRP) have all approved SOLAS and sponsor the international project office.

Broader Impacts

There is increasing evidence that mankind has perturbed the biogeochemical cycles for the building blocks of life, such as C, nitrogen (N_2), and sulfur (S). One example of this premise is the link between atmospheric CO_2 levels and dust deposition shown in Figure 1. These changes have resulted in appreciable impacts and feedbacks in the surface ocean-lower atmosphere region. The exact nature of the impacts and feedbacks are poorly constrained because of sparse observations, especially those observations relating to the interconnections between the major biogeochemical cycles and associated physical controls. It is in these areas that the interdisciplinary research approach, which is advocated by the US-SOLAS community, will provide the greatest impact on scientific understanding. US-SOLAS research will focus heavily on the natural variability of key processes, anthropogenic perturbation of the processes, and the (positive and negative) feedbacks on biogeochemical cycles in the SOLAS domain. A major objective is to integrate results from the process studies, large-scale observations, small- and large-scale modeling, and remote sensing efforts to improve our mechanistic understanding of biogeochemical incidents, physical phenomena, and feedbacks.

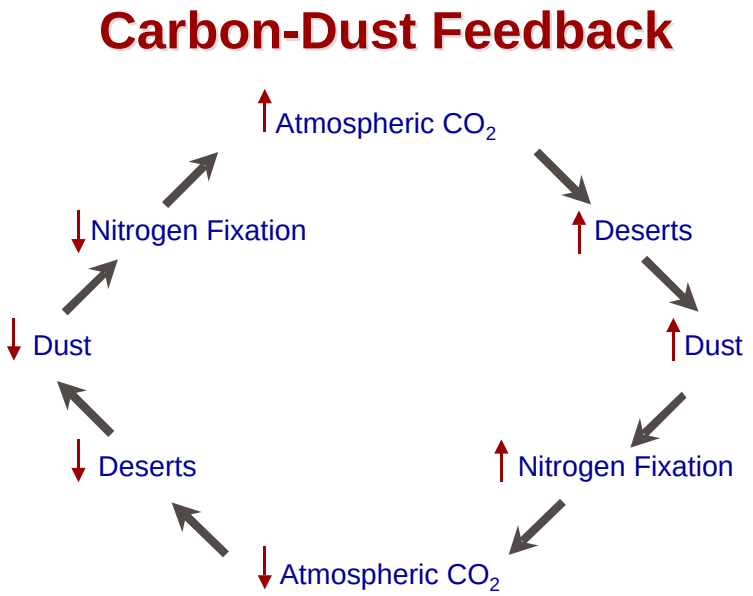

Figure 1: The hypothesized link between atmospheric CO_2 levels and dust deposition is one example of the tight connectivity between lower atmosphere and surface ocean processes (courtesy of T. Michaels, USC).

The SOLAS Approach

In this Science Implementation Strategy document, we identify critical questions and hypotheses, as well as goals to quantify the rates and variability of various important processes. SOLAS will focus on important research issues that are not being emphasized by other projects and that require scientific

collaboration. It will concentrate on research that can be expected to produce results within a 10-year period, although some aspects will need to be continued beyond this timeframe.

The general approach to the implementation is to assess the ambient situation as thoroughly as possible, identify the weak links in understanding, and then undertake laboratory work and focused field studies to resolve those issues. The SOLAS community will then place the new understandings into process models and test those models with carefully designed observations that bridge scales from the micro level to the global level. In many cases, observations with high temporal and spatial resolution will be of great value for both process understanding and process model testing. In some cases, simultaneous observations from multiple platforms, such as ships, aircraft, buoys, and satellites will be required. The final stage will be to integrate this process understanding into diagnostic models, which will then be expanded to regional and global scales for use in climate models.

SOLAS will be testing several key hypotheses that will require numerical modeling studies for systematic evaluation and quantitative assessment. Generally, SOLAS modeling activities will fall into the following broad classes:

- Contributing to process studies
- Monitoring the integration of spatial and temporal scales
- Integrating SOLAS subsystems with Earth System models

SOLAS expects that remote sensing data, mainly from satellite sensors, will make vital contributions. Satellites allow global observation of marine biogeochemical signatures such as ocean color, trace gases, and aerosols, and satellites also have good temporal coverage. With their four- to five-year missions, satellites also provide observations over an extended time period. In particular, satellite observations can place field experiments into a larger temporal and spatial perspective. The SOLAS community will need to integrate the data sets from satellites, models, and the field.

Many of the key questions in the SOLAS domain can be addressed by time-series studies. Ideally these investigations should be conducted at strategic sites that either are representative of large biomes or that are likely to exhibit substantial interannual variability over large areas. Furthermore, these field investigations should be continued for at least several decades in order to distinguish natural variability from changes induced by human activities. Such observations, in combination with proxy records preserved in peat bogs, soil/dust deposits, firn, ice, and lake/marine sediments, have clearly established which trends are occurring in many individual components as well as in their gross budgets. The studies have implicated human activities as the cause of change in many cases. Despite their well-recognized value, the number of systematic, long-term, and direct biogeochemical observations of the atmosphere is relatively small; while the number of observations of the ocean habitat is even smaller.

Considering the sizeable resources required to set up and maintain time-series measurement sites, wherever possible the sites should address the goals of several SOLAS foci/projects and be shared with other projects. Examples of such projects include the Ocean Carbon and Biogeochemistry (OCB) program, the International Global Atmospheric Chemistry (IGAC) project, the Integrated Marine Biogeochemistry Ecosystem Research (IMBER) project, the Integrated Land Ecosystem-Atmosphere Processes Study (iLEAPS) project, the North American Carbon Program (NACP), and the Global Energy and Water Cycle Experiment (GEWEX) project. The studies should also build on results from current time-series stations. Because SOLAS has a strong emphasis on process-driven research, it may not be an obvious main sponsor for such time-series studies, but the SOLAS Implementation Groups need to specify their long-term measurement needs for both satellite and ground-based routine

observations and then, along with the SOLAS Science Steering Committee (SSC), support the efforts of those groups mandated to make the observations.

The ethos of SOLAS is to use a multi-discipline approach, which includes biology, chemistry, physics, and other disciplines, to study biogeochemical interactions in the ocean-atmosphere domain. In achieving this vision, these disciplines should be seen as tools to pursue the larger aim. So, for example, SOLAS will not carry out research to study the physics of air-sea exchanges of heat and momentum for its own sake, but will and must use the best physical knowledge available together with knowledge from other disciplines, to quantitatively address the issue of how matter is exchanged across the air-sea interface.

The SOLAS Domain

SOLAS will focus on research topics of ocean-atmosphere interactions at a multitude of space and time scales in each medium. This approach results in an unavoidable mismatch in time and space scales of processes (and hence measurement needs) because atmospheric transport is more rapid than oceanic circulation. A distinctive feature of the ocean surface and surrounding air and water boundary layers is the progressive change in scale and progressively greater interdependence of different processes as the interface is approached. Processes that might be usefully explored in isolation at depth/height must be considered with a host of competing and interacting effects close to the interface. The scales of the interacting phenomena become smaller and start to overlap, and the nonlinear interactions increase in strength as the interface is approached.

The interdisciplinary nature and broad domain of SOLAS are illustrated in Figure 2.

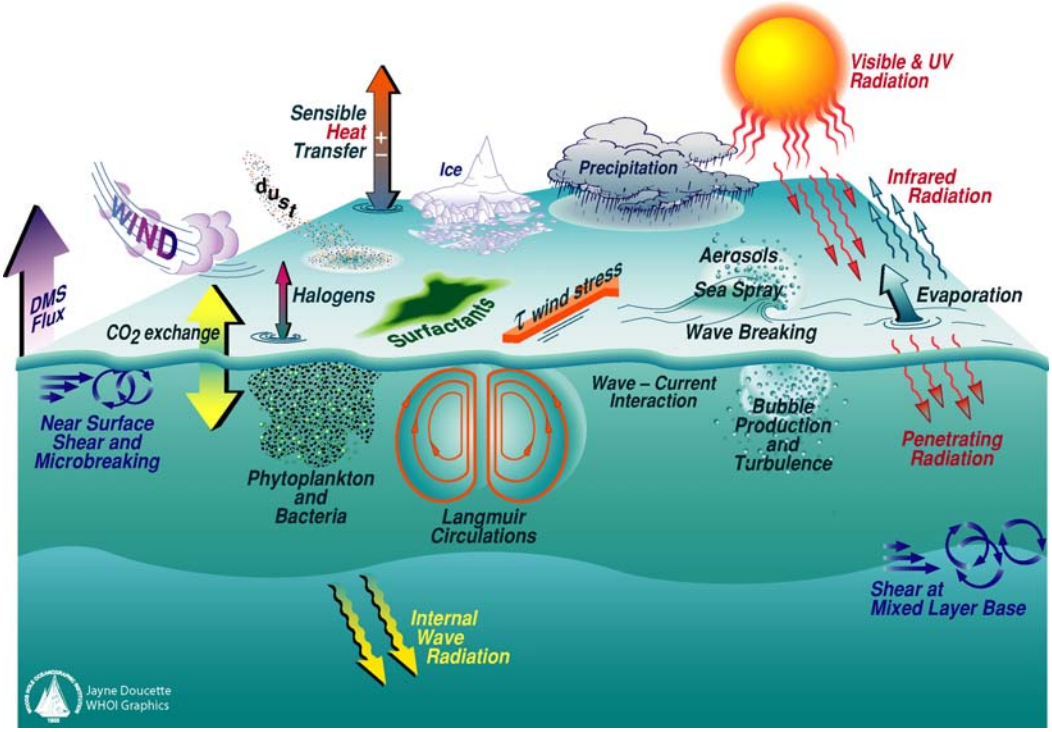

Figure 2: Diagram to illustrate SOLAS, its interdisciplinary domain, and the major operative processes (courtesy of Jayne Doucette, WHOI and Wade McGillis, Columbia University).

Figure 3 shows the complex structure and dynamics of the air-sea interface.

Figure 3: Photos of sea surface at 1 m/s (top) and 35 m/s (bottom).

The vertical domain of SOLAS is focused on processes at the air-sea interface and includes a natural emphasis on the atmospheric and upper-ocean boundary layers, while recognizing that some of the processes to be studied will, of necessity, be linked to significantly greater depth/height scales (illustrated in Figure 4). The atmospheric boundary layer can be functionally defined as extending to the top of the boundary-layer clouds (typically to about 1 km). The upper-ocean boundary layer functionally includes the actively mixed or euphotic zone (typically 100-200 m).

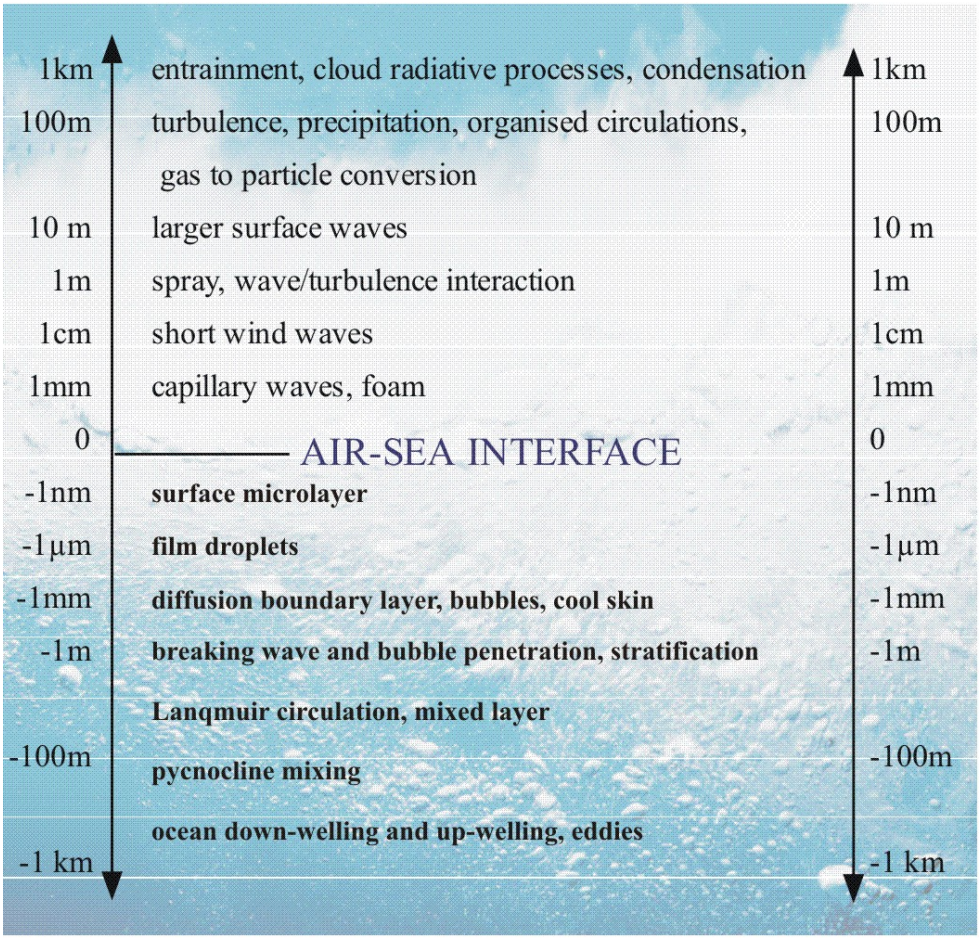

Figure 4: Vertical Scales of Processes Important for Air-Sea Exchanges.

In the horizontal dimension, SOLAS research can be focused anywhere over the ocean, extending into coastal areas and estuaries, as well as ice-covered regions. Coastal ecosystems are characterized by higher primary production than open ocean systems, along with high rates of carbon burial that are significant to the global carbon budget. In addition, coastal seas are dominant marine sources of some trace gases, such as nitrous oxide (N_2O), carbonyl sulphide (COS), and methane (CH_4). Coastal seas are important production sites for almost all trace gases. Coastal research is spread across the whole of the SOLAS research agenda and will be linked to the Land-Ocean Interactions in the Coastal Zone (LOICZ) program. Likewise, processes that occur at ice edges and in ice-covered seas are important for emission of trace gases, such as dimethyl sulphide (DMS) and organohalogens. Each focus in SOLAS includes research in these important regions.

In the temporal domain, SOLAS will need to be concerned with a continuum, from the past through the present to the future. Measurements of oceanographic and climatic indicators of past ocean and atmospheric chemistry and climate will be needed to determine how a variety of factors related to air-sea interactions varied in relation to one another in the past. Long-term, regular observations at important sites are needed to provide an understanding of interannual to interdecadal variability of important global processes. Models need information from paleoindicators and from studies of present-day processes, in order to develop the ability to predict environmental variability and responses of global systems to the effects of human perturbations. Models also provide the capability to extrapolate measurements up and down across scales and to integrate data from different sources. Model studies conducted in parallel with experimental and observational studies will allow a systematic evaluation and qualitative assessment of the different hypotheses emerging from the data. Needing both paleo and modeling expertise in SOLAS illustrates the basis for strong cooperation between SOLAS and the Analysis, Integration and Modeling of Earth Systems (AIMES) Task Force and between SOLAS and the Past Global Changes Project (PAGES) especially its International Marine Global Changes Study (IMAGES).

Data assimilation techniques, similar to those being used at numerical weather prediction centers and developed by the Global Ocean Data Assimilation Experiment (GODAE) for oceanographic applications, will be required to handle the complex and disparate data sets generated by SOLAS field campaigns

The chemical domain of SOLAS will include many of the natural elements (and their compounds) that play an important role in biogeochemical cycling, such as carbon (C), nitrogen (N_2), oxygen (O_2), phosphorus (P), sulfur (S), Group 1 and 2 elements, halogens, iron (Fe), manganese (Mn), and other trace metals and metalloids. Some inert gases and low chemical reactivity substances (lanthanides, natural and anthropogenic radionuclides), as well as a variety of persistent organic pollutants (POPs), will also be included in SOLAS, but only where their study can yield information useful in elucidating the ocean-atmosphere behavior of biogeochemically and/or climatically active elements.

Societal Relevance

SOLAS can also contribute to our understanding of the important role that the ocean-atmosphere interface plays in relation to issues relevant to society, such as climate change, air quality, and the health of the ocean. For each of these topics, SOLAS will seek to develop collaborative research with related international projects. Likewise, SOLAS and the International Human Dimensions Program on Global Environmental Change (IHDP) can work together to identify societal issues and important human drivers of changing biogeochemical fluxes with respect to the ethical, legal, and financial implications of the research.

The Montreal and Kyoto Protocols marked a change in attitude within the international policy community to the issues of global change related to ozone (O_3) and atmospheric CO_2. Ozone depletion and greenhouse gas emissions are increasingly recognized as threats to the quality of human life, the global economy, and ecosystems. Such threats require close observations and forecasts. As a practical matter, nations must plan to meet the commitments made in these agreements. Transparent and accountable verification of greenhouse and ozone-depleting gas sources and sinks is required. Within its area of research, SOLAS can help to better quantify the global emissions of these compounds and thereby help to address major societal needs. Presently, however, political imperative seems to be running well ahead of scientific knowledge. For example, from models that interpret atmospheric and marine measurements of CO_2, we know that the Northern Hemisphere land biota is taking up 1-2 PgC

(petagrams of C, 1 PgC = 1 GtC) of atmospheric CO_2 per year, and the global ocean a similar amount. But beyond this understanding, little scientific consensus exists as to where these sinks are (which continent or ocean), why these sinks exist (what processes are responsible), and what is the variability of these sinks on seasonal to decadal time scales.

A second example of a knowledge gap is related to aerosols, which are now recognized as having a significant effect on global climate change, but aerosol generation, chemistry, and fate have received relatively little attention. Without a substantial maturation and deepening of our knowledge about the complex aerosol system, scientists will be unable to provide verification techniques or reliably forecast trends.

Similar arguments apply to O_3 depletion where, in spite of the success of the Montreal Protocol, O_3 recovery is being delayed by the continued increases in brominated gases and chlorofluorocarbon (CFC) replacements and potentially, by global warming. This perturbation should be evaluated within the context of the large scale and uncertain air-sea exchange of biogenic halogen gases [Bromine (Br), Chlorine (Cl), and Iodine (I)]. Another example is the proposal to fertilize large parts of the open oceans with Fe in order to enhance the oceanic sink for CO_2. In this case, the proposed industrial application is running substantially ahead of scientific understanding. All these topics, together with many others, are some of the major scientific issues facing the SOLAS program. SOLAS research can help to build sound scientific foundations for future policy making.

Simulations of future climate are only now beginning to incorporate the biological and chemical feedbacks that may arise as the atmosphere-ocean system changes in response to climate and other environmental forcings. These simulations give divergent predictions, depending on which feedbacks are included and how they are modeled. Substantial changes in natural sources and sinks of climatically active gases are possible and indeed probable after climate change effects become obvious. Even though CO_2 is the most closely studied example, DMS and other chemically active trace species, such as organohalogens may also have important effects. To date, all of these species are infrequently addressed. These deficiencies lead to uncertainties in the timing and magnitude of global change effects by many decades. The social and economic implications of these uncertainties are clearly profound. Adaptation strategies are highly dependent on the time scales of change. SOLAS is designed to address these issues, with the purpose of substantially reducing the uncertainties in our predictions of the timing and effects of future global and climate change.

The US-SOLAS has a strong outreach activity to entrain young scientists with the participation in the International SOLAS Summer School led by Corinne LeQuéré and Veronique Garcon. Many international participants meet near the Mediterranean Sea at Institut d'Études Scientifiques de Cargèse in Corsica. One of the purposes of the School is to introduce graduate students and young researchers to different components of SOLAS. The interdisciplinary nature of the International SOLAS summer school offers a wide range of educational opportunities. It also provided an opportunity for the participants to meet one another and the lecturers.

The course has a theoretical framework and uses practical exercises and laboratory experiments to create an intense learning environment. Lectures take place in early morning and late afternoon alternated with practical lessons and student presentations. Lecture topics focus on broad overviews of the large-scale processes that control the distribution of the compounds relevant to climate in the surface ocean and lower atmosphere. Specifically, there are lectures on the global carbon cycle, biogeochemical modeling,

gas exchange, physical and biogeochemical processes in the coastal zone, data assimilation, marine ecology, and atmospheric chemistry.

Support for the US-SOLAS participation in the 2003 and 2005 International Summer Schools was gratefully provided through generous grants from: the National Aeronautics and Space Administration (NASA) by Charles Trees and Paula Bontempi; the National Oceanic and Atmospheric Administration (NOAA) by Lisa Dilling and Kathy Tedesco; the National Science Foundation (NSF) by Don Rice and Anne-Marie Schmoltner; and the Office of Naval Research (ONR) by Ronald Ferek.

SOLAS and the Global Carbon Cycle

SOLAS cannot address all issues related to the ocean's present and future role in the global carbon cycle. Rather, it will address an important subset of carbon cycle issues that are compatible with its overall goals, domain, and technical approaches. These topics can be summarized as:

- Quantification of the present-day exchange of CO_2 and carbon-related properties between the atmosphere and the surface ocean
- Understanding of surface-layer processes that can change the future air-sea CO_2 flux with potential implications for altered sequestration of C within the ocean

SOLAS will focus on providing a description of the contemporary geographical and temporal structure and variation of air-sea CO_2 fluxes, as well as the mechanistic understanding of surface-layer processes that determine these fluxes, both now and in the future. This description should include a strong emphasis on continental margins where forcing and fluxes can be particularly large. SOLAS is not the appropriate home for a global-scale pCO_2 measurement system, but its work will help guide the development and progress of such a program, which the SOLAS SSC will strongly support. The limited SOLAS objectives above will provide a foundation for broader global carbon cycle science activities in the Global Carbon Project (GCP), particularly for the evaluation and parameterization of processes in the models required to predict future ocean C sequestration.

Interdisciplinary Research and Integration

More than is usually the case, meaningful developments in SOLAS will depend on research that is not only interdisciplinary, but that also involves closely coordinated field studies. These field studies will combine the different research components to produce comprehensive data sets. Achieving an understanding of processes that occur at the ocean-atmosphere interface will require an enhanced level of cooperation in planning and execution of research among many different disciplines in the environmental sciences. The success of SOLAS will depend on the effectiveness of such cooperation and ability to integrate measurements and analyses of many different types.

These challenges call for efforts to bring together young and established researchers from different countries for the exchange of ideas and experiences. The first and second International SOLAS Summer School sessions were held in 2003 and 2005 with participants from a variety of backgrounds. In addition and most importantly, research involving the coherent study of linkages between environmental compartments (in the case of SOLAS, atmosphere and oceans) will require a shift in attitude within the

academic community and research funding agencies, both of which are generally organized on a medium-by-medium basis. Bridging such barriers is vital because knowledge of atmosphere-ocean interactions is key to understanding climate and other global changes.

Mission of the US-SOLAS Science Steering Committee

The US-SOLAS Science Steering Committee (SSC) currently consists of Chairs, Wade McGillis (Columbia University) and Eric Saltzman (University of California at Irvine) with fifteen scientists recommended by NSF, NOAA, and NASA. The group works closely with the US Ocean Carbon and Biogeochemistry Program (OCB), the International SOLAS Program Office (IPO), and the World Climate Research Program (WCRP). It is also developing strong interactions with other IGBP Programs, such as IMBER, LOICZ, CLIVAR, and the Joint Carbon Project (JCP). The US-SOLAS SSC is currently comprised of ad-hoc, volunteer experts from the diverse SOLAS domains.

The main objectives of the US-SOLAS SSC include:

- Encouraging, soliciting, collecting, and compiling US-SOLAS projects under a developed protocol
- Generating an ongoing database for past, present, and future observational, modeling, and theoretical US-SOLAS activities
- Producing and maintaining this Science Implementation Strategy, which will be updated and revised periodically
- Meeting at conferences and workshops
- Annually reporting to the NSF, NOAA, and NASA oceanic and atmospheric directorates
- Coordinating activities with those of the other complementary program such as OCB and IMBER, particularly with data management efforts
- Making contributions to US-SOLAS workshops and representing US-SOLAS in other program workshops
- Working closely with the international SOLAS program and their complementary working group
- Fostering collaborations with other IGBP, SCOR, and WCRP-sponsored international programs such as IMBER, LOIDC, CLIVAR and Joint Carbon Project (JCP)

Recommended US-SOLAS Initiatives and Projects

1.1 Global Ocean Trace Gas Surveys
1.2 The North-Atlantic African Dust-Aerosol Experiment (NafDAE)
1.3 Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS)
1.4 Climate Modeling in SOLAS (CLIMAS)

2.1 World Ocean Gas Exchange Process Studies
2.2 Surface Spray *In-Situ* and Modeling Studies
2.3 Halogens in the Troposphere - US-SOLAS (HiT-US)
2.4 Cape Verde Air-Sea Interaction Time-series Station

Project

1.1

Global Ocean Trace Gas Surveys

Goals

Understand the global seasonal and interannual variations in surface trace gases including surface reactive and noble gases such as, dimethyl sulphide (DMS), volatile organic chemicals (VOCs), and isoprene.

Understanding to Date:

The production of a climatology of sea surface saturation state and mixed layer trace gas levels over the major oceanographic regimes in all four seasons is recommended. This pursuit may involve a combination of surveys aboard ships of opportunity, as well as dedicated cruises. It may also include intensive studies in conjunction with existing water column process and gas exchange studies. This mission is essentially already underway, but only in an informal sense. It would be useful to formalize a program of work and create a US working group to address standardization and data management issues, as well as develop new deployment opportunities for global coverage. Existing oceanographic time-series stations, such as the Hawai'i Ocean Time-series (HOT) station and Bermuda Atlantic Time-series Study (BATS), could serve as hosts for this long-term monitoring program of the surface trace gases and their concentration and sea surface saturation state in oceanic environments. The critically needed air-sea fluxes of trace gases on a time series will begin to provide an understanding of the budgets of these gases in our oceanic and atmospheric biospheres. Obtaining global trace gas concentrations will further our understanding of the exchange across the air-sea interface and the processes that control them in the atmospheric boundary layer.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What are the dominant features of the spatial distributions of trace gases?
- What controls the global distributions of trace gases in the surface ocean?
- Will a concerted effort to survey trace gases in the surface ocean allow one to assess changes in time concurrent with physical climate change?

Project Description

Target 1: Conduct long-term global surveys of climate reactive gases in the surface ocean.

Target 2: Assess various methods of augmenting station data with satellite measurements.

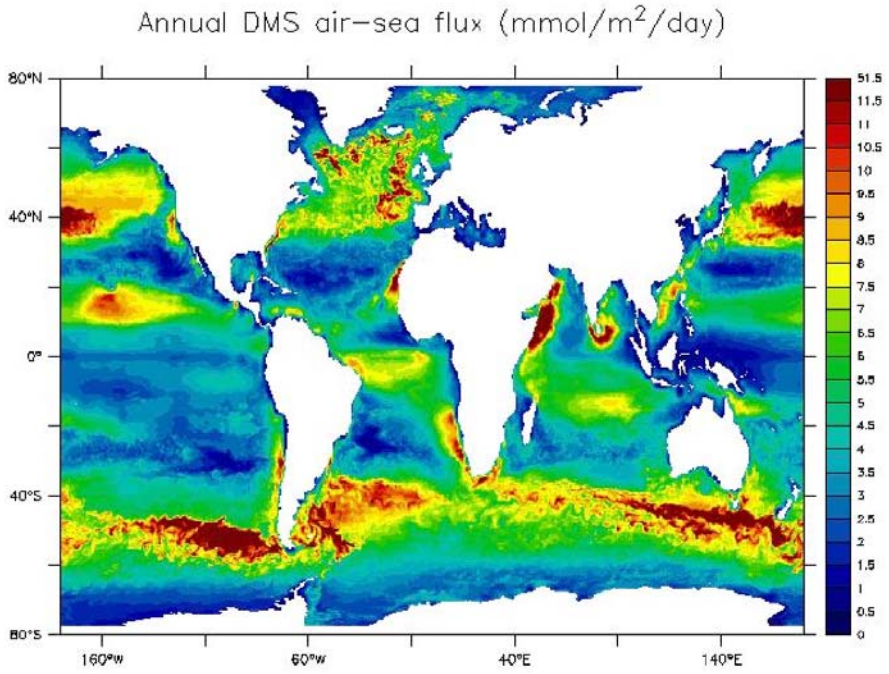

Figure 5: Modeled global air-sea DMS flux. A global survey of other climate relevant compounds, in collaboration with carbon dioxide global surveys, may provide a significant contribution to understanding the global cycling of these compounds (courtesy of S. Chu *et al.*, 2004).

International Interactions

Global trace gas surveys complement the international activity of ascertaining the global surface concentration field of carbon dioxide (CO_2). This project requires complete international collaboration to successfully cover the global domain.

Research Needs

- Buoys
- Moorings
- Weather stations and towers

Project Contributors

- David Erickson, Oak Ridge National Laboratory (ORNL)
- Richard Feely, National Oceanic and Atmospheric Administration (NOAA)
- William Jenkins, Woods Hole Oceanographic Institution (WHOI)
- Ronald Kiene, University of Alabama
- William Miller, University of Georgia
- Eric Saltzman, University of California at Irvine

References

Chu, S., S. Elliott, M. Multrud, J. Hernandez, and D. J. Erickson III, 2004: Ecodynamics and eddy-admitting dimethyl sulfide simulations in a global ocean biogeochemistry/ circulation model, *Earth Interactions* 10, 1175/1087-3562.

Project

1.2

The North-Atlantic African Dust-Aerosol Experiment (NafDAE)

Goals

Understand Biogeochemical Interactions and Feedbacks Between Ocean and Atmosphere.

Understanding to Date:

Iron and Marine Productivity: Natural and anthropogenic changes in climate and global biogeochemistry alter the atmospheric input of aerosols containing iron (Fe) and other essential trace metals to the ocean. These changes may cause adjustments in planktonic productivity and food web structure, resulting in altered carbon partitioning and biogenic air-sea gas fluxes.

Determine the Exchange Processes at the Air-Sea Interface and the Role of Transport and Transformation in the Atmospheric and Oceanic Boundary Layers.

Understanding to Date:

Exchange Across the Air-Sea Interface: Understanding physical and biogeochemical processes near the air-sea interface is critical for predicting the air-sea exchange of gases and aerosol particles. It is also important to determine how these processes will affect and be affected by global change.

Processes in the Atmospheric Boundary Layer: Understanding atmospheric boundary layer physics and biogeochemical processes is crucial for predicting the air-sea exchange of gases and particles. It is also vital to determine how these processes will affect and be affected by global change.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- How is the transport and deposition of dust and associated aerosols to the eastern Atlantic linked to large-scale meteorological processes over North Africa and the tropical Atlantic?
- How is dust-aerosol deposition in individual rain events over the eastern Atlantic quantitatively related to atmospheric conditions over the region?
- How do oceanic Fe concentrations and speciation in the deposition area respond to these sporadic inputs?
- How does this response contrast to conditions when dry deposition is dominant in these same regions?
- What are the chemical responses to the inputs of dust-iron and other aerosol species as a result of biological processes in the surface waters?

Project Description

Iron (Fe) is a limiting nutrient in many high-nutrient, low-chlorophyll (HNLC) regions of the global ocean. Experiments show that *in situ* additions of Fe to these waters can greatly stimulate primary productivity. It is hypothesized that Fe associated with wind-transported mineral dust is a major source of Fe to many of these HNLC regions. While there is considerable evidence that supports the importance of dust-iron on ocean biogeochemisty, there have been no major efforts to directly characterize and quantify the impact of the natural additions of mineral dust to ocean waters. Moreover, scientists have not developed an understanding of the meteorological processes that carry dust to the marine atmosphere and remove it to the ocean. Neither have they quantitatively related the deposition of dust to the ocean surface to the iron-related processes in the underlying water column.

The aeolian dust and Fe input to the ocean takes place through both wet (by precipitation and scavenging) and dry deposition. Our current knowledge of wet deposition fluxes of mineral dust rests upon a relatively limited set of measurements that were carried out primarily on a few island stations. While wet deposition can be measured with acceptable accuracy, dry deposition can be estimated only coarsely. In order to address the deposition of dust to the global oceans, it will be necessary to have a much better quantitative understanding of both of these processes over the oceans. This understanding is essential to the further development of the global dust models that will ultimately be required to gain a quantitative picture of dust impact on the present day oceans and future impacts from climate change. While global dust models have improved considerably over the past few years, the parameterization of removal processes remains crude.

On smaller scales, we need a better understanding of how atmospheric processes, especially the incorporation of mineral dust into precipitation, could affect the solubility of Fe and its bioavailability to phytoplankton in the surface ocean (Kieber *et al.*, 2001). The biological

uptake of Fe largely depends on its solubility and chemical speciation in seawater (Wells *et al.*, 1995). Photochemical reactions in more acidic cloud waters and precipitation may promote dissolution of Fe in dust, and thus the input of Fe by precipitation may be particularly important.

Although the central focus of this science activity is on Fe, there are many other chemical species present in the aerosol clouds that emerge from the coast of Africa. Prominent components in these clouds include nitrate (NO_3^-), ammonium (NH_4^+), and other various organic nitrogen species. These are produced from a wide variety of natural and anthropogenic sources in Europe and Africa. Dust also includes substantial quantities of phosphorous (P). Both dissolved inorganic nutrients (DIN) and P might be expected to play a role as nutrients in this region. For example, as noted below, a prominent plume of excess DIN is observed in waters that underlie the dust plume in the tropical Atlantic. The deposition of this complex mix of species is expected to impact biological processes in the region. The changed processes could then affect the emissions of a wide range of species, including various biogenic trace gases, such as dimethyl sulfide (DMS), methyl bromide (CH_3Br), bromoform ($CHBr_3$), and other halocarbons.

To address these issues, we propose an experiment to be carried out in the eastern Atlantic Ocean to focus on three primary target investigations:

Target 1: Characterize the transport and removal processes of mineral dust and related aerosol particles over the tropical Atlantic.

A critical issue is to link the understanding of dust transport on a large scale to precipitation processes on small scales. Over the last several decades, much has been learned about the transport of dust over the Atlantic. This knowledge is based on field studies on North Africa, on islands in the Atlantic, and aboard ships and aircraft. These measurements show that large quantities of dust are carried over this region during much of the year. Satellites allow extrapolation of these studies to higher resolution on both the temporal and spatial scales. There have been, however, only a few *in situ* physical and chemical studies of the temporal and spatial distribution of dust with respect to meteorological forcing. *In situ* investigations will help elucidate the meteorological processes that affect dust transport and removal.

Dust generation appears to be closely linked to the presence of African Easterly Waves (AEWs) and the mesoscale cyclonic systems (MCS) that are typically embedded in the AEWs. These systems move across West Africa and into the tropical Atlantic. In the Atlantic, many evolve into tropical storms and some develop into hurricanes. During the summer months, AEWs move across the coast of Africa in a cycle of 5-6 days. In satellite images, each wave is preceded by and then followed by dust. Dust is strongly associated with the Saharan Air Layer (SAL), a layer of hot, dry air that has its origins over the deserts. The close association of the SAL with the AEWs and the Intertropical Convergence Zone (ITCZ) (see Figure 6) and the intense cloud and precipitation that occurs in these regions provides a good mechanism for the frequent and efficient removal of dust by precipitation.

This phase of the study would be carried out by coordinated measurements from an aircraft (such as the NCAR C-130) and a ship (such as the NOAA Research Vessel *Ronald H. Brown*), which would focus on the passage of AEWs. Measurements would involve a wide variety of aerosol properties, precipitation, and cloud microphysics. Radar aboard the ship would provide information on cloud distribution, cloud properties, and the distribution and intensity of rainfall. The ship would also carry a wide range of aerosol and precipitation chemistry instrumentation.

The optimal time of year for this study is July when there is a lot of dust being transported across the region and when rainfall is relatively plentiful and frequent.

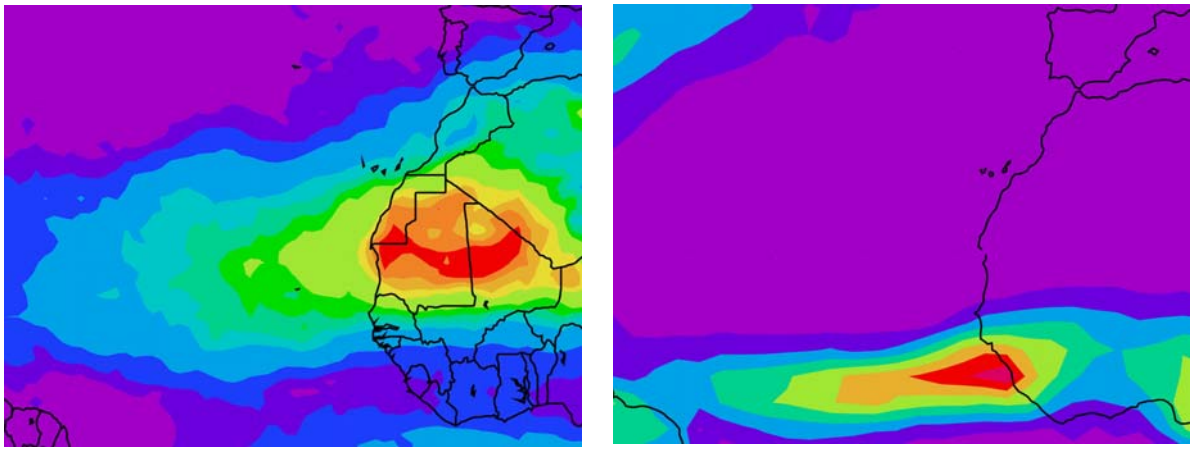

Figure 6: The July mean TOMS aerosol index over the tropical Atlantic (on the left) and July monthly mean precipitation. The research focus area would be between ca. 10°N and 15°N (courtesy of Joseph Prospero and Chidong Zhang, University of Miami).

An aircraft carrying a broad range of aerosol instrumentation and operating out of the Cape Verde Islands could penetrate AEWs and the associated dust clouds. Flights would be coordinated with the ship. Satellites, such as the MODIS and MISR, would provide information on aerosol distributions and in some cases gross physical properties. The lidar satellites, GLAS and CALIPSO, would provide sporadic altitude distribution. Ground-based and ship-based lidars could provide vertical profiles on a continuous basis. These data sets, integrated with aerosol prediction models, will help to guide the ship and aircraft to areas of interest.

The best year for this study would be 2007 when a large-scale program, called the African Monsoon Multidisciplinary Analysis (AMMA), is being carried out over western Africa and the tropical Atlantic. AMMA is an international project with the goal of improving our knowledge and understanding of the West African monsoon (WAM) and its variability on daily-to-interannual time scales. AMMA, primarily a European effort, will be involved in several field campaigns that would provide a broad range of meteorological and source-region data, which would also be valuable to NafDAE. For more details on AMMA, see the International Interactions section of this chapter.

Target 2: Measure the deposition rate of dust and associated chemical species [such as Fe, aluminum (Al), P, nitrogen species, organic carbon (C), and perhaps trace elements] to the ocean surface in individual rain events. Follow the subsequent changes in the concentration of these species in the surface waters.

The ultimate objective of this study is to develop a quantitative link between processes on the atmospheric side of the water interface and those in the underlying water column. The shipboard component would target individual cumulus cloud rain events using ship radar information, cloud properties, and precipitation intensity. Rain deposition areas would be identified based on the mapping of surface water concentration of hydrogen peroxide (H_2O_2) using towed detectors. Precipitation penetration would be based on profiles of the H_2O_2 distribution in the short term and beryllium-7 (^7Be) distributions in the long term. The Fe, Al, and other element distributions would be mapped concurrently using *in situ* detection systems where possible. Periodic grab samples would be collected to make high-precision measurements of the dissolved and particulate Fe, Al, and other elements.

Although the major focus is deposition of dust and its associated chemical species, nitrogen species would also be measured in aerosols, precipitation, and ocean surface waters. It is noted that the ocean region underlying the dust plume in Figure 6 is also the region where a large plume of excess DIN is present in the upper thermocline (Hansell *et al.*, 2004). A study in the Sargasso Sea has shown that the concentration of excess DIN is highly correlated with African dust concentrations as measured on Bermuda. It has been believed that nitrogen gas (N_2) fixation in the surface layer, in part supported by dust-borne Fe, was the primary source of the excess NO_3^- in the thermocline. Given the high N:P ratio of dust, and the high dust flux to the region, it is likely that some of the excess NO_3^- signal is carried to the region by deposition of dust. The extent of this contribution is unknown, but must be determined.

Target 3: Document the chemical responses to these atmospheric inputs as a result of biological processes in the surface and thermocline waters.

The tropical Atlantic is not an iron-limited region. Thus, it would not be warranted to carry out an extensive biological-response field study. Instead, the major efforts should focus on characterizing the first-order response to dust inputs and the temporal-spatial variability related to dust deposition events. In addition, the input of terriginous dissolved organic matter (DOM) to the surface ocean during dust events should be examined. For example, a dust event that carries DOM and is co-located with the large DIN pool mentioned above could result in enhanced dissolved alkyl nitrate concentrations.

To this end we need continuous and discrete water measurements of a wide range of biogenic trace gases: DMS, CH_3Br, $CHBr_3$, and other halocarbons; inert physical tracers such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs); and photochemically produced compounds, such as alkyl nitrates. Existing and ongoing measurements of surface chlorophyll and fast repetition rate (FRR) fluorometry could be used to determine short-term biological responses to dust and could be coupled to ocean

color observations (SeaWiFS and MODIS). Depending on preliminary results, more detailed biogeochemical studies involving characterization of key phytoplankton, such as diazotrophs, would be undertaken. These studies would examine the response of the biogenic trace gases over time to inputs, the effects on primary production and N_2 fixation, and the dynamics of the gases in inorganic nutrient and CRC pools. An appropriately located mooring, which would be similar to the Bermuda Testbed Mooring, with physical, bio-optical, and chemical sensing/sampling devices would be a valuable addition to the experiment.

International Interactions

Many of the activities proposed in this effort are complementary to a number of objectives of international programs, in particular the African Monsoon Multidisciplinary Analysis (AMMA), the International Global Atmospheric Chemistry (IGAC) Project, and the Integrated Land Ecosystem Atmosphere Process Study (iLEAPS).

African Monsoon Multidisciplinary Analysis (AMMA)

The main goal of this international project (www.amma-international.org) is to improve our knowledge of the West African monsoon (WAM), its variability on daily-to-interannual time scales, and the impact of WAM on the meteorology of the tropical Atlantic. AMMA is motivated by an interest in fundamental scientific issues and by the societal need for improved prediction of the WAM and its impacts on West African and American nations (through its impact on the tropical Atlantic). Incorporated into AMMA is an extensive atmospheric chemistry program. The objectives of this program address the following questions:

- What is the impact of various sources of environmental processes, such as lightning, biomass burning, mineral dust, and pollutants?
- What are the relative roles of humans and natural processes?
- What are the links between small-scale phenomenon and climate processes?

AMMA will take place across a broad region of West Africa and the tropical Atlantic. It will provide to NafDAE valuable upstream meteorological data and information on source region processes, as well as an extensive array of chemical measurements. Augmented AMMA field programs will be carried out through 2007. In this regard, the summer of 2007 would be an advantageous time to carry out the NafDAE study.

The IGAC Science Steering Committee (SSC) endorsed the atmospheric chemistry activities in AMMA on 25 October 2004, under the title: AMMA-Atmospheric Chemistry (AMMA-AC) with C. Mari and J.M. Prospero as Task Coordinators. The expectation is that International Geosphere-Biosphere Program (IGBP) will designate AMMA as an Integrated Regional Study (IRS). As an IRS, it would interact with other programs, such as DIVERSITAS and the International Human Dimensions Program on Global Environmental Change (IHDP), with specific links with individual projects within the IGBP and World Climate Research Program (WCRP).

International Global Atmospheric Chemistry (IGAC)

The objectives of IGAC are to provide "a fundamental understanding of the processes that control the distributions of chemical species in the atmosphere and their impact on global change and air quality" and to "improve our ability to predict the chemical composition of the atmosphere over the coming decades by integrating our understanding of atmospheric processes with the response and feedbacks of the Earth System." The NafDAE program addresses many of the central issues of IGAC. These linkages are more specifically identified within the iLEAPS and AMMA programs, both of which are endorsed by IGAC.

Integrated Land Ecosystem Atmosphere Process Study (iLEAPS)

This project is a land-atmosphere project within IGBP and is the complementary land program to SOLAS. The main goal of iLEAPS is to provide an understanding of how interacting physical, chemical, and biological processes transport and transform energy and matter through the land-atmosphere interface. To help reach its goal, iLEAPS is studying the emissions from and deposition to land surfaces including various feedbacks, such as aerosol influences on cloud properties and precipitation. These activities are parallel to NafDAE's study on these same processes over the Atlantic. The iLEAPS project will be active within AMMA during its field program in North Africa. The iLEAPS measurements will provide vital information on aerosol properties over some of the source regions that feed the tropical Atlantic.

Research Needs

- NCAR C-130 aircraft
- NOAA research vessel, the *Ronald H. Brown*

Project Contributors

Joseph M. Prospero, University of Miami

Project

1.3

Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS)

Goals

Determine the importance of the chemical, physical, and biological exchange processes of Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS) on tropospheric chemistry, the cryosphere, and the marine environment. Ascertain the feedback mechanisms of OASIS in the context of a changing climate.

Understanding to Date:

For the most recent version of the OASIS Science Plan, please visit http://www.oasishome.net/oasis_science.htm. In January 2005, an open meeting was held in Rome, Italy to prepare the Implementation Plan (http://www.oasishome.net/implementation.htm). A schematic of the biogeochemical and SOLAS processes are shown in Figure 7.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What is the solar influence on physical, chemical, and biologically mediated chemical exchange processes involving halogens, dimethyl sulphide (DMS), nitrogen oxides (NO_x), ozone (O_3), volatile organic chemicals (VOCs), persistent organic pollutants (POPs), mercury (Hg), S-constituents, organic matter, and carbon dioxide (CO_2) in the Arctic?
- What is the importance of OASIS exchange processes on the chemistry, physics, and biology of aerosol particles and cloud/snow formation?
- What is the impact of seasonal and climatic changes in ocean, ice, and snow cover on OASIS chemical exchanges?

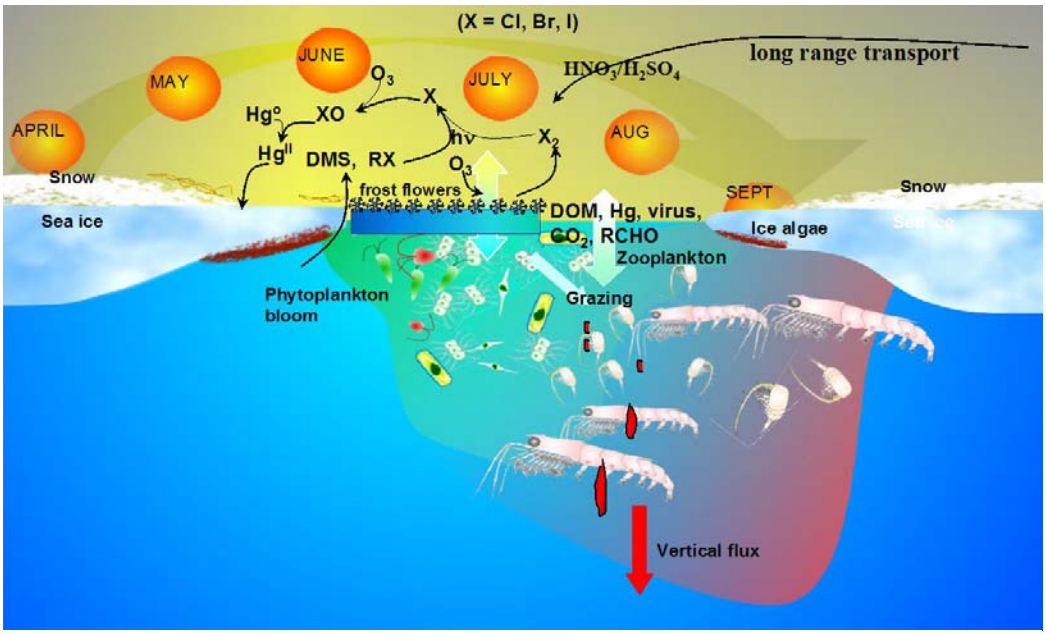

Figure 7: Seasonal variations of CRCs in the OASIS.

Project Description

The Executive Summary on the OASIS Web site describes the project (http://www.oasishome.net/Docs/OASIS%20Executive%20Summary.pdf).

International Interactions

- Accepted as a project by International SOLAS, IGAC/AICI, and WCRP/CliC
- Submitted as a project for the International Polar Year 2007-2008 (http://www.ipy.org/)
- The first workshop was held at Purdue University (West Lafayette, Indiana) with 40 attendees from 11 countries

Research Needs

- Ice breaker(s)
- Ice camp(s)
- Ice-tethered buoys

Project Contributors

- Patricia Matrai, Bigelow Laboratory for Ocean Sciences
- Paul Shepson, Purdue University

Project

1.4

Climate Modeling In SOLAS (CLIMIS)

Goals

Address the ocean-atmospheric biogeochemical coupling through modeling activities.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- How does the air-sea flux of atoms, molecules, and aerosols impact climate and climate prediction using global Earth System models?
- How does the air-sea flux of trace species impact spatial distribution of climate variables?
- What feedbacks can be identified and explicitly treated in global climate models that are grounded in SOLAS observational data sets?

Project Description

The realization that the sources and sinks of long-lived trace species have multiple non-linear feedbacks within the climate system requires that climate models explicitly treat the transport and fluxes of CO_2 and other trace species. Understanding and quantifying the air-sea fluxes of trace gases and aerosols is a SOLAS goal.

The air-sea flux of CO_2 is an important term in the global atmospheric CO_2 budget. Therefore, SOLAS provides the framework for including the details of air-sea trace gas exchange in climate models. Ocean biogeochemistry plays an important role in determining the surface ocean concentration of the trace gases that are rapidly exchanged with the atmosphere. Changes in ocean circulation due to changing climate; as well as upwelling, surface turbulence, and trace gas production/uptake; all influence the trace gas flux between the ocean and the atmosphere. While this feedback is particularly important for CO_2, it is probable that feedbacks exist for many other trace gases and aerosols. This possibility also should be a focus of SOLAS studies. Because aerosols are closely related to atmospheric trace gas composition through multi-phase interactions and because aerosols interact with the radiative balance of the atmosphere, these processes also need to be included in climate

models. Trace species that impact global biogeochemical cycles, such as dust aerosols that contain a varying amounts of iron (Fe), nutrients, and participate in multi-phase atmospheric chemistry; are also important factors in creating fully interactive biogeochemistry-climate Earth System models.

A recent realization in climate modeling is that the full carbon system must be included explicitly in the climate simulation. This inclusion is necessary because as CO_2 increases in the atmosphere, there may be compensatory effects related to the uptake of CO_2 by the ocean. These effects may change over the next several decades. The possibility of uptake change requires that CO_2 be treated like water vapor in that it interacts with the radiation code at every time step in the climate model. Also, the many feedbacks between climate and air-sea CO_2 fluxes should be allowed to operate freely in the climate simulation. A similar treatment is required for dimethyl sulfide (DMS), carbon monoxide (CO), methylated halogens, and many other chemical species. Including the full carbon system is essential in identifying the critical feedbacks and ensuring that these feedbacks are accurately understood and portrayed in future suites of Earth climate simulations.

Target 1: Include CO_2 and DMS in the flux coupler in the Community Climate System Model (CCSM) version 3.0 series of coupled models.

Target 2: Ensure that the atmospheric component of the Global Climate Models (GCM) have advection and perform chemical reactions, including aerosol production, on species that flux to the atmosphere from the ocean.

Target 3: Evaluate the atmospheric CO_2 and sulfur (S) budget within the context of oceanic sources. Figure 8 shows the seasonal distribution of ocean surface DMS concentrations.

Target 4: Calculate radiative forcing in the atmosphere from DMS.

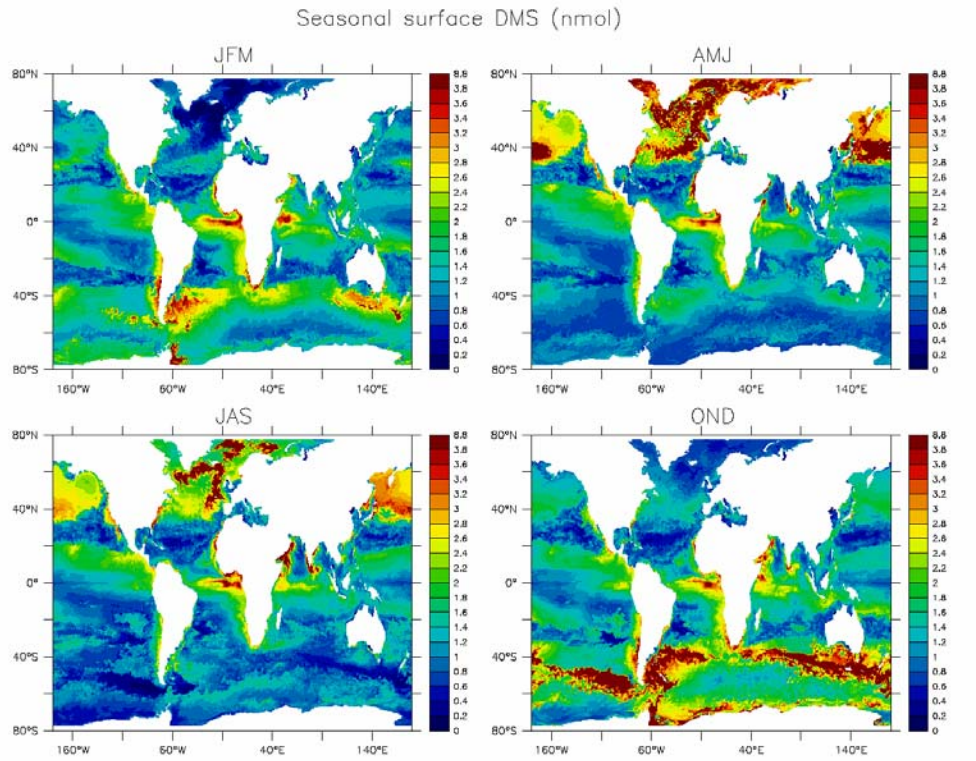

Figure 8: Seasonal variations in ocean surface DMS concentrations (Chu *et al.*, 2004).

Target 5: Evaluate atmospheric circulation, precipitation, and radiation changes due to DMS.

Target 5 will serve as a starting point for ensuring that SOLAS-related fluxes of trace gases, aerosols, and precipitation related to a complete representation of biogeochemical cycles actually impact atmospheric circulation, precipitation, and radiation changes in quantitative climate prediction.

International Interactions

- Australia - Griffith University
- European Union - Atmospheric Chemists
- France - Institute Pierre Simon Laplace (IPSL)
- Japan - Earth Simulator Research Project
- New Zealand - National Institute of Water and Atmospheric (NIWA) Research
- Spain - Institute Ciencias PG Maritim Barceloneta
- United Kingdom - Hadley Centre for Climate Prediction and Research

Research Needs

- Assimilation data products
- High performance computational platforms
- Version 3 of CCSM and related numerical climate models

Project Contributors

- Scott Elliot, Los Alamos National Laboratory (LANL)
- David Erickson, Oak Ridge National Laboratory (ORNL)

Project

2.1

World Ocean Gas Exchange Process Studies

Goals

Improve the parameterization of marine gas exchange using process studies that rely on the following:

- **Direct eddy correlation flux measurements of dimethyl sulfide (DMS), ozone (O_3), carbon dioxide (CO_2), sulfur dioxide (SO_2), and any other species for which fast analytical methods exist**
- **Deliberate tracer releases (such as ^3He and SF_6) for integrated measurements of gas transfer velocities**
- **Simultaneous measurements of as many potential controlling parameters as possible**

Understanding to Date:

Lab and field studies have demonstrated that many factors other than wind, control gas transfer velocities (Wanninkhof and McGillis, 1999). Among these factors are: sea state, capillary waves, wave breaking, bubble spectra, air-water turbulence and mixing, rainfall, and surface films. To a large degree our inability to develop quantitative flux algorithms results from our earlier inability to measure gas transfer velocities on sub-hour time scales that could clearly relate condition changes to flux changes. Now that we can measure some of these gas fluxes, such as DMS, we can quantify the impacts of many more controlling factors.

Conduct these flux process studies in all of the important geographical regions of the world's oceans to develop data sets that include the entire range of regionally specific controlling factors that could impact global gas flux and climate models.

Understanding to Date:

Reducing the uncertainty in air-sea gas fluxes has been an ongoing research activity. Air-sea fluxes under a variety of environmental regimes are not well understood or parameterized. The CO_2 transfer velocity in coastal zones has been reported to be substantially higher than open-ocean predictions (Weseley *et al.*, 1982). Under open-ocean and lake conditions, observations show a dependence of k, the transfer velocity, on wind speed and stability (Cole and Caraco, 1998; Liss and Merlivat, 1986; Nightingale, 2000; Wanninkhof and McGillis, 1999; Erickson, 1994; McGillis *et al.*, 2001). Increasing evidence suggests that wind waves play a dominant role in controlling k (Bock *et al.*, 1999; Jähne *et al.*, 1987) at scales ranging from microbreaking (Zappa *et al.*, 2001; Zappa *et al.*, 2004) through whitecapping via bubble-mediated transfer (Asher and Wanninkhof, 1998; Farmer *et al.*, 1993). In streams, the generation of turbulence by bottom friction dominates (O'Connor and Dobbins, 1958), and k scales with hydraulic characteristics, such as depth and water velocity.

One way to understand geophysical processes is to study spatial variability. For example, biota are different across the Southern Ocean, from the upwelling regions west of the continents to the oligotrophic central gyres. Likewise, surface films, swell characteristics, winds, typical bubble spectra, and vertical mixing vary from one region to the other. By carefully measuring fluxes and transfer velocities in each of the nine SOLAS regimes, we should encounter the necessary range of controlling factors and ensure that each region has one flux data set for comparison with regional models. These regional data sets can help to reduce the chance of mistakes in modeling any one type of ocean region.

Where appropriate, couple these flux process studies to marine biology and seawater sulfur chemistry studies or atmospheric sulfur chemistry, aerosol, and cloud studies; so that the related disciplines can benefit from quantifying these surface fluxes.

Understanding to Date:

Two other major types of experiments come together naturally with surface flux studies:

- Ocean mixed-layer biology and chemistry studies [often done to try to constrain sulfur (S) and carbon (C) fluxes]
- Atmospheric chemistry studies that constrain either ozone-related photochemistry or S gas reactions, aerosol formation, and the indirect effect of aerosols on clouds

In both cases, well-constrained surface gas fluxes can limit the number of assumptions and parameterizations that are needed to derive climatically important conclusions. The GasEx-1998 and GasEx-2001 studies demonstrated the feasibility of performing direct flux measurements over the ocean and the resulting ability to constrain the surface water inorganic carbon budget. The proposed effort focuses on using similar direct flux techniques to provide robust constraints on the sulfur cycle, as well as to further elucidate the hydrodynamic controls of gas transfer.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- How do changes in physical and biological controlling factors affect air-sea gas transfer velocities?
- How do transfer velocities and fluxes vary spatially?
- What factors are responsible for those transfer velocity and flux changes?
- Which rate constants, branching ratios, and condensation rates should be used in models of marine boundary layer sulfur and oxidant chemistry?
- Which seawater biological and chemical processes could be modeled more accurately if gas flux measurements were available?

Project Description

Air-sea gas fluxes must be modeled accurately for many geophysical problems, including the sequestration of atmospheric carbon and the formation and growth of climate-controlling marine aerosols. For more than a decade, however, the most widely used parameterizations of air-sea gas exchange (Liss and Merlivat 1986, Wanninkhof 1992, and subsequent authors) have used wind as the only correlate for gas transfer velocities.

Regional Air-Sea Exchange Campaigns

US-SOLAS recommends nine major field campaigns spanning all four foci during its ten-year lifetime (see introduction). These campaigns will combine sustained observations, intensive process studies, remote sensing, and modeling. Focus 2 will play a strong role in at least seven of these campaigns. The campaigns are designed to allow the broad sweep of experiments called for in this plan to converge. In particular, a set of regional air-sea exchange experiments would allow investigation of non-wind speed forcings of air-sea exchange (such as surfactants, fetch, rainfall regime, wave field, spray, and bubbles). Investigating regional experiments is critical as these non-wind speed forcings of air-sea exchange are often geographically unique.

The studies should be done in areas where there is a significant flux of climate relevant gases and where the auxiliary forcing is distinct and separable from wind forcing (see Figure 9). Seven of the target studies that are described here that take advantage of infrastructures or other programs that have a strong interest in flux parameterizations.

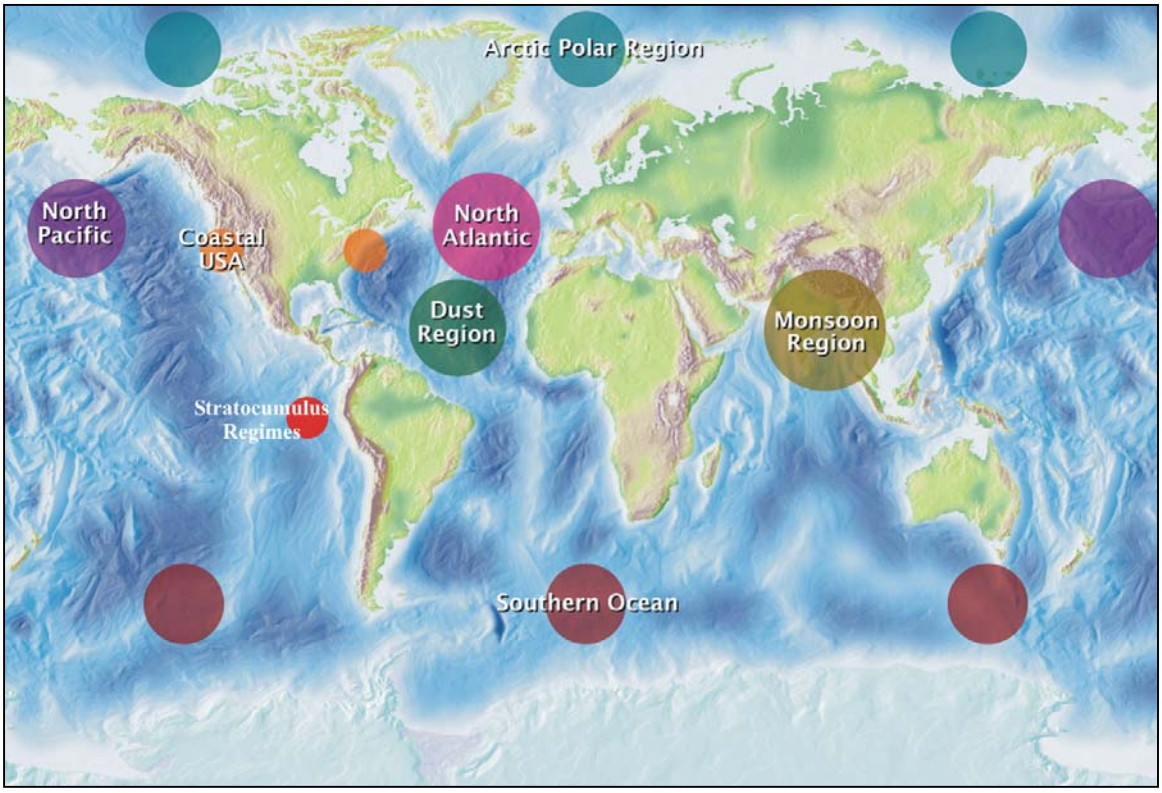

Figure 9: Air-sea gas exchange regions recommended for study.

The scope of the studies is ambitious and provides infrastructure and synergism with several other efforts within SOLAS and other international programs. It is envisioned that these studies would occur in concert with other regional process studies, see Table 1.

Table 1: Air-Sea Gas Exchange Regions Recommended for Study

Study Region	Infrastructure	Processes	Climate Relevant Compounds	Program Linkages
Coastal United States	Sustained-tower fluxes	Surfactants Fetch Bottom-boundary friction Air-sea temperature difference Stratification Heterogeneity	CO_2 fluxes Methane (CH_4) fluxes Halocarbon fluxes	Land Ocean Interaction in the Coastal Zone (LOICZ II) CarboEurope North American Carbon Program (NACP) Ocean Carbon and Biogeochemistry (OCB)
Southern Ocean	Large buoys may need to be developed and deployed	High wind Swells Understand unknown CO_2 variability	CO_2 fluxes Bubble - mediated fluxes Aerosols	CLIVAR (Climate Variability and Predictability) sponsored by the World Climate Research Programme (WCRP)
North Pacific and Atlantic	Voluntary Observing Ships (VOS) Buoys	Coastal upwelling Eckman cells	Bubble-mediated fluxes Aerosols	The Ocean Observatories Initiative (OOI) The NEPTUNE Project (To establish a regional cabled observatory in the northeast Pacific Ocean) NACP
Monsoon Region	Capture episodic events Riverine inputs	Coastal upwelling Seasonal forcing	CO_2 fluxes Nitrous oxide (N_2O) fluxes	ENSO

Study Region	Infrastructure	Processes	Climate Relevant Compounds	Program Linkages
Tropical Pacific	Hawai'i Ocean Time-series (HOT)	Persistent low winds El Niño-Southern Oscillation (ENSO) Often oligotrophic High heat fluxes High CO_2 outgassing	CO_2 fluxes	Tropical Atmosphere Ocean Project (TAO) ENSO
Dust Region	Cape Verde monitoring, BATS monitoring station	Fe deposition phytoplankton blooms chlorophyll correlations	Aerosols DMS CO_2	CARBOOCEAN Tenatso
Stratocumulus Regimes	Radiator fin Aircraft Buoys	Particle formation CCN Light/DMS response	DMS Halogens Aerosols	CLIVAR-VAMOS Ocean-Cloud-Atmosphere-Land Study (VOCALS)
Arctic Polar Region	Canadian ice-breaker	Transport in polynas Leads Ice melts	DMS CO_2 Bromine monoxide (BrO) O_3 Persistent organic pollutants (POPs)	International Polar Year (IPY) 2007-2008 Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS)

The design of the studies mentioned above will have many commonalities including the ability to:

- Capture a range of forcing
- Measure gas fluxes with micrometeorological techniques
- Use independent means to constrain gas fluxes through mass balance approaches
- Characterize the forcing parameters accurately

Comprehensive background information should be available or should be obtained prior to the studies to characterize the scales of variability and heterogeneity in surface concentrations and forcing. Remotely sensed information is particularly useful in this regard.

The studies also have commonality in experimental design in that they should cover a representative spectrum of spatial and temporal variability encountered in the regime. The processes to be studied are often so strongly non-linear that episodic events can have a

disproportionate effect on the fluxes. Several of the designs include a nested approach of intensive (shipboard) studies at locations of sustained flux and surface water measurements on autonomous platforms. Measurements from the autonomous platforms should cover one to two years to capture phenomenon associated with the seasonal cycles, such as winter storms, monsoons, and spring blooms.

Atlantic Coastal Study

The heterogeneous nature and local focus of coastal studies have hampered quantitative and integrative understanding of this region. The LOICZ I and II programs (www.loicz.org) have made major inroads into upscaling and extrapolating biogeochemical fluxes. One area where US-SOLAS can make a contribution is to improve the constraints of air-water fluxes through development of robust algorithms.

The gas fluxes from coastal areas are poorly quantified. The air-water disequilibrium anomalies of climate relevant gases such as CO_2, CH_4, and N_2O are often quite large due to enhanced biological productivity and remineralization in the water column and sediments. Gas fluxes are not well constrained where magnitude and sometimes even the directions of fluxes on regional scales are uncertain.

Coastal regimes have several unique features that might yield different flux algorithms compared to algorithms of the open ocean. Several of the parameters that affect coastal gas transfer, such as fetch and surfactants, also operate in the open ocean, but at smaller levels. Therefore, the information gleaned from the coastal areas where certain processes dominate, will lead to refinements in open ocean bulk algorithms.

Surfactants, a generic description of a large number of compounds with varying levels of hydrophobicity, are known to have a significant effect on gas transfer by suppressing formation of capillary waves. Surfactants are so ubiquitous in the coastal ocean that the surfactant effects should be pronounced. Studies should incorporate determination of key physical parameters of the surfactants along with good measurements of surface stress, near surface turbulence, and (capillary) wave field. Because of the ephemeral nature of surfactants and patchiness, direct flux measurements with high frequency are essential in this context.

Fetch effects heavily influence the coastal environment. Depending on location and wind direction, fetch can range from less than one kilometer to several thousand kilometers. Fetch has a dramatic influence on friction velocity and presumably on air-sea gas fluxes. The same applies for sea-spray aerosols. Wind direction is the controlling factor on fetch effects and direction can change on daily scales. Therefore, a direct flux measurement at high frequency is the preferred method of determining air-sea fluxes as well as the generation of sea-spray aerosols.

The protocol for the execution of experiments must take the small scales of variability into account and preferably also capture the full range of forcing. A design that includes an Eulerian component to capture the temporal variability over month and year time scales, along with a survey intensive component to address spatial variability is recommended. This design follows the successful MAGE project of the Air Sea Gas Exchange program (ASGAMAGE), but with measurements covering longer time scales. Using a tower for the

Eulerian component is optimal from a logistical perspective because it provides a stable platform for micrometeorological and near surface measurements. Many towers have sufficient power for sustained measurements. An optimal time scale to capture most scales of variability would be two years. Several surveys should be undertaken to capture the spatial variability during the study. During these intensives, measured frequency and measured parameters should increase to the level of the ship-based campaign.

Tower measurements for the two-year observation period should include surface water measurements of temperature, salinity, pCO_2, DMS, chlorophyll, and O_2. High-resolution meteorological measurements should also be taken. One or more of the micrometeorological techniques should perform continuous flux measurements of DMS and CO_2.

During the intensives, both the tower and ship should augment these measurements with surface and profile measurements of nutrients, inorganic C, and productivity estimates. Tower and ship measurements should include concentration of CO_2 and DMS in bulk surface water at 10-minute intervals or less. Automated water profiling systems would also be advantageous.

As with all the proposed gas exchange studies, this framework is such that many of the efforts outlined in other sections of the implementation plan can be performed synergistically. This framework augments the focus of the studies: to provide robust physically based parameterizations of gas transfer with environmental forcing. The North Sea and North Eastern US continental shelf are suggested as prime locations because of the accessibility of towers and their proximity to major research institutions.

Southern Ocean Study

The Southern Ocean has several unique characteristics that warrant dedicated studies (in concert with the CO_2 Project 3.2). It is a region with frequent high wind events and long fetch that both lead to large swells. The remoteness of the region and the environmental conditions have made it one of the last unexplored frontiers in oceanography. Many of the discrepancies and inconsistencies in mass balances and biogeochemical rate estimates are in this region. Numerical global circulation and biogeochemical models are very sensitive to parameterizations of processes within the Southern Ocean. Of note for US-SOLAS is the significant discrepancy between uptake estimates of CO_2 in the Southern Ocean. Estimates determined from atmospheric and oceanic (inversion) models yield one set of values; while measurement-based estimates obtained from estimates of ΔpCO_2 and gas transfer velocity yield a significantly higher set of values. The latter method suffers from a dearth of pCO_2 observations and from a lack of a firm knowledge of gas transfer velocities in this energetic region.

The process study to parameterize transfer velocities in the Southern Ocean will be centered on the deployment of a large surface mooring as part of the CLIVAR and GEO mooring network. The proposed mooring (12 meters in diameter) with possible diesel generators, will have sufficient space and power to install the relevant flux and marine air surface water measurement instruments. Ship-based process studies providing higher resolution and a larger suite of measurements will provide the proper details for interpretation.

To elucidate and quantify the controls on gas transfer at high winds from the buoy, accurate wind and friction velocity measurements must be made along with pertinent and automated measurement of wave parameters, such as wave height and period. Much of the instrumentation for measurement of physical forcing is available as part of the high resolution meteorological packages, such as the ASIMET system (http://uop.whoi.edu/) and would be provided by the main project. Robust gas flux measurement systems that can operate autonomously for 6 to 12 months with minimal power have to be improved. Autonomous measurement of CO_2 fluxes by eddy correlation and eddy accumulation methods should be attainable with a modest development effort. Instrumentation for measurement of DMS fluxes and fluxes of other climate relevant gases are not at the level for sustained autonomous measurements and would have to be done during the ship component of the study. Water column measurements should include CO_2, DMS, O_2 and total gas tension. The last two parameters can be used to assess the effect of bubble dissolution and gas transfer.

Performing the ship component as part of an iron (Fe) fertilization study as recommended in the *SOLAS Focus I Implementation Plan* (http://www.uea.ac.uk/env/solas/SPIS/pdfs/FOCUS1_IMP_plan.pdf) would be an optimal use of resources and would provide several important assets to the gas exchange studies. By adding ^3He to the sulfur hexafluoride (SF_6) tag of the fertilized patch, the gas transfer velocity can be determined over 1- to 3-day time scales. This technique provides an additional constraint to the higher frequency direct flux measurements. (A similar technique was used in the New Zealand-led SAGE experiment.) The fertilization may also cause a drawdown of CO_2, which would increase the accuracy of the direct CO_2 flux measurements. Previous Fe fertilization studies have also shown significant increases in DMS, halocarbons, and hydrocarbons, such as terpenes. Flux measurements of these compounds by gradient and conditional sampling techniques will provide additional constraints on the effect of solubility and diffusivity on gas exchange, particularly in the presence of bubbles.

North Pacific Study

The proposed NEPTUNE cable network provides an excellent opportunity for deployment of sensors with significant power and data transfer requirements. The funded Canadian portion and the proposed US design will cross the coastal upwelling regime that is characterized by large concentration anomalies of climate relevant gases. The region also experiences strong currents where the effect of wind-wave interaction on gas transfer can be studied in greater detail. An augmented study design patterned after the Canadian SOLAS Station Papa mooring is recommended. A series of moorings is proposed covering the different coastal regimes including a near-coast riverine dominated system that experiences large salinity gradients, strong buoyancy fluxes, and low pCO_2 levels. The second regime would be in the active upwelling areas, which are characterized by low SST and high pCO_2. The third regime would be just beyond the upwelling regime. This regime is where there are frequently strong currents that are both parallel to the coast and occasionally perpendicular to the coast as coastal jets. The sites of these phenomena are liable to change location over time because of changing winds, river flow, and other forcing factors, which means that the moorings will not always be centered in the regime of interest. The regimes can often be distinguished from satellite SST, color, and radar images. Optimal locations for deployment

along the NEPTUNE network can be determined by examining past satellite data. The advantage of the longer duration studies is that the particular regime can be studied in detail, despite the spatial variability.

Of particular interest in the coastal work along the western boundaries of continents is the effect of near shore air-sea fluxes on modifying air masses that flow across the continent. Some of the most robust estimates of sources and sinks of long-lived climate relevant gases, such as CO_2, are obtained from inverse models. In these models the inferred magnitude of sources and sinks are directly related to the concentration of the particular compound of interest. Current inverse models use large regions and they do not account for strong fluxes in smaller areas that can influence the adjacent boxes. For the North American continent, the concentration in the air masses entering over the west coastal region must be measured in a sustained fashion. Thus aside from the very precise air measurements necessary for the direct flux measurement, the concentration must be measured at great accuracy as well.

Monsoon Region Study

The Monsoon Region study will focus on air-sea gas fluxes in an area with extreme variation in forcing due to the effects of monsoons, such as changes in wind direction, in wind intensity, and in the amount of rainfall. Significant air-sea interaction and biogeochemical information has been obtained from the Arabian Sea over the past decades. In particular, the International Geosphere-Biosphere Program's (IGBP) study called the International Joint Global Ocean Flux Study (JGOFS) and associated work on an air-sea interaction buoy funded by the Office of Naval Research (ONR) has provided important seasonal information. No dedicated air-sea gas transfer studies were performed as part of these studies.

The focus of this gas exchange study will be on the contrasting fluxes due to monsoonal forcing. To successfully capture the effects of rain on air-sea gas transfer and boundary layer stability, the project area should be situated off the Indian Coast (Ho *et al.*, 1997). Direct flux instrumentation will have to be adapted to perform measurements under rain conditions (Ho *et al.*, accepted). Little is known about the stabilization of the water column due to formation of a fresh water lens and its effect on air-sea gas fluxes. Waterside stability can be determined with profiling floats.

Aside from surface pCO_2 measurements with levels exceeding 1000 μatm, elevated CH_4 and N_2O levels are also encountered near the coast during the monsoon period. Although the three gases have some similar characteristics, they also have important differences that can be used to elucidate gas transfer mechanisms. Carbon dioxide (CO_2), CH_4, and N_2O have similar Schmidt numbers. Therefore, their gas transfer velocity over a smooth and wavy surface should be the same, but CH_4 has a much lower solubility than CO_2. This difference can be used to separate gas transfer enhancement into turbulence and bubble components when compared to CO_2 transfer velocities. Nitrous oxide (N_2O) is an analog to CO_2, but N_2O is not buffered in the water column, nor does it experience any possible chemical enhancement effects due to hydration as CO_2 does. Therefore, studying N_2O and CO_2 gas transfer simultaneously could offer insights into possible chemical influences on air-sea CO_2 exchange.

Equatorial Pacific Study

The equatorial Pacific is one of the best-studied regimes because of its importance in the global heat, water, and carbon budgets along with the large interannual variability caused by the ENSO cycle. From the US-SOLAS perspective, the regime has many unique attributes that warrant quantification. The large fluxes of heat and several climate relevant compounds (CRCs) facilitate the measurements by improving the signal to noise. The large heat fluxes and surface currents combined with low to intermediate winds make this an ideal environment to study parameters (other than wind) that control gas and particle fluxes.

The process study in the equatorial Pacific will build on several studies of S, C, halocarbon, and productivity limitation that have been performed in the last decade. The study's objectives include the following:

- Quantifying DMS and sulfur dioxide (SO_2) fluxes and gas transfer velocities using micrometeorological techniques
- Investigating the response of the ecosystem to increased Fe availability with a focus on DMS and halocarbon production
- Discerning the environmental forcing that affects the exchange of CRCs
- Computing the effects of near surface chemical and physical gradients on fluxes
- Validating, extending, and tuning air-sea exchange models, such as the Tropical Ocean Global Atmosphere Coupled Ocean Atmosphere Response Experiment (TOGA COARE) model
- Using the results from the US-SOLAS process study, previous process studies, *in situ* synoptic observations, and remote synoptic observations to model fluxes of CRCs in the equatorial Pacific regime

This recommended study will be integrative over different CRCs and time scales through a multi-platform execution. This study will take advantage of the large infrastructure available through TAO's TRITON project, which is an array of approximately 70 moored ocean buoys in the tropical Pacific Ocean, see http://www.pmel.noaa.gov/tao/proj_over/-tour/tao_tour.html for more information. The area and scope also call for an international endeavor of the TOGA COARE study. This study will include an Fe fertilization study that perturbs the ecosystem in a systematic fashion and follows the response over its full perturbation back to its background state. This methodology has been lacking in the previous Fe perturbation studies performed in the equatorial Pacific and other regions. During the study, comprehensive micrometeorological measurements of heat, water vapor, momentum, CO_2, and halocarbons will be performed, as well as detailed near surface profiles of temperature, salinity, and pH (and other parameters that can be measured at a frequency 1 Hz). These studies will all be done in conjunction with the *SOLAS Focus 1 Implementation Plan* (http://www.uea.ac.uk/env/solas/SPIS/pdfs/FOCUS1_IMP_plan.pdf), which focuses on biogeochemical responses in the water column.

Polar Regions

The Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS) team will lead this regional activity that coincides with the IPY 2007-2008. The polar region study is aimed at filling major gaps in our knowledge of the physical and chemical variables involved with polar ocean surface

ozone and mercury depletion and radiatively active trace gas budgets. For the Arctic Ocean, we will collaborate with the International Arctic Buoy Project, the North Pole Environmental Observatory, and the proposed Arctic Ocean Observing System. Coordination is also envisioned with the satellite communities that are involved with measurements of halogen oxides, sea surface characteristics, and other chemical and physical parameters. We will conduct coordinated ice camp, icebreaker, and aircraft studies of OASIS chemical exchange, for the following species:

- DMS
- CO_2
- Volatile organic chemicals (VOCs)
- O_3
- Nitrous oxide compounds ($NO_{x/y}$)
- Mercury (Hg)
- Relative gaseous mercury (RGM) and particulate phase Hg
- POPs
- Halogen oxides and molecular halogens
- Oxygenated volatile organic chemicals (OVOCs)
- Organohalogen compounds
- Snow-phase ions
- Snow, ice, and ocean bacteria and micro-algae
- Aerosols

The impact on and by the physical state of the local environment will be a key topic of these studies, as will cloud optical properties and meteorological parameters.

Our quantitative understanding of the many processes controlling air-sea exchange has been limited in large part by the dearth of measurements of gas fluxes at the ocean's surface. Until recently, ambient fluxes had to be measured using budget methods with day-to-year time scales, but now it is possible to make eddy flux measurements of DMS (Huebert *et al.*, 2004), SO_2 (Thornton *et al.*, 2002), O_3 (Lenschow *et al.*, 1981), and CO_2 (McGillis *et al.*, 2001) on time scales of less than an hour. Therefore, now we can undertake experiments in which we measure both controlling factors and gas fluxes on time scales that allow us to quantify their covariance.

In these experiments, direct flux measurements will be accompanied by measurements of bulk fluxes and ancillary data necessary to develop, and then verify transfer velocity parameterizations. The measurements include the following variables:

- Deliberate tracers (*e.g.* ^{3}He and SF_6)
- Ocean surface wave properties (such as, period, significant wave height, and small-scale roughness)
- Oceanic and atmospheric DMS
- Surface tension (as an indicator of surface films)
- Standard bulk meteorological variables (such as wind speed, air temperature and humidity, sea surface temperature and salinity, cloud cover, boundary layer properties, rawinsondes, and precipitation)

A variety of satellite products will also be used for the foundation of parameterizations based on the remotely sensed variables of wind, sea state, and so on.

The following examples indicate the kinds of experiments that are needed and will be performed over the next year. It is important that similar experiments be planned in each of

the SOLAS regimes, from equatorial to polar waters, because many of the potential controlling factors have a unique range of values in each regime.

Target 1: CLIVAR-VAMOS Ocean-Cloud-Atmosphere-Land Study (VOCALS)

One of the fundamental issues impeding our understanding of the weather and climate system is our lack of understanding and quantification of the indirect effect of aerosols on cloud radiative properties. Another issue is the errors in simulating boundary layer clouds and their radiative properties (*e.g.* Mechoso *et al.*, 1995; Ma *et al.*, 1996). The VOCALS program is an international program in which modeling, extended-time observations[1], and intensive field observations[2] are being coordinated to address these two issues. This program is set to be operational from 2003 to 2010, including an intensive ship-based and aircraft-based campaign during a four-week period in October and November 2007.

Observations in the south equatorial Pacific (SEP) made during the EPIC 2001 field campaign (Bretherton *et al.*, 2004) suggest that drizzle production is modulated by cloud droplet number concentration. This cloud droplet number concentration is, in turn, directly related to aerosol concentration. Potentially significant evidence has been presented suggesting a direct link between drizzle and cloudiness in marine boundary layer (MBL) clouds. Open cellular convection describes the process where regions of broken cloud, embedded within otherwise overcast stratocumulus, roughly organize themselves into polygonal lattices. The regions have been termed pockets of open cells (POCs). Measurements suggest that POCs tend to be associated with low aerosol concentration (Petters *et al.*, 2004) and intense drizzle production. This link between drizzle production and cloudiness is central to the hypothesis of Albrecht (1989), that states that increases in anthropogenic aerosol may lead to a reduction in precipitation and a corresponding increase in global cloud cover and thickness. The hypothesis continues that the re-filling of POCs with clouds is probably controlled by the nucleation and growth of sulfate aerosols. The nucleation and growth of sulfate aerosols is limited by the DMS source and the sulfate aerosols' oxidation chemistry. Therefore, there is a strong need for detailed observational studies of POCs and their associated aerosol dynamics, particularly studies with collocated aircraft *in-situ* measurements and ground/shipborne remote sensing. These studies would help determine whether POCs show a fundamental mechanism in which aerosols can influence MBL cloudiness.

US-SOLAS interests include both biogeochemical issues, such as the role of biogenic gases in forming the aerosols that control marine cloud properties, and studies of the many physical factors that control air-sea exchange. We need to study the ocean chemistry and biology that modulate DMS (and other trace gas) production, including DMS flux and exchange velocity measurements, and to characterize the natural and anthropogenic aerosols

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1 These extended-time observations are made by collecting data from a relatively new group of satellite sensors and from buoy, island, and coastal measuring devices.

2 These field observations include annual buoy maintenance cruises in the south equatorial Pacific (SEP).

in the MBL. With CLIVAR, US-SOLAS should assemble an aerosol measurement team to study the chemical and physical processes controlling the aerosols inside and outside of POCs.

Target 2: DOGEE

The UK-SOLAS program has been funded to conduct two Deep Ocean Gas Exchange Experiments (DOGEE). These experiments are tentatively slated for November/December 2006 and May 2007. These months were chosen to maximize wind speeds and biological activity in the eastern Atlantic Ocean. Rob Upstill-Goddard, the DOGEE Lead Investigator, has invited US-SOLAS scientists to participate in these cruises. They plan a full suite of gas exchange and related measurements that are linked to deliberate tracer (SF_6 and ^3He) estimates of gas transfer velocities. Shipboard activities will include measuring key meteorological variables; evaluating the role of whitecaps, wave breaking, bubble distributions and surfactants during gas transfer; measuring direct air-sea fluxes of CO_2, DMS, sensible heat, latent heat and momentum by direct covariance and inertial dissipation; and measurements in the microlayer. Measurements of DMS fluxes by eddy covariance and ^3He deliberate tracers will be included. The comprehensive set of controlling factor measurements will enable the development of new, more inclusive exchange velocity parameterizations. Having several types of exchange measurements (eddy accumulation and ocean mixed-layer tracer loss) will also support some technique inter-comparisons.

International Interactions

We will work with other IGBP and WCRP international programs to supply accurate measurements and parameterizations of surface gas fluxes. US-SOLAS is already playing an important role in VOCALS, the multi-national CLIVAR initiative. We will invite the International Global Atmospheric Chemistry (IGAC) project to contribute to the MBL sulfur and aerosol studies. We will seek to and continue to work with other nations on flux measurement programs. Sponsoring research vessel cruises requires significant resources, so the US-SOLAS scientists are already and should continue to seek international collaboration, wherever possible.

Research Needs

- Integrated field programs
- NCAR C-130 and other flux-measuring aircraft
- NOAA research vessel, the *Ronald H. Brown* and other flux-measuring ships

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Project

2.2

Surface Spray *In Situ* Modeling Studies

Goals

Understand and characterize the physical processes involved in the production of bubble-mediated and spume droplets from the ocean-air interface.

Understanding to Date:

When bubbles reach the water surface, they burst and produce two types of drops. Film drops are produced by the film cap opening and are produced only by bubbles larger than about 1200 μm. The number of film drops produced has been reported to be 100-1000 per bubble (Blanchard, 1963). The opening bubble leaves a hole at the water surface from which a vertical jet rises. In the air the jet breaks into no more than six droplets that are called jet drops. The number of jet drops depends on the bubble size; bubbles larger than 1700 μm produce no jet drops, the smallest bubbles produce about six jet droplets (Spiel, 1997). High wind speeds (> 9 m s^{-1}) lead to the formation of spume drops by direct tearing from the wave tops (Monahan *et al.*, 1986; Marks, 1990). This tearing of the wave tops enhances the effective surface area for exchange of constituents that are transferred across the air-water interface. Film, jet, and spume droplets are collectively referred to as sea-spray aerosol.

The rate at which the sea surface produces spray droplets is roughly estimated as the third power of the 10-meter wind speed, U_{10}. Andreas and DeCosmo (1999) estimated that when U_{10} exceeds 20 m s^{-1}, the surface area of the airborne spray above a unit area of sea surface is equal to 10% of that unit area. In other words, at high winds, spray rapidly increases the effective surface area of the ocean and therefore, should enhance the exchange of any constituent or property normally transferred across the air-sea interface. A further spray-producing process is the formation of spume, which creates droplets that are typically larger than 20 μm. Both rain drops and spume striking the surface can produce splash droplets (Andreas *et al.*, 1995). Spume droplets account for most of the spray volume flux, but are deposited more rapidly than the smaller drops typical of bubble bursting. Small droplets can be dispersed throughout the boundary layer and can act as cloud condensation nuclei.

The magnitude of the sea-spray effect as a function of wind speed however, is a subject of debate. The main reason that such diverse opinions can exist is our uncertainty in the spray generation function (the rate at which droplets of a given size are produced per unit area of sea surface). For any given wind speed and droplet radius, the spray generation functions

available in the literature range over six orders of magnitude. Because modeled spray effects generally correlate linearly with this function, such a range means that modeled spray effects are fraught with uncertainty. Andreas (2001) has reviewed the available spray generation functions to look for some consensus. On applying theoretical tests and indirect evidence, he discarded many of the reported spray generation functions as unrealistic and recommended four as the most plausible. These four agree within half an order of magnitude. Recent determinations of the sea-spray generation functions, using various techniques based on new approaches are within similar uncertainty limits (Schulz *et al.*, 2003).

The fundamental problem is that both bubble-mediated and spume-droplet production models are usually formulated in terms of wind speed or whitecap coverage rather than the fundamental physical driving forces of the system (wave breaking, turbulent surface stress, and near-surface wind speed variability). Theoretical, experimental, and numerical efforts are required to make progress in this area.

Understand and characterize the physical processes involved in the turbulent and gravitational transport of droplets in the near-surface atmospheric-wave boundary layer region and the resultant export of droplets into the atmospheric boundary layer.

Understanding to Date:

A complete understanding of the scaling properties of droplet production (Goal 1) is only one step in solving the problem. The surface source of aerosol particles is a complex convolution of the initial ejection trajectory of the droplets (different for bubble-film, bubble-jet, and spume-droplet production modes), the surface wave displacements, and the three-dimensional velocity field over the waves. The droplet production is clearly a function of location on the waves. For small droplets, the initial ballistic trajectory is brief and of modest significance; while large drops may or may not re-impact the ocean while on their ballistic trajectory.

In principal, for a given forcing condition, the source might be characterized as $S_n(r,z,$ *wave phase)*. This formula is far too complicated for virtually all anticipated applications. A typical application would be in a numerical aerosol budget equation with horizontal averaging on 10-100 km scales, where the lowest level of the model, z_1, is tens of meters above the surface. Most of the processes discussed here are subgrid scale to the model and therefore, the source must be represented in the simplest possible fashion - as an effective surface flux at the interface. If we assume the source is used to specify the lower boundary condition in a model for the concentration of particles, *n(r)*, then the first level of the model is computed (leaving dependencies on *r* as implicit) as:

$$\frac{\partial n}{\partial t} = -\frac{[F_{z1} - F_0\ ]}{\Delta z} = -\frac{[-\kappa z_1 u_* \partial n / \partial z - V_g n - F_0\ ]}{\Delta z} \qquad (1)$$

where $\Delta z = z_1$ is the total thickness of the first model layer. The effective surface source, F_0, can be found in several ways. The simplest way is to define it as:

$$F_0 = S_{n\_eff}(z_1) - V_{d\_eff}(z_1) n(z_1) \quad (2)$$

where S_{n_eff} is the effective source strength and V_{d_eff} the effective deposition velocity (Hoppel *et al.*, 2005). At a minimum, the effective source strength is a function of the forcing and some characteristic source height; it is a parameterization derived from the physics of $S_n(r, z, \textit{wave phase})$ and the turbulent dispersion properties of particles in the flow field over waves. Understanding the interactions of the interfacial droplet production, the wave boundary layer (BL) flow field, and the convolution that leads to the effective source strength is Goal 2. Note that reaching this goal must be done in the context of an effective deposition velocity. The development of the deposition velocity parameterization is Goal 3; however, it is recognized that the true deposition velocity, that is, the rate of loss of particles to the surface in the absence of a surface source, may be different.

Understand and characterize the turbulent, inertial, and gravitational processes involved in the deposition of particles to the ocean surface. This information is needed because deposition velocity is required to relate measurements of particle fluxes and concentrations to the surface source strength.

Understanding to Date:

At present, the most reliable approach for estimating the dry deposition of particles to the ocean surface requires measurements of size-resolved aerosol composition (and inferred density), and the corresponding wind speed, relative humidity, and temperature. Deposition fluxes are then calculated based on a model originally developed by Slinn and Slinn (1980), or improved variants thereof (*e.g.* Williams, 1982; Hummelshøj *et al.*, 1992), which consider gravitational settling, impaction, and Brownian diffusion as a function of particle size both above and within the laminar sublayer at the ocean surface. The generation of such intensive input data is limited to short-term field experiments. Consequently, no long-term data records based on this approach have been produced. Currently, there is no technique for accurate direct estimation of dry deposition fluxes. Research is required to improve estimates of dry deposition velocity, as well as to develop novel techniques for direct estimation of dry fluxes.

Alternative approaches have been used to infer dry deposition rates from measurements of the chemical composition of aerosol sampled in bulk and "average" or "representative" deposition velocities. The dry deposition fluxes of many particulate species of interest [*e.g.* NO_3^-, SO_4^{2-}, and iron (Fe)] however, are typically dominated by larger aerosol size fractions (Huebert *et al.*, 1996; Turekian *et al.*, 2001), which vary greatly over space and time. Therefore, such approaches are very uncertain. Micrometeorological (*e.g.* Sievering, 1987) and inferential (*e.g.* Meyers *et al.*, 1998) techniques have been employed to estimate the dry deposition fluxes of finer-fraction (<2 mm diameter) aerosol constituents over continents.

To our knowledge, however, such approaches have not been successfully deployed in marine regions, nor have they been extended to the larger aerosol size fractions that typically dominate the dry deposition of many species to the ocean surface. The most reliable estimates of particulate dry deposition in marine regions are uncertain by a factor of at least two and probably more.

Present theories of dry deposition are based on representation of the molecular diffusion, gravitational settling, and inertial impaction. For large particles the deposition velocity must approach the gravitational settling velocity. For very small particles, molecular diffusion dominates the flux. There are some issues in defining the proper size dependence of the diffusive sublayer, but these are still tractable. The characterization of the inertial impaction, which is important for particles that dominate the optically relevant sizes, is not well understood. Present parameterizations of inertial impaction give a wide span of deposition velocities and there is little experimental evidence available to discern an accurate characterization. For example, fig. 39 in Lewis and Schwartz (2004) shows four orders of magnitude variation estimates in the deposition rate for nine representations at $r=0.1$ μm.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What are the fundamental processes to parameterize the production of sea spray (*e.g.* wind stress, energy of wave breaking, wave properties, and molecular transfer variables)?
- What are the fundamental parameters for characterization of the droplet source function (*e.g.* effective height, size spectral shape, and particle slip velocity distribution with height)?
- What is the theoretical relationship among the source function, the deposition velocity, and measurable properties of the system?

Project Description

Target 1: Characterize the scaling properties of the inertial impact component, or Stokes flow, of particle deposition.

Deposition velocity is a combination of molecular diffusion, inertial-impaction, and gravitational settling. For large particles ($r>10$) gravity dominates; for small particles ($r<0.1$) diffusion dominates. For particles in between, all mechanisms are relevant. The inertial impaction mechanism and present parameterizations are not well understood. Understanding this mechanism is critical because particles in this size range dominate the optical properties and Cloud Condensation Nuclei (CCN) spectrum of the Atmospheric Boundary Layer (ABL). This problem is best tackled with Direct Numerical Simulation (DNS) solutions over waves. These simulations would allow exploration of particle motions down to molecular sublayer scales.

Target 2: Characterize the scaling properties of the flux of whitecap-produced bubbles to the ocean surface.

For production of sea spray by bursting air bubbles, the principal quantity of interest is the flux (concentration multiplied by vertical velocity) of bubbles to the interface as a function of bubble size and location in wave phase. This issue is a subset of the more general problem of bubble-mediated gas transfer where much more information is required about the vertical distribution of bubbles. This work could be done in conjunction with gas transfer studies.

Target 3: Characterize the scaling properties of breaking wave-produced spume droplets.

Spume droplets are principally produced near the tops of breaking waves under strong wind forcing. The physics of the interactions of the turbulent circulations in the water near the wave crest are uncertain. It has been hypothesized that the spume processes is forced by the energy being dissipated by the breaking wave. When the air-water interface breaks down into a bubble/droplet mixture, the wind is able to blow some of the droplets off the top of the wave and into the wavy boundary layer. The scaling of these processes can be studied in wind-wave tanks and verified with carefully constructed field measurements from fixed platforms, such as a FLoating Instrument Platform (FLIP) or an offshore platform.

Target 4: Characterize the scaling properties of the vertical distribution of sea spray droplet properties in the near-surface atmosphere-wave layer.

Models of aerosol budget in the atmospheric boundary layer require simple representations of the particle source strength, for example, a droplet flux spectrum at an effective height. Such a simple representation should follow from a more detailed understanding of the particle ejection and transport processes in the wavy boundary layer. A combination of Large eddy simulation (LES) or DNS velocity fields over waves and laboratory studies can provide most of this information. This model could be verified in the field with simple measurements of profiles of droplet concentration spectra.

International Interactions

- EU effort led by Michael Smith (University of Leeds)
- The North Atlantic African Dust Aerosol Experiment led by US-SOLAS

Research Needs

- DNS and LES or DNS velocity fields over waves
- Offshore instrumented research platform (such as the Martha's Vineyard Coastal Observatory)
- Research platform FLIP
- Wind-wave tanks

Project Contributors

- Christopher Fairall, National Oceanic and Atmospheric Administration (NOAA)
- Gerrit de Leeuw, TNO, The Hague, The Netherlands

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Project

2.3

Halogens in the Troposphere - US-SOLAS (HiT-US)

Goals

Reliably characterize biogeochemical factors controlling spatial and temporal variability in fluxes of halogen-containing particulate species and reactive trace gases emitted from the surface ocean to the lower atmosphere.

Understanding to Date:

Available evidence suggests that the emission of inorganic chloride ion (Cl^-) and bromide ion (Br^-) in association with sea-salt aerosol produced by wind stress at the ocean surface is the dominant source of reactive chlorine (Cl) and bromine (Br) in the marine boundary layer (MBL) (Keene *et al.*, 1999; Sander *et al.*, 2003; and references therein). Production fluxes of sea salt (and its constituent halogens) are uncertain by factors of 6 or more; (Lewis and Schwartz, 2004, and references therein) and consequently, rates of Cl and Br cycling through the MBL are poorly constrained.

The production of iodine(I)-containing organic compounds, such as methylene iodide (CH_2I_2), chloroiodomethane (CH_2ICl), bromoiodomethane (CH_2IBr), and methyl iodide (CH_3I) by marine phytoplankton and their subsequent volatilization from the ocean surface is thought to be the primary source of reactive iodine in the open-ocean MBL (Carpenter, 2003). Limited data for the more photolabile of these compounds, except for CH_3I, preclude reliable estimates of emissions fluxes from the global ocean. The recent detection of significant iodine (I_2) in coastal air at Mace Head, Ireland (Saiz-Lopez and Plane, 2004) and at southern Maine, USA (Stutz *et al.*, 2005) suggests the possibility for direct production at the ocean surface, although the mechanism is uncertain and the associated fluxes are virtually unconstrained.

Evaluate the multiphase chemical cycling of reactive halogens, their associated influences on the chemical and physical evolution of the MBL, and their feedbacks on the surface ocean.

Understanding to Date:

The overall importance of reactive halogens in the chemical and physical evolution of marine air is uncertain and is currently the focus of intense study. Our understanding is limited in part because few comprehensive field investigations have been conducted in open-ocean regions. One example of such an investigation was published by Pszenny *et al.*, (2004). In addition, many key reactant and product species such as molecular and atomic halogens, iodine bromide (IBr), iodine monochloride (ICl), bromine chloride (BrCl), halogen nitrates, and hypohalous acids, either never have been measured directly in ambient marine air or have been measured only rarely [*e.g.* chlorine (Cl_2) and iodine (I_2)] (Spicer *et al.*, 1998; Saiz-Lopez and Plane, 2004). Halogen oxides [bromine monoxide (BrO), iodine oxide (IO), and iodine dioxide (OIO)] have been quantified at several locations, but most of the data correspond to coastal conditions that are not representative of the open-ocean MBL. The broadest observational evidence of active halogen chemistry in the open-ocean MBL is the nearly universal depletion of Cl and Br and the enrichment of I relative to seawater in super-μm sea-salt aerosol. These departures may be partially explained by acid displacement or redox processes that do not involve halogen radical chemistry. Model calculations indicate that particulate Cl^- and Br^- are initially activated and subsequently recycled via autocatalytic pathways involving hypohalous acids (Vote *et al.*, 1996):

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \quad (1)$$

$$HOCl + Br^- + H^+ \rightarrow BrCl + H_2O \quad (2)$$

$$HOCl + Cl^- + H^+ \rightarrow Cl_2 + H_2O \quad (3)$$

Then, the bromine (Br_2), BrCl, and Cl_2 volatilize and photolyze in sunlight to produce atomic Br and Cl. At high hydrogen chloride (HCl) concentrations in polluted regions, significant atomic Cl is also produced via

$$HCl + OH \rightarrow Cl + H_2O \quad (4)$$

Atomic I originates from photolysis of organoiodine compounds and I_2, but may also recycle subsequently via multiphase pathways analogous to 1 through 3.

Following production, halogen atoms catalytically destroy ozone (O_3) via:

$$X + O_3 \rightarrow XO + O_2 \quad (5)$$

$$XO + HO_2 \rightarrow HOX + O_2 \quad (6)$$

$$HOX + h\nu \rightarrow OH + X \quad (7)$$

where (X=Cl, Br, and I). Formation of halogen nitrates via XO + nitrogen dioxide (NO_2) and their subsequent scavenging accelerates conversion of NO_x to particulate nitrate ion (NO_3^-) and thereby contributes to net O_3 destruction. Halogen chemistry also impacts O_3 indirectly by altering hydroxyl radical/hydroperoxyl (OH/HO_2) ratios ($XO + HO_2 \rightarrow HOX + O_2 \rightarrow OH + X$). These chemical pathways destroy O_3 in near-surface air during polar sunrise (Martinez *et al.*, 1999) and have also been hypothesized to explain O_3 anomalies in the MBL at lower latitudes including post-sunrise O_3 depletions over the western subtropical Pacific Ocean (Nagao *et al.*, 2000), the temperate Southern Ocean (Galbally *et al.*, 2000), and the tropical Indian Ocean (Dickerson *et al.*, 1999).

In addition to O_3 destruction via reaction 5, atomic Cl also oxidized hydrocarbons (HCs) primarily via hydrogen abstraction to form HCl vapor and products. The enhanced supply of odd-H radicals from HC oxidation leads to O_3 production in the presence of sufficient NO_x. Evidence from the Texas Air Quality Study indicates that Cl-radical chemistry may be a significant net source for O_3 in polluted coastal/urban air (*e.g.* Tanaka *et al.*, 2003).

Halogen radical chemistry also provides alternate reaction pathways for sulfur (S) cycling in the MBL. Bromine monoxide (BrO), IO, and atomic Cl efficiently oxidize dimethyl sulfide [$(CH_3)_2S$] (von Glasow, 2002; von Glasow and Crutzen, 2004) into sulfur dioxide (SO_2) in the gas phase; while hypochlorous acid (HOCl) and hypobromous acid (HOBr) oxidize S_{IV} into S_{VI} in acidic aerosol solutions (Keene *et al.*, 1998). Both sets of transformations are potentially important, but as yet inadequately quantified, influences for the nature and rate of S cycling in marine air.

Finally, bursts of ultrafine particles that coincide with elevated levels of iodine oxides have been observed at Mace Head, Ireland (O'Dowd *et al.*, 1999, 2002). Laboratory studies confirm that mixtures of CH_2I_2 and O_3 rapidly produce ultrafine particles in the presence of light (Hoffmann *et al.*, 2001; Jimenez *et al.*, 2002). The actual formation mechanism is not known, but evidence suggests that the key species are IO, OIO, and/or I_2O_2. O'Dowd *et al.* (2002) proposed that the presence of I oxides helps to overcome the coagulation loss barrier and therefore leads to an increase in the number and lifetime of particles. If such nucleation events are widespread geographically, the production of cloud condensation nuclei via iodine radical chemistry may significantly influence the microphysics of clouds, radiative transfer, global climate, and related feedbacks on the surface ocean.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What are the major precursors for I radicals in the MBL?
- What are the primary factors regulating the production of I radicals and associated emission from the surface ocean?
- What are the spatial and temporal variables in halogen radical chemistry over the world's oceans?
- What are the major variables that control production and recycling rates of halogen radicals?

- What is the overall influence of halogen radical chemistry on the oxidation capacity of the MBL?
- Does the chemical processing of marine-derived halogens represent a significant global sink for tropospheric O_3?
- Does halogen radical chemistry significantly influence S cycling through the MBL? If so, what are the implications for radiative transfer?
- Does I radical chemistry drive widespread aerosol nucleation events over the open ocean? If so, what are the associated climatic implications and feedbacks?

Project Description

This project is envisioned as a collaborative effort that will build on and augment companion projects within US-SOLAS that focus on the air-sea exchange of gases and aerosols, see Projects 2.1 and 2.2, and global modeling, see Project 1.4. It will also contribute to ongoing, planned, and future international research programs investigating details of reactive halogen chemistry in the SOLAS realm. Examples of the latter include:

- The international Halogens in the Troposphere (HitT) program, an activity of the International Geosphere-Biosphere Program (IGBP) jointly sponsored by the SOLAS and International Global Atmospheric Chemistry (IGAC) organizations For more information, see www.uea.ac.uk /env/solas/org/HitT%20 brief%20report.pdf
- Reactive Halogens in the Marine Boundary Layer (RHaMBLe), a major field investigation of halogen radical chemistry at the Cape Verde Islands under the auspices of UK-SOLAS

The halogens in the troposphere project will target these interrelated areas of research:

- Study the emissions of halogen-radical precursors
- Conduct comprehensive field experiments
- Work to develop global models
- Work to improve measurement methods

There will be Cape Verde workshop in January 8-10, 2007, called "Integrated, long-term ocean-atmosphere observations in the tropical Atlantic." For more information, see www.york.ac.uk/capeverde/CV%20workshop%20advert.doc.

Target 1: Study the emissions of halogen-radical precursors.

These efforts dovetail with the projects described in Projects 2.1 and 2.2 of this implementation plan.

Particulate Halogens: Reliable estimates for emission fluxes of particulate halogens from the ocean surface to the atmosphere require reliable estimates of the following:

- Aerosol production rates
- The halogen contents of fresh aerosols

This analysis will draw on the improved estimates for size-resolved particle fluxes generated through Project 2.2. Because multiphase chemical transformations rapidly modify the

composition of sea-salt aerosol within seconds or minutes of injection into the atmosphere (Erickson *et al.*, 1999), the initial composition of fresh aerosol cannot be resolved unequivocally based on samples collected in ambient air. It is widely assumed that the halogen content of fresh aerosol is conservative with respect to seawater at the time of injection, but this assumption has never been rigorously tested. Relative to surface seawater, fresh sea-salt aerosols are highly enriched (factors of 10^2 to 10^3) in marine-derived organic compounds, and the relative enrichments increase with decreasing size (*e.g.* Turekian *et al.*, 2003). Some organic compounds in the surface ocean contain halogens and, consequently, it is possible but not likely, that fresh aerosols are enriched in organohalogens relative to bulk seawater.

To estimate the composition of fresh aerosol, artificial aerosol will be generated with a bubbler-type device (*e.g.*, Hoffman and Duce, 1976) deployed on a ship at sea or in a laboratory plumbed with representative open ocean seawater. Fresh droplets will be dehydraded into equilibrium with a representative relative humidity (RH) of about 80%; sampled with cascade impactors; analyzed for sodium (Na), magnesium (Mg), and total halogen content via neutron-activation analysis (NAA); analyzed for Na+, Mg2+, and ionic halogens by ion chromatography (IC); and analyzed for total organic content by combustion techniques.

Feed seawater would be similarly characterized. Enrichments or depletions relative to seawater will be evaluated based on ratios with the conservative, base-cation tracers. The organohalogen fractions will be inferred by difference (total minus ionic) and, if significant concentrations are evident, more comprehensive analyses will be implemented in an attempt to speciate the major halogenated organics. Results would then be applied to model size-resolved emission fluxes of particulate inorganic and organic Cl, Br, and I and of particulate organic carbon (C) from the ocean surface.

Iodocarbon Gases: As discussed in Project 2.1, the flux of a given gas across the air-sea interface is a function of the saturation state of the surface ocean with respect to overlying air and the physically controlled transfer velocity. To the extent possible, reactive iodocarbons will be measured in the surface ocean and overlying air during the field campaigns mentioned in Project 2.1 and the corresponding exchange fluxes modeled. Results of this effort will allow a preliminary assessment of spatial and temporal variability in emission fluxes of major iodine radical precursors.

Target 2: Conduct comprehensive field experiments.

To provide the necessary complement of information for evaluating the potential influences of halogens on the chemical and physical evolution of marine air, two things must occur. One is to conduct field investigations, which incorporate relevant, available measurement techniques. The second is to couple those experiments with focused modeling efforts. Based on current capabilities, a minimal set of measurement and modeling components should include the following:

- Cl_2 and Br_2 (tandem mass spectrometer)
- HCl, nitric acid (HNO_3) (mist chambers/IC or tunable diode lasers)

- BrO, IO, OIO, I2, O_3, NO_2, formaldehyde (HCHO), nitrate (NO_3), nitrous acid (HONO), and SO_2 [long-path and/or multi-axis (MAX) differential optical absorption spectrometers (DOAS)]
- Total volatile inorganic Br and I (filterpack/NAA)
- Non-methane hydrocarbons and halocarbons [flask, resin, or cryotrapping/gas chromatograph and mass spectrometer (GC/MS)]
- Ionic, elemental, and organic C content of size-resolved aerosol [cascade impactor/IC, NAA, and organic-carbon (OC) analyzer]
- Aerosol number/size distributions (aerodynamic particle sizer, differential or scanning mobility particle sizer, and ultrafine particle sizer)
- Iodocarbon fluxes (see Iodocarbon gases, page 47)
- Actinic flux (scanning spectralradiometer)
- Local meteorology (temperature, RH, wind speed and direction, pressure, and back trajectories)
- Multiphase photochemical model (*e.g.* MOCCA, MECCA, and MISTRA)

To the extent possible, field deployments will be coordinated with those for other projects to benefit from economies of scale and to broaden the base of information. For example, vertical profiles of aerosol composition and boundary layer structure would add substantial value to the above suite. Each deployment would correspond to an observation period of 4 to 6 weeks within a representative marine region.

Several comprehensive field investigations focusing on halogen cycling have been conducted previously in the relatively clean coastal region of western Ireland and in the heavily polluted coastal region of New England. Additional campaigns are currently planned for coastal locations in Europe and North America over the next two years. Consequently, this project will focus on processes over the open ocean, which has received less attention, but corresponds to substantially larger fractions of Earth's surface.

The RHaMBLe project is pending, but the timing of the first field deployment could coincide with that program, which is currently scheduled for June and July 2007 at the UK-SOLAS observatory on São Vicente, in the Cape Verde Islands. Letters from US-SOLAS scientists expressing their intent to collaborate in RHaMBLe were included in the project's proposal. The Cape Verde Islands lie in biologically rich waters influenced by the Mauritanian upwelling zone at ~16° N and approximately 700 km west of Senegal off the west African coast. One of the particular aims of the RHaMBLe experiment will be to examine the importance of biogenic halocarbon emissions in driving halogen (and particularly I) radical chemistry. Relatively high levels of BrO (up to several pptv), which are indicative of active Br radical chemistry, have also been measured previously in that region (Leser *et al.*, 2003). In addition, this region has been impacted intermittently by Saharan dust during some summers, which would provide opportunities to investigate the potential influences of transition metals on halogen cycling over the ocean (Behnke and Zetzsch, 1989).

Recommended locations for subsequent deployments include but are not limited to the following:

- Christmas Island near the equator in the Central Pacific
    - Low relief
    - Relatively low sea salt fluxes
    - Relatively low biological productivity

    - Remote from significant sources of pollutants
    - Remote from significant sources of mineral aerosol
- A low-relief location or cruise in the high latitude Southern Ocean during summer
    - Low relief
    - Relatively high sea salt fluxes
    - Relatively high biological productivity
    - Remote from significant sources of pollutants
    - Remote from significant sources of mineral aerosol
- A low-relief location or cruise in a marine region, such as the western South Atlantic Ocean or the northern Indian Ocean, that is significantly influenced by biomass-burning emissions

Target 3: Work to develop global models.

This task dovetails with Project 1.4. We expect the investigators at the Max Planck Institute for Chemistry to publish results based on the first working model that explicitly treats multiphase halogen radical chemistry in the MBL on a global scale by the latter half of 2006. Currently, this model, called the Modular Earth Submodel System (MESSy), considers only one sea-salt size bin, which limits the evaluation of some important and highly nonlinear aspects of multiphase halogen chemistry. These aspects include the production flux of particulate precursors and atmospheric lifetimes of conservative particulate reaction products. The Canadian Aerosol Model (CAM) (Gong, 2003) includes multiple sea-salt size bins. During winter 2005-06, a collaborative effort involving German, Canadian, and US-SOLAS scientists was initiated to merge CAM with MESSy. When complete, the coupled model will provide a unique and powerful tool. Scientists will be able to evaluate halogen radical chemistry on a global scale and assess related implications for Earth Systems, including oxidation processes and climate.

Target 4: Work to improve measurement methods.

Aerosols: The poor temporal and vertical resolution of current measurement techniques for the chemical composition of super-μm-diameter aerosols is a major impediment to progress in understanding chemical processes in the MBL. Many reactive trace gases can be reliably quantified by various techniques on time scales of seconds to tens of minutes. The composition of sub-μm aerosol size fractions can be quantified by aerosol mass spectrometers (AMS) (*e.g.* Jayne *et al.*, 2000), aerosol time of flight mass spectrometers (ATOFMS) (*e.g.* Gard *et al.*, 1998), and particle-into-liquid sampler (PILS) techniques (*e.g.* Weber *et al.*, 2001) on similar time scales.

In contrast, characterization of the super-μm aerosol size fractions (in which both reactive trace gases and sub-μm aerosols are chemically coupled) typically requires sampling with cascade impactors deployed over many hours to a day or more, followed by extraction and chemical analysis (*e.g.* Pszenny *et al.*, 2004). Such sampling techniques obscure temporal variability and limit resolution in deconvoluting chemical dynamics of the multiphase system as a whole. They also prevent evaluation of the internal versus external mixing state of similarly sized particles and exacerbate inherent problems associated with artifact reactions caused by mixing compositionally distinct, but similarly sized particles in individual samples (*e.g.* Keene *et al.*, 1990). In addition to the above factors, reliable measurement techniques for

many non-ionic and reactive-transient species associated with aerosols do not yet exist. Finally, inlets on many research aircraft do not pass super-μm aerosol efficiently (Huebert *et al.*, 1990). Consequently, vertical distributions of sea salt composition are not well understood. US-SOLAS strongly encourages the following efforts:

- Extend the analytical range of current aerosol mass spectrometers to super-μm size fractions and/or develop new approaches to reliably quantify the composition of larger aerosol size fractions at high temporal resolution and to determine their internal/external mixing state
- Develop new analytical techniques to reliably quantify non-ionic and reactive transient species in marine aerosols
- Develop, rigorously characterize, and deploy inlets on aircraft that efficiently pass super-μm aerosols
- Quantify vertical distributions in the size-resolved number concentrations and compositions of atmospheric sea salt over representative ranges of atmospheric conditions

Gases: The lack of direct, specific measurement techniques for many of the inorganic halogenated species (hypohalous acids, halogen atoms, halogen nitrates, interhalogens, and some of the halogen oxides) seriously constrains resolution in deconvoluting chemical pathways. US-SOLAS strongly encourages efforts to develop new measurement techniques and to improve the resolution of existing techniques for halogen-containing inorganic gases.

International Interactions

- HitT
- IGAC
- UK-SOLAS

Research Needs

NOAA research vessel, the *Ronald H. Brown*

Project Contributors

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Project

2.4

Cape Verde Air-Sea Interaction Time- Series Station

Goals

Assist in establishing long-term monitoring of atmospheric and oceanic conditions relative to global change in the critical tropical eastern North Atlantic Ocean region.

This project will be an international collaboration among Cape Verde, Germany, the United Kingdom, and the United States. It will provide a state-of-the-art air-sea exchange mooring at the Cape Verde ocean-atmosphere observing facility, which is off the island of São Vicente, Cape Verde.

Provide scientists and West African nations with information so they can assess the impact of changing oceanic and atmospheric conditions on regional natural resources and the environment.

Integrate the monitoring site and its data products into the International Global Earth Observation's activities.

Contribute to long-term monitoring of relevant compounds for biogeochemical cycles influencing climate.

Understanding to Date:

Long-term observation is fundamental to understanding of global changes in air quality, atmospheric oxidation capacity, and climate. Such changes impact marine ecosystems and the atmosphere, which are then influenced by ocean physical and biogeochemical processes. Many impacts and feedbacks are focused in the tropics. In collaboration with international partners, the UK-SOLAS program has funded ground-based observations in the tropical eastern North Atlantic Ocean region, specifically at São Vicente, Cape Verde (16 ºN, 24 ºW; www.york.ac.uk/capeverde/). Atmospheric observations should start in late August/early September 2006.

Funding has been requested through the German SOLAS program to establish an instrumented oceanic time-series site, as shown in Figure 10. Funding has also been requested to refurbish the *Islandia*, a Cape Verde research vessel. This refurbished vessel could then make monthly visits to the mooring to collect samples for physical and biogeochemical parameters. Close links between the atmospheric observation site (currently UK-led) and the oceanic time-series site (currently German-led) will be established with joint steering committee memberships and shared data management plans.

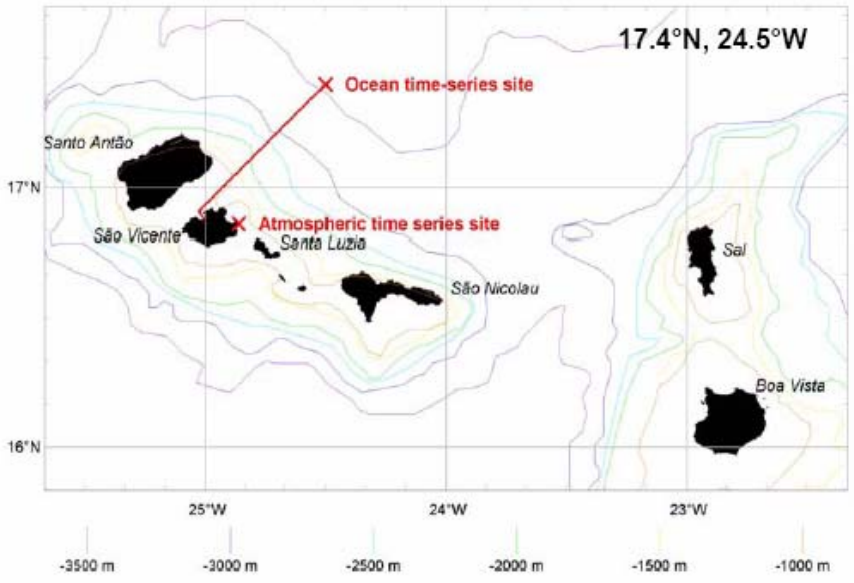

Figure 10: Map of the Cape Verde Ocean and Atmosphere observatory.

The tropical eastern North Atlantic Ocean region plays a key role in atmosphere-ocean interactions of climate-related and biogeochemical parameters, including greenhouse gases. This region is located downwind from an area of high primary productivity in the Mauritanian upwelling. Being located here, the observatory can provide information on connections between upwelling and atmospheric composition changes. The location is also ideal for other climate studies and for investigating impacts of dust on the marine ecosystem. The SOLAS atmospheric station will measure meteorological parameters, greenhouse gases, short-lived gaseous species, and aerosols. The scientist will then integrate the data into the Global Atmospheric Watch (GAW) program of the World Meteorological Organization (WMO). The measurements of air-sea fluxes, temperature, salinity, ocean current, oxygen (O_2), CO_2, and atmospheric trace gases will also be incorporated into the Ocean Research Interactive Observatory Networks (ORION) program and other international observation programs.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- Does the net flux of non-anthropogenic carbon (C) go from the atmosphere to the ocean through the ocean's biological pump?

- Is a large component of the biological O_2 flux from the upper ocean to the atmosphere across the air-water interface?

- Is the atmospheric deposition of iron (Fe), in the form mineral dust from Africa, critically important with respect to controlling phytoplankton productivity in large areas of the Atlantic Ocean, where Fe is a limiting nutrient?

- Is the dissolution of Fe, following mineral dust deposition in the upper oceans, a key process that connects the atmospheric deposition of continental soil with the regulation of biological productivity?

- Does mineral dust, which is a source of dissolved Fe, play a major role in the ecology of nitrogen-fixing plankton? Knowing that this plankton is a major source of organic C and nitrogen (N_2) to the oceans.

- Can we reduce the amount of uncertainty in flux estimates and parameterizations at high wind by explicitly considering the sea state?

- Episodic events accomplish a disproportionately large amount of air-sea exchange and therefore, can adequate sampling of these events help to accurately quantify air-sea exchanges and help to understand the dynamics of ocean-atmosphere coupling?

- Are atmospheric aerosols contributing to a significant reduction in surface incoming short-wave radiation, perhaps at a magnitude of 10 W m^{-2}, averaged over the surface of the Earth (including the oceans)?

- Do the feedbacks between sea surface temperature and air-sea exchanges of heat govern the coupled evolution of the atmosphere and the ocean?

- Do feedback processes that link atmospheric convection also reduce insolation and increase precipitation to the sea surface temperature field?

- There are phase lags in the diurnal cycle between maximum heating by insolation and maximum freshwater flux due to atmospheric convection. Are these lags a critical component of the atmosphere-ocean dynamics that maintain shallow ocean mixed layers in the tropics?

- The greatest shortcoming of present state-of-the-art ocean models stems from the inaccurate surface flux fields used to drive these models. With more accurate surface fluxes, can these models reproduce observed ocean structure and variability?

- If air-sea fluxes are the dominant mechanism for water mass formation, can spatiotemporal variability in formation be tracked to space/time variability in the surface fluxes?

Project Description

The overall project of the Cape Verde mooring is to establish the physical and human infrastructure and basic equipment required for long-term monitoring of atmospheric and oceanic conditions in the tropical eastern North Atlantic Ocean region. Establishing a Cape Verde observatory will involve creating both an atmospheric site and an ocean-monitoring site. The observatory should welcome the open exchange of scientific expertise and ideas, and focus on outreach and collaboration.

Atmospheric Monitoring Site

The physical site for the monitoring station has been established on the island of São Vicente. There, US-SOLAS will assist in establishing and maintaining infrastructure for long-term measurement of the following:

- Key meteorological and climate parameters
- Long-lived greenhouse gases
- A set of key trace gas species relevant to pollution and tropospheric chemistry
- The size and chemical composition of the aerosols and dust

Ocean Monitoring Site

The project will establish long-term oceanographic observations at a pelagic site representative of open ocean conditions and immediately upwind of the atmospheric monitoring site. Two major sampling modes will be established: monthly and continuous. The Cape Verde research vessel, *Islandia*, will make visits to the site and perform conductivity, temperature, and density (CTD) profiling and water sampling for nutrients, dissolved gases, and plankton for the monthly sampling mode. The continuous measurement of atmospheric and oceanic parameters will be conducted with a long-term mooring. This project will measure both physical and basic chemical parameters.

Air-Sea Flux Component: There are three basic methods for obtaining time series of the air-sea fluxes from unattended observatories:

- Direct covariance
- Bulk aerodynamic
- Inertial-dissipation methods

Using the sensible heat flux as an example, the three approaches can be summarized as follows:

$$Q_{SHF} = \rho c_p < w'\theta' > \cong \rho c_p u_* \theta_* \cong \rho c_p C_H U_r \Delta\Theta \qquad (1)$$

Where ρ is the density of air, c_p is the specific heat of air at constant pressure, w' and θ' are the turbulent fluctuations of vertical velocity and potential temperature, u_* and θ_* are scaling parameters for velocity and humidity, C_H is the transfer coefficient for sensible heat (the Stanton number), U_r is the wind speed at some reference level relative to the surface current, and $\Delta\Theta$ is the difference between potential temperature at some reference level and at the sea surface. The most direct estimate of the flux is the direct covariance (DC) method where the correlation between the turbulence fluctuations, $<w'\theta'>$, provides an estimate of the ensemble averaged flux. The inertial dissipation method (ID) represented by the second to last term in (1), uses high frequency turbulence measurements of velocity, temperature, and humidity to estimate the scaling parameters from the corresponding dissipation estimates and empirical formulae (Edson *et al.*, 1991). The bulk aerodynamic (BA) method represented by the last term in (1), estimates the fluxes using mean surface variables together with empirical formulae for the transfer coefficients. The empirical formulae for the ID and BA methods are derived ideally from DC fluxes and mean profiles (*e.g.* Businger, 1988; Vickers and Mahrt, 1999; Edson *et al.*, 2004).

The BA method is the most widely used approach to estimate the fluxes over the ocean. The acceptance of this position is largely due to these factors:

- The DC and ID methods require fast response instrumentation with power requirements that limit their operation on oceanographic moorings.
- The empirical formulae required by the ID method are believed to have larger uncertainties than those required by the BA method. These uncertainties are in the parameterizations of the energy transport terms in the Turbulent Kinetic Energy (TKE) equation (*e.g.* Janssen, 1999; Edson and Fairall, 1998).
- The fluctuating turbulent velocity measurements required by the DC method need to be corrected for platform motion. This correction requires additional instrumentation and power to measure the translation and rotational motion of the platform (*e.g.* Edson *et al.*, 1998).

Therefore, researchers have relied most heavily on the BA method to obtain long, continuous, and autonomous time series of momentum, heat, and gas fluxes from oceanographic moorings.

Estimates of momentum, heat, and gas fluxes require accurate measurements of wind velocity, surface currents, air temperature, sea surface temperature, barometric pressure, sea surface salinity, and relative humidity. Estimates of gas fluxes, such as CO_2, require additional measurements of the air-sea gas concentration differences (McGillis *et al.*, 2004). The transfer coefficients have been shown to vary with height, stability, wind speed, and sea state (*e.g.* Fairall *et al.*, 1996, 2003; Donelan *et al.*, 1993). Therefore, parameterizations that attempt to account for sea state require measurement of surface waves.

An exciting era is beginning with what promises to be a time of substantial progress both in understanding the detailed mechanisms of air-sea gas exchange and in integrating this knowledge into the gas flux calculations required for biogeochemical modeling. A confluence of many factors will feed this progress including: new experimental techniques, global sustained observing capabilities from ORION, and the reinvigorated societal needs to understand air-sea exchange. Without the dedication and hard work of many scientists and engineers over the past several decades, no progress could be made today. The study of air-sea gas exchange is not new; over 40 years ago the manuscripts of Bolin (1960) and Kanwisher (1963) hypothesized that wind stress and surface waves would play a key role in determining gas transfer rates. These concepts are the cornerstone of today's research efforts.

Dissemination, Outreach, and Collaboration Component: In general, it is easier to maintain an observation site if there is an exchange of scientific expertise and ideas. This principle is particularly critical for observation sites that are located in developing countries. At the Cape Verde observation site, there will be many opportunities for collaboration with European and other international science programs. For example, because the air-sea flux buoy will depend on local personnel for operation, the air-sea flux specialists will train local scientists, engineers, and technicians. It is envisioned that the Antarctica service ships (from the United Kingdom/Germany) could help support the air-sea interaction buoy maintenance, if necessary.

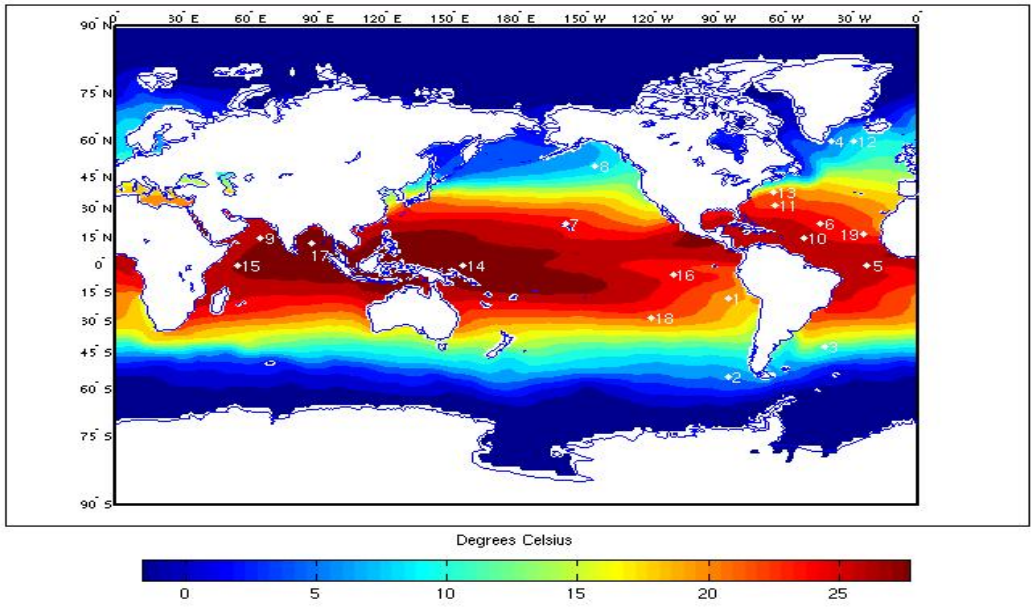

Figure 11: Map showing the Cape Verde air-sea exchange ocean time-series mooring with the 19 air-sea exchange sites plotted over an average mean sea surface temperature field.

Establish a Cape Verde mooring for an oceanic time-series station and maintain it for ten years.

Target 1: Select a suitable open-ocean site for an oceanic time-series station as shown in Figure 11.

Target 2: Employ and train necessary personnel for the operation of the oceanic time-series station.

Target 3: Maintain air-sea flux buoy with atmospheric and aqueous oxygen and carbon dioxide (CO_2) measurements.

Target 4: Install the necessary CTD equipment, acoustic Doppler current profilers (ADCP), and turbulence equipment on the mooring.

Target 5: Deploy and maintain the mooring that will measure profiles of physical and chemical parameters through the water column down to approximately 100 m below the water surface.

Target 6: Visit the oceanic time-series station using the research vessel, *Islandia*, on a regular basis (monthly) to measure biogeochemical and physical parameters.

Target 7: Visit the buoy using the research vessel, *Islandia*, quarterly for regular maintenance.

Target 8: Service and re-deploy marine mooring.

The air-sea exchange consortium is finalizing the details of which instruments will be deployed at each site. At this point, the list of instruments includes:

- Improved mean meteorological sensors that have been adapted for severe environments (similar to the surface radiation sensors that were deployed at Baseline Surface Radiation Network land sites)
- Ventilated air temperature and humidity sensors
- Ventilated, stabilized, self-cleaning Kipp and Zonen short-wave and long-wave radiations
- Reference radiometers exposed for short intervals
- Direct covariance flux sensors for heat, water, and gases
- Oxygen (O_2) and nitrogen (N_2) sensors
- Dust collection and analysis instrumentation
- Atmospheric profilers (including automated radiosonde launcher, radar, sodar, and lidar)
- Cloud base sensor

- All-sky camera
- In-water sensors (hyperspectral) for penetrating radiation
- Motion sensors to remove platform motion from the velocity measurement before computation of the fluxes (these motion sensors also serve as surface wave and swell sensors for wave height, frequency, and directional spectra)

SOLAS plans to coordinate these payloads with the other users of the platforms and other disciplinary consortia. We also anticipate working with them to ensure that other resources are in the field. Examples of these resources are autonomous gliders (to maneuver around the buoy observatory for at least a year), subsurface and surface moorings (to track the space/time evolution of the upper ocean), and aircraft and remote sensors (to map spatial variability around the site).

International Interactions

Understanding and detecting global change requires relevant, long-term data collection in critical areas around the globe. This proposed Cape Verde mooring site is in an area where atmosphere-ocean interactions of climate-related and biogeochemical parameters occur. Another benefit is that this location experiences massive dust transport from land to the ocean and aerosols here are believed to have a large impact on the climate, atmospheric chemistry, and marine processes. Locating the mooring in the tropics gives the US-SOLAS team the opportunity to collaborate with European and other international science programs. Finally, the living marine resources of the West African region in general, and Cape Verde's enormous economic zone (742,438 km^2) in particular, are of high economic value to Europe and the United States. Infrastructure improvements, training of local scientific personnel, and long-term environmental monitoring data of this project will strengthen Cape Verde's ability to manage its marine resources. Specifically, an oceanographic ORION monitoring site could be used by other programs or by the Cape Verde partners themselves to measure biological parameters. Presently, Cape Verde has no resources available to conduct such long-term monitoring of its ocean waters.

Research Needs

- Establish a flask-sampling program for studying greenhouse gases
- Install and operate a MAX-DOAS system for measuring halogen oxide
- Purchase, install, and operate meteorological, gas, and aerosol analysis equipment

Project Contributors

- Lucy Carpenter, University of York
- Dennis Hansell, University of Miami
- Barry Huebert, University of Hawai'i
- William Keene, University of Virginia

- Wade McGillis, Columbia University
- Daniela Turk, European Science Foundation
- Doug Wallace, Christian-Albrechts-Universität zu Kiel

Project

3.1

Air-Water Carbon and Volatile Carbon Compounds in the Coastal Margins

Goals

To establish an extensive sampling network in the coastal margins. This network will make possible calculations of air-sea flux of carbon dioxide (CO_2) and other volatile carbon (C) compounds in various ocean margin provinces. With this data, we can begin to understand which kind of processes contribute and control air-sea fluxes.

Understanding to Date:

It has been suggested that the coastal ocean may absorb atmospheric CO_2 up to 1.0 PgC/yr. This suggestion, however, appears to be an oversimplification. While coastal oceans in the middle and high latitudes do act as a CO_2 sink, coastal oceans at low latitudes may act as a source of CO_2. The continental shelves are undersampled and need a more extensive observation network. In addition to surveys already in progress, long-term, real-time mooring and area-integrated methods are also needed.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What types of ocean margins or margin provinces are annual sources of atmospheric CO_2? What are their respective magnitudes?
- What type of ocean margins or margin provinces are annual sinks of atmospheric CO_2? What are their respective magnitudes?
- What are the characteristic features in the temporal and spatial variability of surface pCO_2 and methane (CH_4) in these margin provinces?
- At the whole shelf ecosystem level, what are the major external (terrestrial and oceanic) forcings and internal physical and biogeochemical processes controlling the nature of CO_2 release or uptake in various margin provinces?

While previous research focused on open ocean basins, recent work has been done in northern temperate areas. This research suggests that the coastal ocean may absorb atmospheric CO_2 up to1.0 PgC/yr, roughly half of the known open ocean uptake. (Tsunogai *et al.*, 1999; Wang *et al.*, 2000; Yool and Fasham, 2001; Frankignoulle and Borges, 2001; DeGrandpre *et al.*, 2002; Thomas *et al.*, 2004; Hales *et al.*, 2005). This conclusion, however, may be overly simplified because of a lack of data for the low latitude areas. Research suggests that coastal oceans in the low latitudes may act as a source of CO_2 (Cai *et al.*, 2003; Cai and Dai, 2004; Cai, 2005). This perspective is suggested again by a recent global compilation of continental shelf air-sea CO_2 flux data (Cai, 2005).

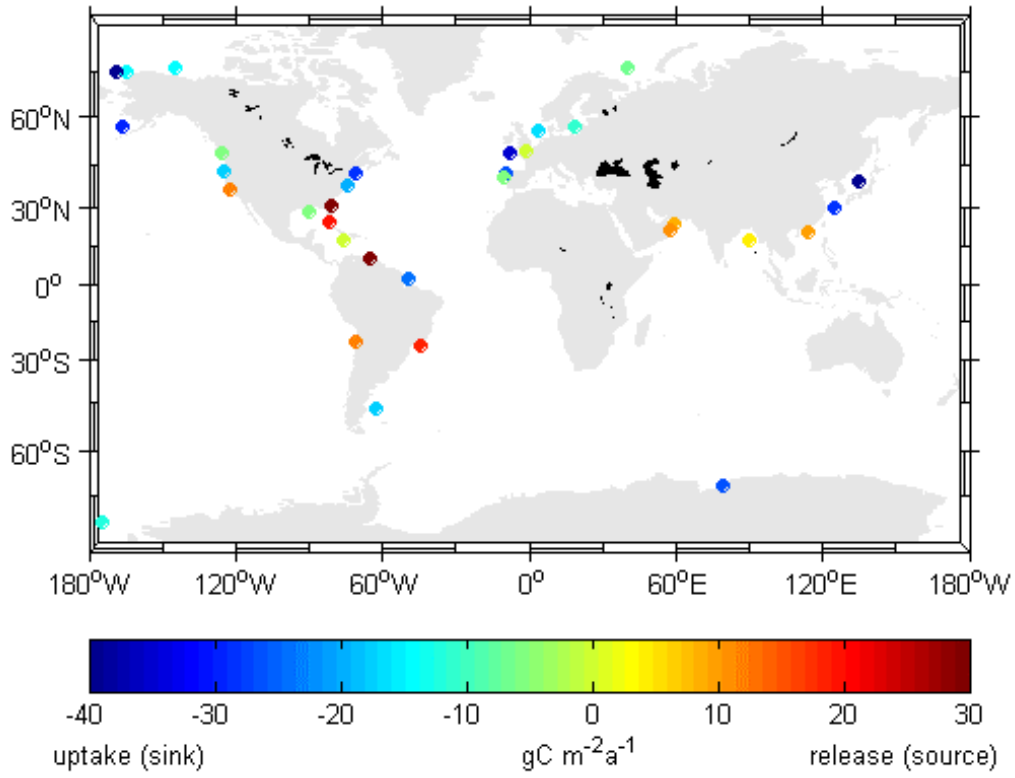

Figure 12: A global distribution of existing database of annual air-sea CO_2 flux measurements. Some of the flux data are not annually averaged. A complete list of individual shelves, references, and explanations are available from W-J. Cai (see appendix for contact information). Flux data from estuaries and embayments are excluded from this compilation except that of the Florida Bay. CO_2 fluxes are reported based on the Wanninkhof 1992 formula and may represent the upper boundary (courtesy of Cai *et al.*, 2006).

Looking at this compilation, one can see that the continental shelves are undersampled and need a more extensive observation network. This lack of observation data is particularly true for some ocean margins. Thus, extrapolating from one area globally or a simple area-weighted average of existing data will be biased greatly in favor of those areas that are relatively data-rich. Coastal oceans, which include continental shelves and slopes, estuaries, and embayments, are highly heterogeneous. Therefore, they call for long-term, real-time mooring and area-integrated methods. An example of an area-integrated method is the atmospheric eddy correlation method. Satellite imagery-based interpretation and extrapolation are also necessary.

To provide an initial estimate of global air-sea CO_2 flux on continental shelves, one must use a suitable classification that accounts for differences in ocean circulation, morphology, latitude, and other differences. The classification must also be consistent with currently available data on shelf CO_2 fluxes. An effort was made to simplify continental shelves into three major types and seven provinces:

- Non-upwelling shelves associated with western boundary currents or marginal sea-loop currents (occupying ~77% of the total area and including two mid-latitude and one low-latitude shelf province)
- Upwelling-dominated shelves associated with eastern boundary currents (~6% of the total shelf area, including one mid- and one low-latitude shelf province)
- Polar ocean margins (17% of total area; including the Arctic and Antarctic provinces)

First, one determines an average air-sea CO_2 flux for each shelf province, and then one calculates a total or net global shelf flux weighted by province areas. An estimate of the global shelf air-to-sea CO_2 flux of 0.2 ± 0.2 PgC/yr has been determined, but a large degree of uncertainty still exists with this estimate because of two factors. First, data sets do not exist in many parts of the world's continental margins. Second, even in those shelves where data sets exist, the number of spatial and temporal coverages is often relatively low.

In North America ocean margins, surface water pCO_2 measurements have been conducted in several areas, see Table 2. For most shelf regions, the studies are preliminary, meaning that the studies have not been verified over a number of years or they lack spatial coverage. Although per unit area fluxes are generally higher in the upwelling West Coast, area integrated fluxes are much higher in the East Coast as the shelves are much wider there. All of data sets except one in Table 2 are based on direct pCO_2 measurements. The Wanninkhof 1992 formula was used to calculate the fluxes in this table.

Table 2: Annual Air-Sea CO_2 Flux Data in North America Continental Shelves[3]

Shelf Name	Latitude (°N)	CO_2 Flux ($molC/m^2/yr$)	CO_2 Flux ($gC/m^2/yr$)	Researcher	Note
Pacific Ocean					
Vancouver Island	49	-0.5	-6	Ianson/ Wong	Modeling extrapolation
Oregon Coast	43	-2.0	-24	Hales/ Takahashi/ Van Geen	Upwelling season
Central California	36.7	-0.5	-6	Friederich/ Chavez	El Niño and weak upwelling year
Central California	36.7	1.5	18	Friederich/ Chavez	La Niño and strong upwelling year
Atlantic Ocean					
Gulf of Maine	42.8	-2.5	-29	Salisbury/ Vandemark	Limited area
Mid-Atlantic Bight (MAB)[4]	38.5	-1.7[4]	-20[4]	DeGrandpre/ Takahashi	Whole shelf
South Atlantic Bight (SAB)[5]	31	2.0	24	Cai/Wang	Limited area
West Florida	25	1.7	20	Millero	
Mississippi River Plume Area	28	-0.5	-6	Cai/Lohrenz	Not annually integrated
Caribbean Sea	18	0	0	Wanninkhof/ Olsen	Including deep water area
Cariaco Basin	10.5	2.8	34	Muller-Karger/ Astor	Over 5 years of data Upwelling site

[3] Positive value represents amount released to the atmosphere; negative value represents amount of uptake by the ocean.

[4] Adjusted atmospheric pCO_2.

[5] Study was limited to central and nearshore area. Recent whole shelf survey suggests a smaller flux $^{+}fCO_2$ calculated from pH and alkalinity.

Compared to the study of air-sea flux, the study of coastal, open ocean interface transport is just beginning and is even more preliminary. Research findings from the Mid-Atlantic Bight (MAB) and the South Atlantic Bight (SAB) suggested a large dissolved organic carbon (DOC) export to open oceans. The dissolved inorganic carbon (DIC) export in the SAB to the open ocean can be as high as three times of the riverine flux. Preliminary work on O_2 balance from the Oregon coast suggests a great export of organic C.

Project Description

To determine what controls coastal carbon fluxes, the entire coastal regime needs to be studied.

Air-sea Fluxes

In the three US coasts (the West, the East, and the Gulf Coasts), surface pCO_2 surveys should be conducted and compared along latitudinal zones. The surveys should include underway, mooring, and satellite imagery-based methods and new techniques, such as the atmospheric eddy correlation method on coastal towers. As many different groups will conduct these surveys, single, alongshore cruises will also be needed. R. Feely and R. Wanninkhof will lead one such effort, funded by NOAA, in 2007. This cruise will provide a quasi-synoptic view and data quality control.

Understanding the coastal carbon system in margins that are not part of the conterminous United States, such as Alaska and Hawaii, should also be considered. Also needed are studies of gas transfer velocity in coastal oceans, particularly in areas of limited wind, and studies of coastal, open ocean interface transport. Determining the amount and mechanism of water (and thus carbon) export is important to the expansion of this area of study.

International Interactions

The activities proposed here are complementary to a number of international programs. Although as a coastal program there is no direct area overlap with other countries, our efforts will contribute to the goal of global synthesis. In the Coastal CO_2 Workshop,[6] scientists from Canada and Mexico showed great interest in collaborating on projects that involved the North American coasts.

[6] Boulder, Colorado/September 21-23, 2005

Research Needs

- Autonomous vehicles
- Research vessels, platforms, buoys, and coastal towers

Project Contributors

Wei-Jun Cai, University of Georgia

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Project

3.2

Southern Ocean Carbon Dioxide Studies

Goals

Understand air-sea flux of carbon dioxide (CO_2) and other long-lived radiatively active gases.

Understanding to Date:

Natural and anthropogenic changes in climate and global biogeochemistry alter the air-sea exchange of carbon dioxide (CO_2) and other long-lived radiatively active gases. These alterations may, in turn, cause changes in the uptake rate by the oceans. Understanding physical and biogeochemical processes at the air-sea interface is critical for predicting the air-sea exchange of gases and determining how these processes will affect and be affected by global change.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What is the sensitivity of air-sea CO_2 flux to climate-related changes in physical forcing?
- How do biogeochemical cycles and air-sea CO_2 fluxes respond to the dominant modes of interannual variability?
- How do biogeochemical cycles and air-sea CO_2 fluxes respond to changes in individual components of meridional overturning circulation, including bottom and intermediate mode water formation and cross-frontal exchange?

Project Description

The Southern Ocean south of 46°S covers 16% of the world's oceans and ventilates about half of the deep ocean waters. Regional measurements suggest this region is a sink of carbon (C) of about 0.9 Pg C yr^{-1} (Takahashi *et al.*, 2002; Figure 13), but atmospheric inversions suggest that the sink is only 0.4 Pg C yr^{-1} (Gurney *et al.*, 2002). Currently, the large uncertainties in the air-sea flux of CO_2 prevent accurately quantifying the partitioning of

anthropogenic CO_2 between the ocean and the terrestrial biosphere on interannual time scales. Uncertainties of approximately 50% are associated with the current global and regional air-sea flux estimates due to inadequacies in the gas transfer parameterizations. These uncertainties limit our ability to realistically model future atmospheric CO_2 levels.

Prognostic model estimates are equally uncertain. Some of the uncertainties stem from the paucity of CO_2 measurements in the Southern Ocean; others come from gas transfer velocity parameterizations. Consequently, the Southern Ocean is of vital importance for the study of air-sea gas exchange. Efforts should be concentrated on measuring CO_2 fluxes directly in the marine air boundary layer; quantifying gas transfer velocities with deliberate tracers; and elucidating the physical, chemical, and biological processes that will allow for parameterizations of gas exchange from physical forcing. Physical forcing data such as wind, wave slope, turbulence, and momentum for the region will be available through remote sensing and sustained *in situ* observations.

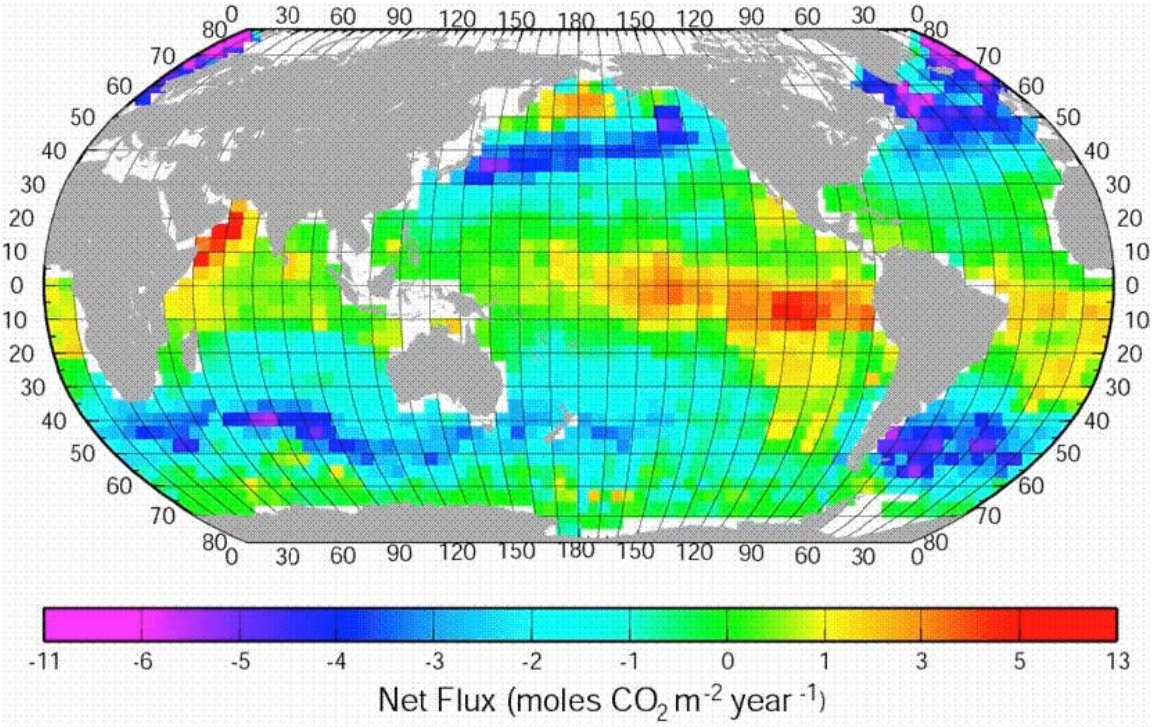

Figure 13: Climatological global air-sea CO_2 flux map based on approximately 1 million ΔpCO_2 measurements over the past 40 years and relationship of gas exchange with climatological wind speed (courtesy of Takahashi *et al.*, 2002).

Until recently, scientists determined the gas transfer velocity exclusively from indirect measurements based on mass balance techniques in the surface mixed layer. These techniques used natural or deliberate tracers that yielded gas transfer velocities averaged over periods of days to weeks. The improvement of direct flux techniques makes it possible to measure the flux and determine gas transfer velocity from collocated ΔpCO_2 measurements on the time scale of the variability of the forcing (on the order of 1 hour). Fairall *et al.*, (2000) demonstrated important technical improvements that allow for direct flux measurements of CO_2 over the ocean. These improvements alleviate previous shortcomings as described by Broecker *et al.*, (1986). Advances in direct flux measurement techniques and airside profile 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 profile method for dimethyl sulfide (DMS) (McGillis *et al.*, 2001b). The ability to measure transfer velocity locally in the field provides the tools to properly relate the gas transfer velocity to the appropriate forcing function. Researchers, however, will continue to use wind parameterizations extensively, both because wind is an important driver of surface turbulence and because synoptic measurements and assimilation products of wind speed are readily available. Improvements in these wind parameterizations, especially in the ability to apply the relationships, should improve our ability to predict air-sea exchange of climatically relevant trace gases.

In the late 1990s, the National Science Foundation (NSF) and the National Oceanic and Atmospheric Administration (NOAA) initiated process studies to improve quantification of air-sea CO_2 fluxes and gas transfer velocities. These studies focused on the determination of gas transfer velocities on regional scales. The GasEx-98 experiment occurred in the CO_2 sink region of an anticyclonic warm core ring in the eastern North Atlantic during May and June of 1998 (Wanninkhof and McGillis, 1999; McGillis *et al.*, 2001a; McGillis *et al.*, 2001b; Feely *et al.*, 2002). A second study, GasEx-2001, took place in the eastern equatorial Pacific in February and March of 2001 (McGillis *et al.*, 2004; Sabine *et al.*, 2004). The low annual mean wind speeds in the equatorial Pacific and high ΔpCO_2 values offered a unique opportunity to directly determine the fluxes in a low wind stress environment and to elucidate the factors controlling the flux. Although the measurements show some agreement at low wind speeds (see Figure 14), there is considerable variability in the transfer rates at high wind speeds. These differences result in a large uncertainty in the processes and magnitude of the Southern Ocean CO_2 sink. Future research must be geared toward concurrent quantification of the flux along with measurements characterizing the near surface turbulence that controls gas transfer. For example, capillary waves are closely related to turbulence, and transfer velocity is strongly affected by these waves (Bock *et al.*, 1999). Moreover, capillary waves generate large radar backscatter returns on altimeters and scatterometers. This equipment is in orbit to measure sea surface height and global winds on monthly and daily time scales. Another promising research avenue is to relate gas transfer to microscale breaking as manifested by perturbation of the cool skin measured by infrared radiometer measurements (Zappa *et al.*, 2002).

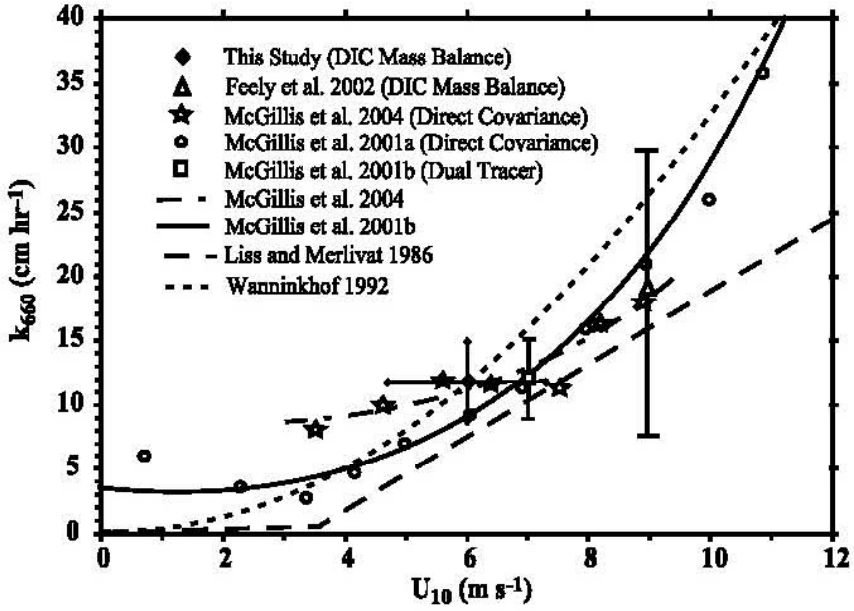

Figure 14: Plot of gas transfer velocity (k660) as a function of wind speed (U_{10}). Dotted line shows Wanninkhof (1992) relationship. Solid line shows McGillis *et al.*, (2001a) relationship. Dashed line shows Liss and Merlivat (1986) relationship. Dash-dotted line shows GasEx-2001 relationship (McGillis *et al.*, 2004b). Open circles and square with error bars show direct covariance and dual tracer estimates, respectively, from GasEx-98 study (McGillis *et al.*, 2001b). Stars show direct covariance measurements from GasEx-2001 (McGillis *et al.*, 2004b). Open triangle with error bars shows the estimate from DIC budget on GasEx-98 (Feely *et al.*, 2002). Solid diamond with error bars shows the estimate from Sabine *et al.*, (2004) using DIC budget models (courtesy Sabine *et al.*)

The overall objective for this gas exchange study is to quantify air-sea gas fluxes over the Southern Ocean's unique range of oceanographic, atmospheric, and biogeochemical conditions. Another objective is to obtain an improved understanding of processes governing air-sea fluxes to adequately constrain and predict the fate of CO_2 in the surface ocean and lower atmospheric boundary layers. This effort will improve the measurement, modeling, and remote-sensing capability in the Southern Ocean CO_2 region. See Table 3 for a list of the necessary research components with corresponding process and method components of a gas exchange study.

Table 3: Southern Ocean Air-Sea Gas Exchange Experiment

Research Project Components	Process and Method Components
Biological Measurements	New Production Primary Production
Bulk Meteorology and Turbulent Fluxes	Atmospheric Boundary Layer Physics and Meteorology IR Heat Flux Solar Temperature Turbulent Fluxes of Momentum Water Vapor
Core CO_2 and Hydrographic Measurements	Conductivity, Temperature, and Density (CTD) Equipment Dissolved Inorganic Carbon (DIC) pCO_2 Spatial and Temporal CO_2 Flux Footprint
Deliberate Tracers	SF_6 and ^3He
IR Remote Sensing	Active Infrared Techniques Microbreaking Processes Ocean Skin Temperature
Nutrients	Nutrients O_2
Sea Surface Roughness	Buoy-based Small Scale Waves Shipboard Radars
Shipboard CO_2 DMS Fluxes	Air-sea Gas Flux Systems Ship Mast
Surface Ocean Processes	Aerosols Atmospheric CO_2 Gradients Bubbles Currents Directional wave field Langmuir Cells Large Waves Oceanic Shear Oceanic Stratification Oceanic Surface Turbulence
Surface pCO_2 Variability	CARbon Interface OCean Atmosphere (CARIOCA) buoy Carbon Modeling Free Rising Temperature Profiler Submersible Autonomous Moored Instrument (SAMI) Surface CO_2 and O_2 Variability

To address these issues, this Southern Ocean gas exchange study should be carried out focusing on these primary targeted objectives:

- Establish the modern net air-sea CO_2 flux in the Southern Ocean
- Determine the sensitivity of Southern Ocean CO_2 uptake to climate variability and climate change, particularly in response to anticipated increase in stratification
- Detect secular trends in stratification and in meridional overturning circulation taking into account natural variability

Target 1: Establish the modern net air-sea CO_2 flux in the Southern Ocean.

These critical issues need to be addressed to meet the first target:

- Improve coverage of the regional estimates of air-sea CO_2 fluxes
- Establish factors regulating ΔpCO_2, such as deep winter convection; the warming, cooling, and mixing of surface waters; and biological use of nutrients
- Establish factors regulating CO_2 flux, such as bubble production and turbulence, near surface shear and microbreaking, Langmuir circulations, stratification, and surfactants

This Southern Ocean gas exchange study should be a multi-disciplinary study focusing on enhancing the understanding of air-sea CO_2 fluxes and the processes controlling them. The primary goal is to measure air-sea CO_2 fluxes, the surface physical processes, and the surface biogeochemical processes that control CO_2 fluxes over short (≈hourly) time scales. The study could provide the necessary knowledge for remote sensing and modeling efforts because it will help us to understand how gas transfer could be parameterized at small time scales and space scales. This understanding, could in turn, make it easier for us to avoid some inherent biases that arise in the cross-correlation terms when values for k estimated from longer-time averages are compared to environmental parameters with much shorter temporal scales. Of the available techniques for measuring air-sea CO_2 fluxes, atmospheric boundary layer micrometeorological CO_2 flux approaches (direct covariance and gradient methods) are well-suited for measuring fluxes over short time scales. In these methods, the gas flux is measured directly with average times on the order of 0.5 hours to 3.0 hours. Continuing studies in controlled environments, such as in a wind-wave tank will improve our mechanistic understanding of the processes that control gas transfer.

Field studies that use micrometeorological measurements (direct covariance, profile flux, and eddy accumulation methods) should be conducted concurrently with water column methods of measuring gas exchange with deliberate tracers, such as $^3He/SF_6$. Water column methods yield gas exchange rate estimates on daily to weekly time scales. Modeling components could be proposed and begun at any time.

Target 2: Determine the sensitivity of Southern Ocean CO_2 uptake to climate variability and climate change, particularly in response to anticipated increase in stratification.

To reach this objective, US-SOLAS will design and deploy an early detection system for physical and chemical parameters. This system will collect records that are sufficiently long enough to distinguish between climate variability and climate change. This phase of the study

will include the deployment of moorings, gliders, and floats that are capable of the appropriate physical and biogeochemical measurements. These measurements are required to detect secular trends and provide input for prognostic models. The data will be used in model development and model-data comparisons to help provide reliable projections of future trends.

By comparing outputs of oceanic and atmospheric inverse models, which yield estimates of fluxes based on oceanic and atmospheric measurements, scientists can verify a regional scale. The results of this study will also be used in data assimilation routines. US-SOLAS should encourage improvement in instrumental analysis. With improved signal to noise ratios in measurements, observations would not need to be limited to only regions with large ΔpCO_2 and CO_2 fluxes.

Target 3: Detect secular trends in stratification and in meridional overturning circulation taking into account natural variability.

To meet this objective, US-SOLAS will initiate the investigation of interannual variability of carbon fluxes in the Southern Ocean and the factors that regulate these fluxes. The Southern Ocean has regular patterns of interannual variability that are associated with coupled modes of ocean and atmospheric circulation. The Antarctic Circumpolar Wave (ACW) propagates around the Southern Ocean with a period of about eight years and a wave number of 2. Sea-ice extent (SIE), sea surface temperature (SST), sea surface height (SSH), sea level pressure (SLP), and wind stress all vary based on the phase of the ACW. The Antarctic Dipole (ADP) is a quasi-stationary wave that is characterized by an out-of-phase relationship between sea ice and temperature anomalies in the Atlantic and Pacific sectors of the Southern Ocean (Yuan and Martinson, 2001). Both the ACW and the ADP have strong statistical relationships to the El Niño-Southern Oscillation (ENSO).

The Southern Hemisphere Annular Mode (SAM) is characterized by an out-of-phase relationship between surface air pressure at the pole and the pressure at the middle latitudes (Thompson and Wallace, 2000). The intensity of the Southern Hemisphere westerlies depends on this pressure gradient. The intensity then influences surface ocean circulation, SIE, and meridional heat transport (Hall and Visbeck, 2002). Surface wind stress, the equatorward extent of sea ice, and SST also vary in systematic fashion in relationship to natural modes of interannual variability. US-SOLAS plans to deploy arrays of instruments to help characterize the modes of variability, the interactions between the ocean and the atmosphere, and the teleconnections to low latitudes. Biogeochemists will coordinate their process studies with the deployment of these arrays. Multi-year studies of ecosystem structure and nutrient utilization efficiency can draw on the natural interannual variability of certain factors. These factors influence light conditions and nutrient supply, while establishing their sensitivity to regional and global climate forcing.

The best year for this study would be in the 2007-09 timeframe to coordinate with the International Polar Year (IPY) carried out in the Arctic and Antarctic regions of the global oceans.

International Interactions

Many of the activities proposed in this effort are complementary to a number of objectives of other international programs, in particular CLIVAR, IMBER, LOICZ, and GLOBEC. Each addresses a specific issue of ocean carbon within the framework of other ocean science topics. For example, SOLAS focuses on the air-sea exchange of CO_2; CLIVAR focuses on large-scale uptake and transport of carbon; IMBER focuses on carbon transport, storage, and transformations; LOICZ focuses on coastal carbon fluxes; and GLOBEC focuses on carbon flow through ecosystems in the higher trophic levels.

These high-level international programs provide a mechanism for developing integrated strategies between the *in situ* and satellite observation communities and for obtaining commitments from the respective governments. Some examples of this integration include the following:

- The Global Observing Systems manages and develops shared networks
- The Global Climate Observing System (GCOS) and the Global Ocean Observing System (GOOS) together to help sponsor the ocean component of the study of climate change
- The Ocean Observations Panel for Climate (OOPC) manages strategy and coordination among the groups
- The SCOR-IOC Advisory Panel on Ocean Carbon Dioxide and its International Ocean Carbon Coordination Project (IOCCP) offer their expertise in the ocean carbon realm
- The International Ocean-Color Coordination Group (IOCCG) shares their expertise in the study of ocean color

Research Needs

- NCAR C-130 aircraft
- NOAA research vessel, the *Ronald H. Brown*
- Research vessel from another nation

Project Contributors

- Richard Feely, National Oceanic and Atmospheric Administration (NOAA)
- David Ho, Columbia University
- Wade McGillis, Columbia University
- Chris Sabine, NOAA
- Rik Wanninkhof, NOAA/Atlantic Oceanographic and Meteorological Laboratory (AOML)

Project

3.3

Global Surface Ocean Carbon Concentration Surveys

Goals

Quantify global regional partial pressure of carbon dioxide (CO_2) in surface water, pCO_{2sw}, and air-sea CO_2fluxes.

Understanding to Date:

Uptake of CO_2 by the global oceans is reasonably well constrained on decadal time scales (Takahashi *et al.*, 2002; Sabine *et al.*, 2004), but there is still significant uncertainty in regional fluxes on seasonal to interannual time scales. Having this regional information will provide constraints for inverse models and serve as a basis for determining the seasonal physical and biogeochemical controls on the ocean carbon cycle. This information will also help to develop a framework to determine interannual and decadal variability in global air-sea CO_2 fluxes.

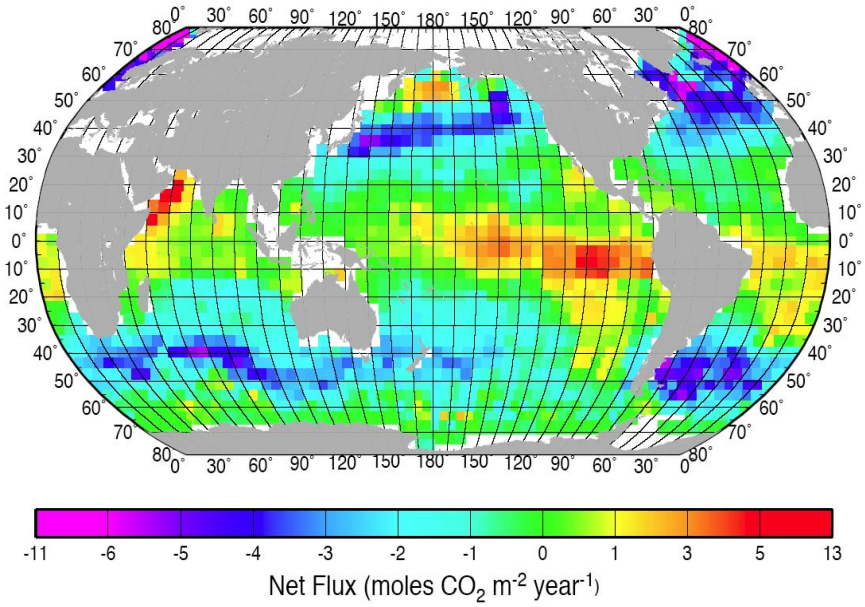

Figure 15: Climatological global air-sea CO2 flux map based on approximately 1 million ΔpCO_2 measurements over the past 40 years and relationship of gas exchange with climatological wind speed (courtesy Takahashi *et al.*, 2002).

The decadal uptake by the ocean is constrained with confidence by inventory measurements (Sabine *et al.*, 2004), but sub-decadal changes still have to be inferred. One method is to infer the changes from atmospheric CO_2 changes in combination with $^{13}C/^{12}C$, or O_2/N_2 measurements (Manning and Keeling, 2005). Another is to determine the flux of CO_2 across the air-sea interface (see Figure 15). For a constraint on carbon cycle models to be meaningful, air-sea fluxes should be constrained on regional scale to about 0.2 Pg C/year. With this level of constraint, models could more accurately forecast future CO_2 levels and studies could focus on a mechanistic understanding of surface water pCO_2 controls.

Based on correlation length scale arguments, the basin wide fluxes can be constrained to 0.2 Pg C/year by taking observations approximately 10° apart 6 to 9 times a year. Temporal and spatial changes in the partial pressure difference of pCO_2 between the atmosphere and ocean (ΔpCO_2) helped to derive this schedule. US-SOLAS does not have the resources to meet this objective alone, but rather can be a contributor to domestic and international efforts.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What is the interannual variability in ΔpCO_2 and in the resulting air-sea CO_2 fluxes?
- What are the causes of the variability?

- How will the oceanic CO_2 uptake change in the future?
- What is the sensitivity of air-sea CO_2 flux to climate-related changes in physical forcing?

Project Description

The goal of the U.S. Volunteer Observing Ship (VOS) pCO_2 Program is to build an observing system of appropriate spatial and temporal resolution. With the observation system, the scientists can constrain regional fluxes and achieve a mechanistic understanding (and ultimately predictive understanding) of the biogeochemical rate processes that give rise to the observed sea surface pCO_2 distributions.

The scientific objectives of this goal can be further separated into three targets as follows:

Target 1: Add data acquired during the project to the extensive database spanning the past 40 years. This additional information will help to improve the seasonal climatological distribution of surface water pCO_2 (Takahashi *et al.*, 2002).

Target 2: In conjunction with CARBOOCEAN and the North Pacific Marine Science Organization (PICES), provide seasonal maps of pCO_2 in the North Atlantic, North Pacific, and equatorial Pacific. Then expand the observation network to the Southern Hemisphere, with an emphasis on the Southern Ocean.

Target 3: Determine seasonal trends of pCO_2 across the Atlantic and Pacific Oceans and assess the effect of large-scale climate reorganizations on surface air-sea CO_2 fluxes.

In addition to the insight a surface water CO_2 observing system will add with respect to ocean regional and global efforts, the underway CO_2 measurements can improve the accuracy of air-sea flux measurements for the North American Carbon Program (NACP). These measurements may also help place the NACP results into more of a global context by monitoring changes in air-sea CO_2 differences in the North Atlantic, North Pacific, and adjacent coastal regions for North America. These measurements may also determine whether the ocean carbon cycle correlates with observed seasonal and interannual changes in the net North American uptake. Surface data on other bioreactive tracers can be collected with only modest additional effort as part of an underway pCO_2 survey. This additional data can provide important constraints on the oceanic, biological, and physical flux rates beyond those available from studying pCO_2 alone.

Our abilities to measure carbon (C), nitrate (NO_3), oxygen (O_2), and silica (SiO_2) have been improved by recent analytical advances. Measuring SiO_2 is particularly important because one can separate the influence of competing processes, such as photosynthesis and respiration; nutrient utilization; and resupply by mixing, production (or consumption), and

gas exchange on surface pCO_2 levels. With a well-organized program that involves analyzing concentrations of bio-tracers, we can dramatically extend our knowledge of the effect of bioactive fluxes due to their interannual variability, mediating processes, and quantitative influence on sea surface pCO_2.

We can take the measurements from the observing network and interpolate them in time and space to create regional flux maps. Creating regional algorithms between pCO_2 and remotely sensed parameters, such as sea surface temperature, can also facilitate such maps. Then using the synoptic information from the satellite product, we can produce maps of high fidelity. A schematic of the steps involved is shown in Figure 16.

A goal of the ongoing effort to measure sea surface pCO_2 in the equatorial Pacific Ocean is to demonstrate the advantages of creating flux maps through interpolation techniques using remotely sensed parameters. A composite of the ΔpCO_2 and air-sea CO_2 fluxes is provided in Figure 17. Similar efforts are underway to create flux maps in the North Atlantic Ocean, North Pacific Ocean, and Caribbean Sea. A limiting factor to date has been the lack of sufficient surface pCO_2 observations.

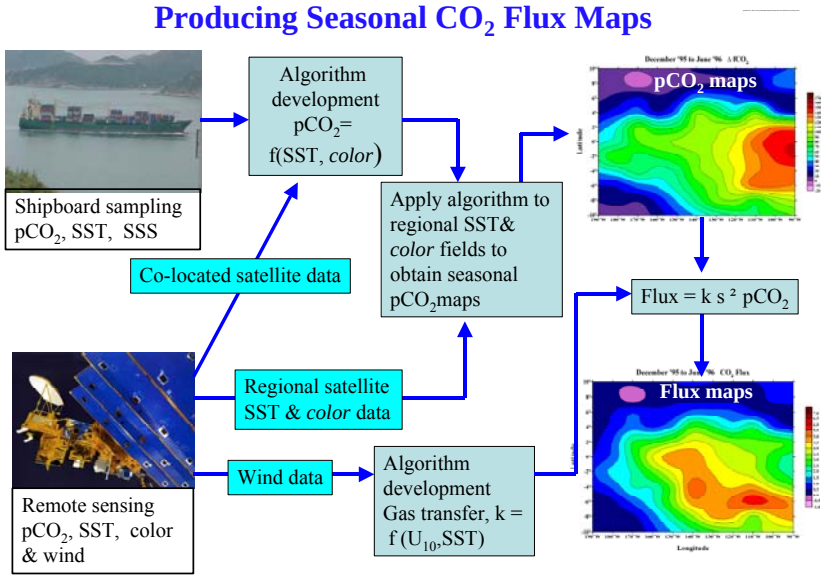

Figure 16: Steps involved in creating CO_2 flux maps (figure courtesy of R. Wanninkhof NOAA/AOML).

To constrain the global air-sea fluxes is one of the important goals of the global ocean CO_2 observing network. A parallel effort is necessary to improve our understanding of the magnitude and controls of gas transfer so we can estimate the fluxes. These efforts are highlighted in US-SOLAS Focus 2. Linking the gas exchange studies to the global observing network should be done by focusing the gas exchange studies on the regions where the observing network is being initiated.

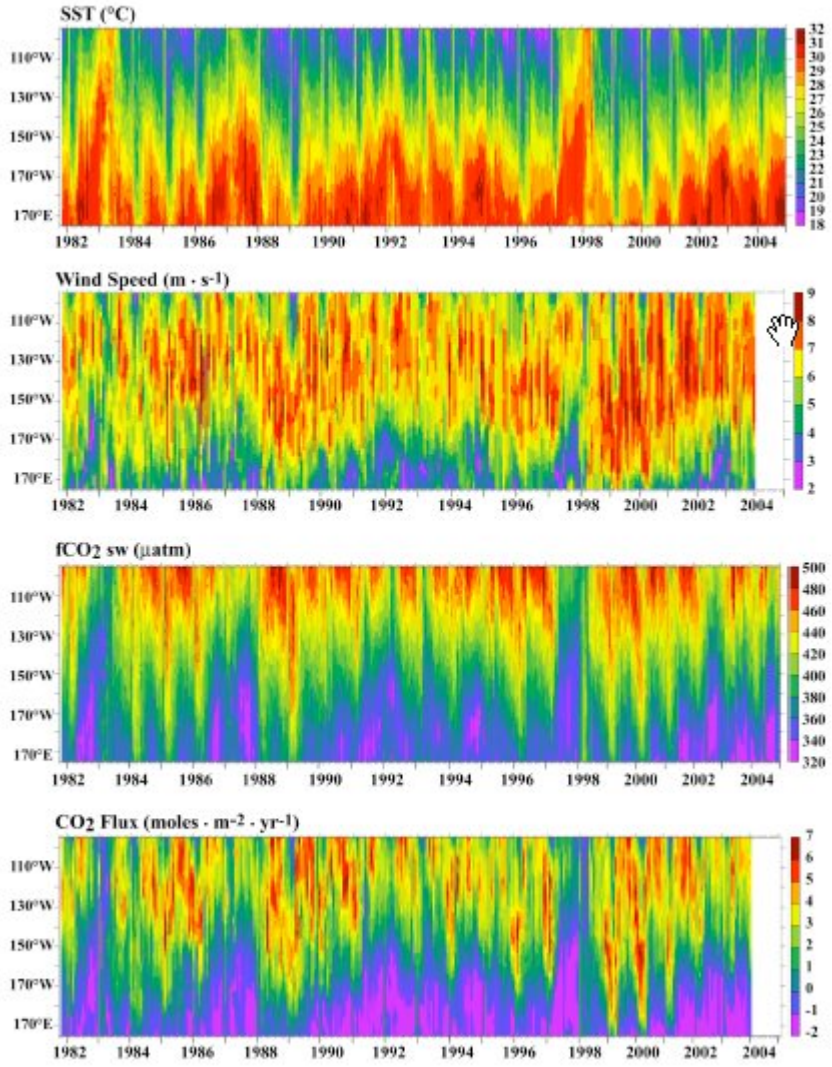

Figure 17: Estimated SST (A), FSU Subjective Analysis wind speeds (B), fCO_2sw (C), and CO_2 Flux (D) between 90°W and 165°E, 5°N to 10°S from 1982 through June 2004. Surface water fCO_2 was calculated by applying the inter-annual and seasonal fCO_2-SST relationships to Reynolds SST data, and CO_2 flux was calculated with FSU Subjective Analysis winds and the Wanninkhof (1992) gas transfer velocity (courtesy, Richard Feely, NOAA).

The network itself should be designed to assure consistency between measurements through the following: administering instrument intercalibration exercises, choosing ship lines so there are opportunities for cross-over comparisons, and assuring that ships used for deploying and maintaining equipment have pCO_2 analysis equipment on board. Research vessels provide a unique platform and are often the vessels of choice for deployments. They often have ancillary equipment and manpower necessary to help ensure that quality measurements are performed in a contextual biogeochemical framework. Therefore, outfitting the US University-National Oceanographic Laboratory System (UNOLS) vessels with CO_2 measuring equipment is a high priority.

International Interactions

This effort depends on collaborations with and the objectives of the International SOLAS program being implemented. Those objectives are being executed under various ongoing and budding national and international efforts, such as the NOAA pCO_2 on VOS and the CARBOOCEAN program, along with the efforts under the sponsorship of the US Ocean Carbon and Biogeochemistry (OCB) program. For more information, see http://www.uea.ac.uk/env/solas/SPIS/SPIS1.html.

Research Needs

- Autonomous pCO_2 systems and instrumentation for ancillary parameters
- Improved access to remotely sensed data, such as SST, color, and winds in near real time
- Surface vessels

Project Contributors

- Scott Doney, Woods Hole Oceanographic Institution (WHOI)
- Richard Feely, National Oceanic and Atmospheric Administration (NOAA)
- Rik Wanninkhof, NOAA/Atlantic Oceanographic and Meteorological Laboratory (AOML)

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Project

3.4

Perturbation Experiments in Ocean-Atmosphere Carbon Dioxide Studies

Goals

Conduct Iron (Fe) addition experiments to understand the different ecosystem response, primary production, and carbon sequestration in Fe-limited ocean domains.

Implement a deliberate biodegradable ocean surface film and measure the subsequent fluxes of momentum, heat, carbon dioxide (CO_2), and aerosols.

Conduct a deliberate ocean acidification experiment.

Perform laboratory studies to explore roles of surfactants, bubbles, spray, fetch, differential gas solubility, carbonic anhydrase, and chemical enhancement.

Understanding to Date:

Feasibility perturbation experiments have been conducted for Fe addition (Cooper *et al.*, 1996; Landry *et al.*, 1996), and surface films (Frew, 1997; McKenna and McGillis, 2004). There has not been a deliberate acid addition to date. Laboratory studies on understanding the role of surfactants, rain, bubbles, spray, fetch, differential gas solubility, carbonic anhydrase, and chemical enhancement, however, have been performed for many years. These experiments should continue as our technical and scientific expertise of these studies continues to improve.

Major Scientific Questions

These major scientific questions should be addressed in the US-SOLAS science activities:

- What are the processes that control air-sea exchange of carbon dioxide (CO_2) during an Fe addition in different ecosystems?
- How significant are *in situ* surface films on air-sea exchange?
- How significant is a strong change in surface acidification on air-sea exchange?

Project Description

Iron (Fe) additions have been a long-standing deliberate addition in processes studies, especially in high-chlorophyll, low-nutrient (HCLN) regions (Cooper *et al.*, 1996; Landry *et al.*, 1996). Iron additions combined with air-sea gas exchange studies are recommended.

Surfactants have long been considered to influence waves (Bock *et al.*, 1999), turbulence (McKenna and McGillis, 2004), and gas exchange (Frew, 1997). Deliberate additions of surfactants, in both the field and laboratories, should be performed.

As the ocean pCO_2 and acidification is rising, the acidity of seawater and the ocean carbonate system are coupled (Roy *et al.*, 1993). A deliberate addition of acid in a gas exchange process study would help elucidate the myriad processes on enhanced acidification on air-sea gas exchange.

Rain has also been found to enhance gas exchange (Ho *et al.*, 1997). Deliberate additions of rain in the laboratories, under different wind and rain conditions, should be performed. Carbonic anhydrases are enzymes that catalyze the hydration of CO_2 and the dehydration of bicarbonate ($CO_2 + H_2O$ <-----> $HCO_3^- + H^+$). There has been significant uncertainty in the amount changes in the rate of air-water CO_2 exchange caused by carbonic anhydrase reactions in the ocean surface microlayer (Goldman and Dennet, 1983; Henry, 1996).

International Interactions

The international global carbon cycle and air-sea interaction community.

Research Needs

- Installations and platforms to conduct precise and deliberate Fe and acid additions in the environment
- Maintaining and using laboratory tanks for the study of air-water gas exchange processes

Project Contributors

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Project

4.1

Autonomous and Lagrangian Platforms (ALPS) for SOLAS

Goals

Improve our understanding and parameterization of upper ocean processes and air-sea fluxes of heat, mass, momentum, and climate relevant compounds.

Develop platforms and sensor suites capable of measuring air-sea exchange processes autonomously in different regions of the world oceans. Systems should have an inherent flexibility to allow sampling with high temporal and spatial resolution during events that may last several days, and low temporal and spatial resolution to provide seasonal and inter-annual variability.

Understanding to Date:

Various sampling platforms and sensors suites have been developed for use in upper ocean research. Of particular interest to US-SOLAS activities are autonomous and Lagrangian platforms (ALPS) (Rudnick and Perry, 2003). There are many different types of ALPS and each has fundamental advantages and limitations based on platform size, power needs, sensor characteristics, deployability from land, ship, or aircraft, range, mission duration, and so on. Science needs will dictate which sampling platform should be used. It is envisioned US-SOLAS activities will benefit in many ways from the use of ALPS, both as stand-alone sampling platforms and in concert with ships or moorings. For example, US-SOLAS could use them to supplement shipboard sampling with high spatial resolution water property measurements around the study region before, during, and after a ship-based campaign. US-SOLAS also could use them to collect data in high sea states or other such conditions when shipboard sampling is impractical. These platforms provide rapid response sampling capabilities, which in turn allow the study of episodic events, such as blooms or dust storms, in remote regions. They also offer a way to extend sampling capabilities into environments that would be impossible to sample shipboard, such as hurricanes.

Sampling Platforms Overview

This section contains a brief overview of some of the active sampling platforms. Differences and limitations are emphasized in each category.

Gliders

Currently, there are three gliders available commercially:

- Slocum Glider, Webb Research, Inc.
- Spray Glider, Scripps/WHOI custom fabrication facility, which was recently licensed to BlueFin Robotics
- Seaglider, University of Washington custom fabrication facility

Gliders, such as the one shown in Figure 18, are used in survey mode for long-range transects and repeat sections. They can also be used in a virtual mooring capacity. Gliders can be used to identify and adaptably chase features, temporarily store data, forward data to other platforms, operate under ice for lengthy missions, function as tracer trackers, and provide over sampling by swarming.

US-SOLAS could implement tracer trackers as part of their experiments. Current sensors include air and water temperature (T), sulfur (S), chlorophyll and colored dissolved organic matter (CDOM) fluorescence, spectral absorption, in-water (ir) radiance, optical (red and blue) backscatter, vertical velocity from dP/dt and fall rate, and oxygen (O_2). At relatively low cost, gliders provide scientists a means to compare estimates of surface variables from satellites, as well as provide vertically averaged values.

Typically, gliders fly in a saw-tooth pattern at 0.45 knots, but can reach 0.9 knots, although at that speed they become much less efficient. It is clear that gliders have very tight power constraints. Using surface flush sensors can minimize drag. Power consumption and space limits the feasibility of adding new sensors, except for short missions. Typically, a glider might use a total of 0.5 W. About 15% (75 mW) of this power consumption is available for all of the onboard sensors. Realistically, these factors severely limit the use of gliders for biogeochemical sampling for anything other than a few low-power and compact sensing technologies, such as chlorophyll fluorescence and O_2.

Figure 18: Spray Glider.

Profiling floats

These floats are used for biogeochemical sensors that have greater power demands because these platforms can carry a larger battery payload. Prototype multi-purpose floats include FERP of the University of Washington's Applied Physics Laboratory. In a workshop report (2003), Rudnick and Perry proposed the development of an even larger profiling float that would be capable of accepting plug-and-play sensors. This float would be designed specifically with standard sampling protocols, size, and power constraints. Such a float would be useful for the rapid transition of advanced prototype sensors into US-SOLAS related activities. With sufficient power, a larger platform could be outfitted with acoustic and high-power optical sensors.

Lagrangian isopycnal and adjustable buoyancy floats

Isopycnal floats allow Lagrangian rates of change of sensed parameters, such as O_2, and thereby respiration rates, *i.e.*, $R=\mathrm{d}(O_2)/\mathrm{d}t$ along the float trajectory. Adjustable buoyancy floats can precisely control buoyancy. This ability makes discrete sampling on multiple isopycnals possible, which is important for several reasons. For one, with this approach, sensors can come to thermal equilibrium before sampling. Equilibrium is important because without it, thermal gradients across the sensing elements of advanced biogeochemical sensors can create significant biases. An isopycnal sample-and-hold approach eliminates many complications associated with non-standard profiling sensors, and in many ways provides a refined vertical-profile sampling platform for any sensor. Using this kind of sampling strategy for slow sensors, such as underwater mass spectrometers, could be beneficial.

Mixed layer Lagrangian floats

A mixed layer Lagrangian float is a variant of the adjustable buoyancy Lagrangian float, see Figure 19. It has a large horizontal drag screen that lets the float follow vertical water movements. A unique advantage of this type of float is the possibility of making waterside covariance estimates. If vertical fluxes by entrainment or air-sea transfer are sufficiently large, the flux can be calculated from $F=\langle w'c' \rangle$, where w' is the float velocity and c' the scalar change. Currently, this approach has been used for estimating heat, salt, and gas fluxes. If other sensors are sufficiently fast and have sufficient precision, vertical fluxes of other properties, such as nutrients, could be measured.

Floats may make possible discrete water sampling for biologically inert gases. Floats have ways to address the change in buoyancy of the platform and options for storing samples.

Figure 19: Mixed layer float.

Autonomous Underwater Vehicles (AUVs)

Propellers power these vehicles, which are suitable for short missions. They have a relatively large payload, and therefore can be especially useful for defining spatial variability in coastal measurements. A picture of the Remus AUV (Hydroid Inc.) is shown in Figure 20.

Figure 20: Remus AUV

Autonomous Surface Vehicles (ASVs)

Historically, these vehicles have been less attractive because users of this class of vehicles may face legal issues and because access to ocean-faring ships was relatively easy (Griffiths *et al.*, 2001). With access to ocean-faring ships decreasing over the past decade, however, different platforms are under development and are being made available through commercial partnerships. A recent addition to this genre of ocean platforms is the Ocean-Atmosphere Sensor Integration System (OASIS[7]) shown in Figure 21. These vessels were developed under a project funded by both the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) as part of an effort to develop new platforms for ocean science.

This vessel has recently been commercialized under a NASA Small Business Innovation Research (SBIR) award to Pacific Gyre, Inc. The OASIS is an 18-foot long vessel, powered by solar energy. It is fully autonomous, with optional station keeping, transect/path following, and wind pointing capabilities in the navigational package. At nominal solar exposure, the vessel is designed to travel 2.5 knots sustained. Under no light conditions, the vessel is designed to operate for three days. The vessel is self-righting and designed to survive hurricane conditions. With 500 lbs. of payload capacity combined with its surface location, this vessel meets many of the platform requirements of many US-SOLAS activities.

[7] The OASIS acronym used here is not related to the Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS) program described in Project 1.3.

Currently, an OASIS vessel is being outfitted with air-sea flux sensors for heat and CO_2. Standard sensors include the following: wind velocity; relative humidity; air temperature; atmospheric pressure; and sea surface salinity, temperature, and chlorophyll. Future plans are to include a profiling system for salinity, temperature, and fluorescence. Communication occurs through Iridium modems to a shore based command center. In part to support US-SOLAS and other similar efforts along the coasts of the United States, NOAA is funding the fabrication of a small fleet of these vessels.

Figure 21: Field Deployment of the Ocean-Atmosphere Sensor Integration System (OASIS) Autonomous Surface Vehicle (ASV). The platform was developed under joint NASA-NOAA funding and commercialized through a NASA-SBIR award. It is being marketed commercially through Pacific Gyre, Inc.

Surface Drifters

Lastly, the simplest of platforms is the surface drifter. There are many designs for these platforms, some of which include drogues to better follow the surface currents. Systems, such as the CARbon Interface OCean Atmosphere (CARIOCA) buoy, which was designed specifically to measure pCO_2, have been deployed for extended periods in the Southern Ocean.

Project Description

Primarily due to limitations associated with shipboard sampling at high winds, up until 2004, measurements of air-sea gas transfer rates have been limited to winds less than 22 ms^{-1}. To measure air-sea gas exchange rates at higher wind speeds, mixed layer floats equipped with fast-response dissolved O_2 and nitrogen gas (N_2) sensors were air-deployed in September

2004 into the path of hurricane Frances. Gas flux estimates were made at wind speeds in excess of 55 ms^{-1}. Figure 22 shows the pre- and post-hurricane dissolved gas profiles that are used in mixed layer budget calculations. These data provided the first waterside covariance flux measurements of O_2, which compared well with mixed layer budgets of O_2 and N_2.

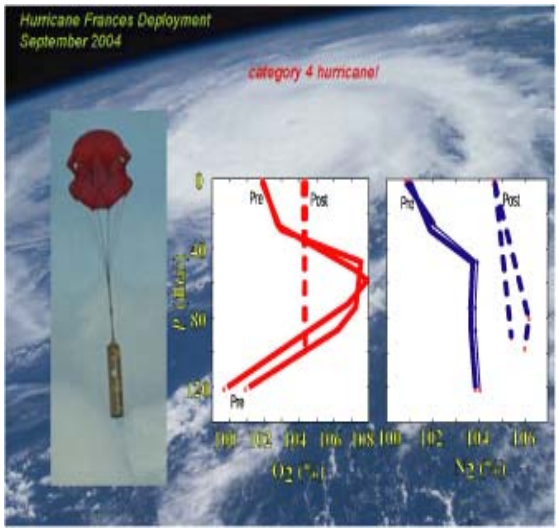

Figure 22: Measurements of upper ocean dissolved gas profiles made before and after the passage of hurricane Frances in September 2004 (courtesy of Craig McNeil, University of Rhode Island).

Target 1: Compare atmospheric and oceanic eddy-flux measurements of gases across the air-sea interface.

Target 2: Compare air-sea gas transfer rates of CO_2, O_2/N_2, and $SF_6/^3He$ at high winds using comparisons of eddy-flux estimates and mixed layer budgets.

These targets complement US-SOLAS activities because they aim for a deeper understanding of the processes that control air-sea fluxes of climate relevant compounds (CRCs). Some CRCs mostly evade the ocean, others mostly invade the ocean. A better understanding of processes that enhance or limit evasion and invasion will lead to improved parameterizations of the processes that control air-sea exchange of CRCs. Rapid response sensors that allow co-variance N_2 flux measurements in the surface ocean are under development. Mixed layer pCO_2 measurements could be made using a newly developed non-dispersive IR absorption pCO_2 sensor. Ambient noise measurements will be used to capture information on wave breaking and wind speed. Floats will be used in tracer release studies, like the recently funded UK-SOLAS Deep Ocean Gas Exchange Experiment (DOGEE).

Research Needs

- Shipborne: deployment of autonomous platforms within specific features and events
- Airborne: P3 aircraft or skydive charters for air-deployable floats
- Research Vessel: ALPS launch and recovery

Project Contributors

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- Eric D'Asaro, University of Washington
- Mary Jane Perry, University of Maine
- John Moisan, NASA

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Project

4.2

Diagnostic Modeling of Air-Sea Trace Gas Exchanges

Goals

Diagnose regional to global patterns of air-sea trace gas exchanges through a synthesis of field observations, satellite data products, and numerical modeling.

Provide a bridge between SOLAS field observations and future predictive models of trace gas fluxes.

Understanding to Date:

The air-sea fluxes of many climatic and biogeochemical relevant gases, such as carbon monoxide (CO), carbon dioxide (CO_2), dimethyl sulfide (DMS), ammonia (NH_3), nitrous oxide (N_2O), oxygen (O_2), and oxygen carbon sulphide (OCS), are poorly constrained on regional to global scales. Though this problem is partly due to uncertainty in the air-sea gas transfer velocity, most of the problem is due to poor spatial and temporal coverages of trace gas concentrations in the surface ocean. While trace gas surveys and time-series measurements will help to reduce this problem (see Projects 1.1 and 1.3), it is likely that uncertainties in regional to global assessments will still be large because of the significant spatial and temporal variability in trace gas distribution processes.

Global coverage by numeric models and remote sensing can constrain some of the key processes. Specifically, ocean circulation models that assimilate observations provide a strong constraint on advection and mixing, both of which dominate the distribution of many trace gases. Also important are light-dependent processes, such as primary production, absorption of ultraviolet radiation by colored dissolved organic matter, and phytoplankton physiological status. Satellites can estimate all of these processes (Antoine and Morel 1996, Siegel *et al.*, 2002, Behrenfeld *et al.*, 2005). Therefore, US-SOLAS will need to blend observations, remote sensing products, and numerical models to better constrain air-sea gas fluxes on large scales. This synthesis of observations and models will produce regional to global scale assessments of trace gas fluxes, which will enable the accounting of uncertainty bounds. Further, this approach will produce parameterizations of important biogeochemical processes that we can then use in predictive models of air-sea gas fluxes. In this way,

diagnostic modeling can act as a bridge between US-SOLAS field observations and future predictive models of trace gas fluxes.

The following sections show examples of how this diagnostic modeling approach can be used for a variety of important trace gases. Some gases, such as CO_2, NH_3, N_2O, and O_2 are regulated largely by primary production and the associated organic matter remineralization. Some, such as CO and OCS, are regulated primarily by photochemistry as modified by other processes, such as microbial consumption and hydrolysis. Others like DMS are affected by both food web dynamics and photochemistry.

Target 1: Quantify the air-sea fluxes of CO_2 and O_2.

To separate terrestrial and oceanic uptake of anthropogenic CO_2, and therefore make future atmospheric CO_2 projections, it is critical to quantify the air-sea fluxes of CO_2 and O_2 and the processes responsible for their variability. In recent years, we have seen an increased emphasis on understanding interannual variability. Although the differences among results from diverse methodologies (mainly atmospheric inversions and forward ocean biogeochemical models) are not as great as earlier comparisons suggested (LeQuéré *et al.*, 2000), they are still substantial. Until these differences are well understood and corrected for, large uncertainty remains in prognostic carbon cycle models and consequently in future climate change predictions.

US-SOLAS studies could combine observations, models, and remote sensing products to constrain air-sea fluxes of CO_2 and O_2 and their interannual variability. An example of this approach applied to the annual cycle of O_2 is the study of Balkanski *et al.*, 1999. They exploited the three-dimensional distribution of Net Primary Production (NPP) determined from satellite ocean color observations (Antoine and Morel, 1996). Respiration in the model is simulated with two parameters: one for the sinking rate of organic matter formed from NPP and another for the rate constant for decomposition of this organic matter. Transport in the model is strictly one-dimensional and driven by observed seasonal variations in mixed-layer depth. The surface O_2 fluxes derived from this model are used to force an atmospheric tracer transport model. Very good agreement was found with observations of the amplitude in the atmospheric O_2:N_2 ratio. The main advantage of this diagnostic approach is that it sidesteps the need to develop a full-blown ecosystem model with multiple phytoplankton species and nutrient limitations.

We could extend this model to three dimensions and include other important components of the carbon cycle, such as dissolved organic matter and calcium carbonate. The three-dimensional advection and diffusion fields product generated from the Estimating the Circulation and Climate of the Ocean (ECCO) consortium is an example of a data assimilation product that could measure ocean circulation (Stammer *et al.*, 2002, Köhl *et al.*, 2003). This biogeochemical model would have only a few parameters (unlike the dozens found in standard prognostic models), and the parameters could be more easily constrained by using one of many optimization techniques (*e.g.* Jones *et al.*, 1998) combined with observations of O_2, dissolved inorganic carbon (C), dissolved organic C, and alkalinity. The result would be temporally varying fields of air-sea fluxes of CO_2 and O_2 with error estimates.

Target 2: Refine our knowledge about sources of ammonia to the atmosphere.

Ammonia (NH_3) serves as the dominant base in the atmosphere and is important for regulating the pH of aerosols and precipitation. We need accurate knowledge of sources of ammonia to the atmosphere to understand a variety of chemical reactions and how anthropogenic forcing and climate variability may affect them. The ocean is thought to be an important natural source of ammonia to the atmosphere, although there is great uncertainty in global flux estimates due to the paucity of ammonium observations in surface seawater. Global estimates of 7 to 13 Tg N yr^{-1} (Dentener and Crutzen, 1994), (Schlesinger and Hartley, 1992) have been made based on one transect of concentration measurements in the Pacific Ocean in 1988 (Quinn *et al.*, 1990). The scarcity of the data precludes a reliable estimate of the error in these fluxes.

Ammonia gas in seawater is at equilibrium with the much larger pool of ammonium (NH_4^+). The amount of ammonia gas can be computed from the ammonium concentration, temperature, salinity, and pH. The distributions of all of these quantities are known reasonably well in the surface ocean, except for ammonium. Ammonium is produced in seawater during organic matter decomposition and is consumed by phytoplankton. Estimates of primary productivity from space (*e.g.* Antoine and Morel, 1996) can be used to quantify the production of organic matter. Previous studies (Balkanski *et al.*, 1999) have shown that the decay of this organic matter can be modeled in an accurate way by calibrating model parameters with observations of dissolved O_2 in the ocean and atmosphere. This model of organic matter cycling could be embedded in a three-dimensional, data-constrained ocean circulation model to simulate the distribution of ammonium in the surface ocean. First, we should perform a data synthesis of ammonium observations and combine the synthesis with results from US-SOLAS trace gas surveys and time-series studies (see Projects 1.1 and 1.3). These data would be used to calibrate the ammonium model, which would effectively act as an interpolator of the ammonium observations.

Target 3: Constrain a global ocean CO model.

Carbon monoxide (CO) is a key regulator of the hydroxyl radical (OH) in the atmosphere. The ocean is thought to be a small, but significant, natural source of CO to the atmosphere. Estimates vary greatly (about 5 to 500 Tg C yr^{-1}), though a recent analysis suggests that the upper bound is far too high (Zafiriou *et al.*, 2003). This CO is mainly produced photochemically and consumed microbially. Loss to the atmosphere is, on average, small compared to these terms (Zafiriou *et al.*, 2003), but can be significant locally (Johnson and Bates 1996). Vertical mixing generally results in a downward flux of CO in the water column.

Improved estimates of the CO source to the atmosphere could be made by constraining a global ocean CO model with satellite-based estimates of CO production, vertical mixing estimated from ocean circulation models, and a model of bacterial CO consumption. The level of CO photoproduction could be determined from observations of the CO quantum yield with satellite estimates of the amount of UV radiation absorbed by colored dissolved organic matter (CDOM) (see Figure 23). An example of this method based upon field observations of the CO quantum yield and satellite-based modeling of incident UV radiation, UV spectral radiation penetration, and CDOM is shown in Figure 24. A recent synthesis of CO microbial consumption rate constants suggests a simple parameterization based on chlorophyll *a* and temperature (Xie *et al.*, 2005), both of which can be retrieved from satellite.

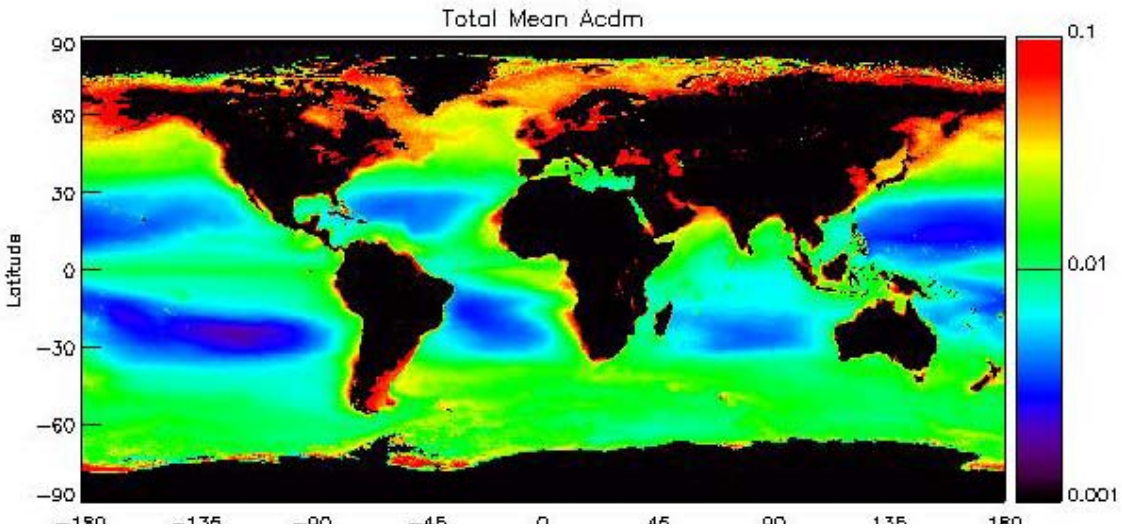

Figure 23: Climatological distributions of the absorption of light by colored dissolved organic matter (CDOM) and detrital particulates at 440 nm (after Siegel *et al.*, 2005). Detrital particulates make a small contribution to the satellite-sensed signal (Siegel *et al.*, 2002) making this an excellent representation of the global CDOM distribution.

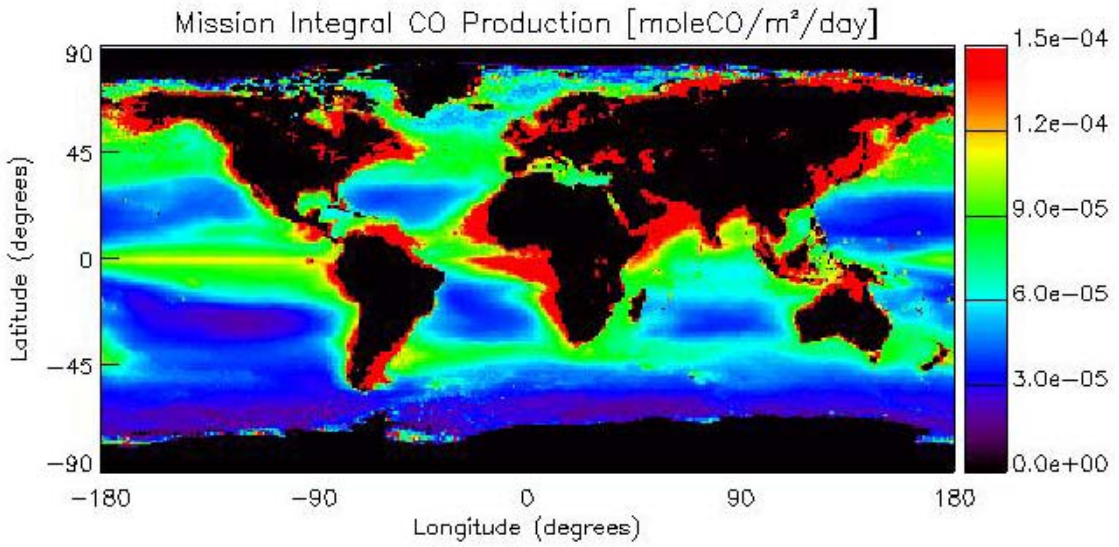

Figure 24: Satellite-based modeling of the average CO photoproduction rate using a CO quantum yield parameterization derived from many field observations (Nelson *et al.*, in prep.). The globally averaged rate is 9.6x10^{-5} mole CO m^{-2} d^{-1}, which corresponds to ~150 T mol CO per year.

Target 4: Develop models that incorporate food web dynamics and the photochemical cycling of dimethyl sulfide and its precursors.

Air-sea fluxes of DMS impact climate change through the cloud albedo feedback mechanism and are of major interest to US-SOLAS. Unfortunately, DMS emissions are regulated by a wide host of processes that span photochemistry to food web dynamics. Recent studies have found some successful predictive relationships for modeling oceanic surface DMS inventories, but due to their empirical formulations, the studies shed little light on how DMS biogeochemical cycling processes will be altered by changing environmental and ecosystem structure conditions (*e.g.* Anderson *et al.*, 2001, Simó and Dachs, 2002).

While these models demonstrate varying degrees of success in certain geographic regions, a review by Belviso *et al.*, (2004) indicates extremely weak correlations between modeled and measured DMS concentrations in all cases. All in all, the results from the suite of surface DMS models differ markedly and do not reach a consensus on the global spatial or temporal distribution of DMS. Furthermore, because the model formulations differ widely, it is unclear whether the models will diverge or converge under changing environmental conditions. Clearly, more mechanistic approaches need to be pursued.

In 2004, Toole and Siegel proposed that ocean DMS cycling could be partitioned into two regimes. In the stress regime, UV radiation and nutrient limitation create elevated intracellular concentrations of DMS and its precursor via the anti-oxidant hypothesis (Sunda *et al.*, 2002). In the bloom regime, increases in phytoplankton biomass drive increases in water column DMS content. Hints of this partitioning are found in the empirical modeling of Simó and Dachs, 2002; however, these correlative models should not be used in a

predictive or forecast setting. Models that incorporate food web dynamics and the photochemical cycling of DMS and its precursors need to be developed.

One path to developing these models is to address the dynamics of each regime separately and develop metrics that distinguish between the two regimes. These models could then be run in a diagnostic fashion to provide assessments of global DMS exchanges, their trends in time, and interactions with other variables. In this way, the DMS feedback hypotheses can be diagnosed. These models could also be used in a predictive or forecast mode. This example illustrates one way that diagnostic modeling can act as a bridge between observations and predictive models.

International Interactions

Many of the activities proposed in this effort complement the activities of a number of international programs.

Research Needs

- Continuous ocean color time series from high-quality satellite imagery
- Large-scale surveys and time-series observations of trace gas concentrations
- Large-scale fields of solar data, climate data, and physical oceanographic parameters
- Numerical models that include physical processes

Project Contributors

- Raymond Najjar, Pennsylvania State University
- Norm Nelson, University of California at Santa Barbara
- David Siegel, University of California at Santa Barbara
- Dierdre Toole, Woods Hole Oceanographic Institution (WHOI)

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Project

4.3

US-SOLAS Linkages to the United States Ocean Carbon and Biogeochemistry (OCB) Program and the Ocean Observing Initiative (OOI)

Summary

The NSF/NOAA/NASA Ocean Carbon and Biogeochemistry (OCB) program and the NSF Ocean Observing Initiative (OOI) are important partners for the US-SOLAS program. Both the OOI and OCB activities complement the US-SOLAS science and implementation Strategy. The OOI and OCB program objectives are multidisciplinary and include the SOLAS domain. The OOI and OCB activities should provide important component to the US-SOLAS program.

Ocean Carbon and Biogeochemistry Program Goals

The Ocean Carbon and Biogeochemistry program (OCB) (http://ocb.whoi.edu) will focus on the ocean's role as a component of the global carbon cycle, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are:

"To promote, plan, and coordinate, collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) program and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous US single-investigator and medium-size research projects funded by NASA, NOAA, and NSF."

Details of OCB

The OCB program consists of Ocean Carbon, SOLAS, and IMBER program science issues. The study of surface ocean-lower atmospheric processes requires a thorough knowledge of the state and variability of (1) marine geochemistry and ecology, (2) air-water gas exchange processes, (3) atmospheric trace gases and particles, and (4) climate and weather. In the past,

these fields of research have mostly progressed in parallel and the state of the art in each of these fields is separately reviewed. The linkages of SOLAS with OCB have opened new opportunities for research.

Key marine biogeochemical topics associated with SOLAS involve better characterizing and understanding the ocean physics, chemistry, and biology dynamics controlling the transfer of gas or particles to and from the atmosphere. Biological productivity occurs at the ocean surface, but as organisms die and sink to the deep ocean, trace elements are transported away and become isolated from the atmosphere through the biological pump. Biological productivity is sustained by the input of nutrients from the atmosphere, rivers and continental margins, and the deep ocean. Whereas nitrate and phosphate are the most common limiting nutrients, recent experiments have demonstrated that iron may also limit biological productivity over large regions of the ocean (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000). These studies also highlight the role of different phytoplankton groups in the efficiency of the biological pump. Efforts are underway to characterize specific properties of the main phytoplankton groups (see for example the iron addition experiments). Biological processes determine the concentration of atmospheric CO_2 on time scales of a few thousand years, while contributing to regional patterns of air-sea CO_2 fluxes on shorter time scales. Biological processes also affect the sulfur cycle. Process studies have established a general link between phytoplankton and dimethylsulphide (DMS) levels, although the exact mechanisms responsible for DMS production are not fully understood. DMS is a direct feedback on climate through its radiative forcing, and an indirect feedback because it is a source of cloud condensation nuclei, and thus can change cloud properties.

The most recent scientific assessment of climate stated that the increase in greenhouse gases and aerosol concentrations likely caused most of the observed warming of the 20th century (IPCC-2001). Changes in the climate system have also been observed in the global water cycle, cloud cover, and the extent and thickness of sea ice, with potential impact on wind patterns and ocean circulation. Better quantification of the physics of climate can account for most of these changes. In particular, in recent years the radiative forcing of greenhouse gases and cloud-albedo feedback were better quantified. From an OCB and SOLAS point of view, I think an equally or even more compelling direction are the physical-biogeochemical feedback mechanisms where by ocean biogeochemistry could either partially ameliorate or accelerate climate change. As a consequence of human activities the role of air-sea gas and particle exchange must be put in a global context. Ocean-atmospheric coupling has already made measurable impacts on several aspects of the global climate system. A main goal of OCB is to combine Ocean Carbon, SOLAS, and IMBER scientific initiatives to understand and quantify the impact of climate change on air-sea processes and to quantify the magnitude of potential feedbacks on climate and weather.

Ocean Observing Initiative Goals

The goals of the Ocean Observing Initiative (OOI) are to develop a long-term ocean infrastructure with the Ocean Research Interactive Observatory Networks (ORION). Information on ORION may be found at http://www.orionprogram.org/. ORION is

being developed to investigate the ocean's roll in a myriad of climate, weather, and geological processes.

"ORION is a program that focuses the science, technology, education and outreach of an emerging network of science driven ocean observing systems. Building on the heritage of the ship-based expeditionary era of the last century, oceanography is commencing a new phase in which research scientists increasingly seek continuous interaction with the ocean environment to adaptively observe the earth-ocean-atmosphere system. Such approaches are crucial to resolving the full range of episodicity and temporal change central to so many ocean processes that directly impact human society, our climate and the incredible range of natural phenomena found in the largest ecosystem of the planet."

Details of the OOI and ORION

Observatory Networks (ORION) consists of a coastal, regional cabled, and global components. The OOI review identifies the following "Blue Ribbon" science issues for ORION:

[1] What is the ocean's role in storing anthropogenic carbon and how will the long-term increase in atmospheric CO_2 affect ocean chemistry and ecosystem structure and interactions?

[2] How will climate change and human activity alter coastal ecosystems, habitats and living marine resources?

[3] What is the impact of storms and other extreme events, especially in the poorly studied Southern Ocean, on exchanges of heat, gases and nutrients within the earth-ocean-atmosphere system?

[4] What is the planetary significance and evolutionary importance of microbial activity in the ocean and in the newly discovered sub-seafloor biosphere?

[5] What processes control the size and frequency of earthquakes at oceanic transform and subduction zone fault systems?

SOLAS science is significantly related to issues 1, 2, and 3 of the high priority, Blue Ribbon, science questions of ORION. ORION also contributes to the study, understanding, and prediction of hazards from the ocean, including:

Hurricanes and Storms: Absolutely need surface gravity waves, wind. Locations proposed might be optimized, however current proposed sites will be hit in SAB. The ability to study intensification is not covered if we do not have assets in the Gulf; however the ability to study ocean thermal resource, high wind physics, storm surge, and the impact of the event will be conducted. Improved wind wave physics will also be key to geomorphology processes. An unexamined biological/chemical forcing function. Pioneer arrays may provide a unique tool here.

Aeolian Dust, Volcanic (Dust), Air Quality, Atmospheric Brown Clouds (ACBs), Atmospheric Pollution: Impacts reefs via airborne fungus? We understand very little and ORION will help understand these processes in the atmospheric boundary layer. The entire network should

be used and complement other efforts (NASA). How much is coming from Asia? Urban vs pristine locations?

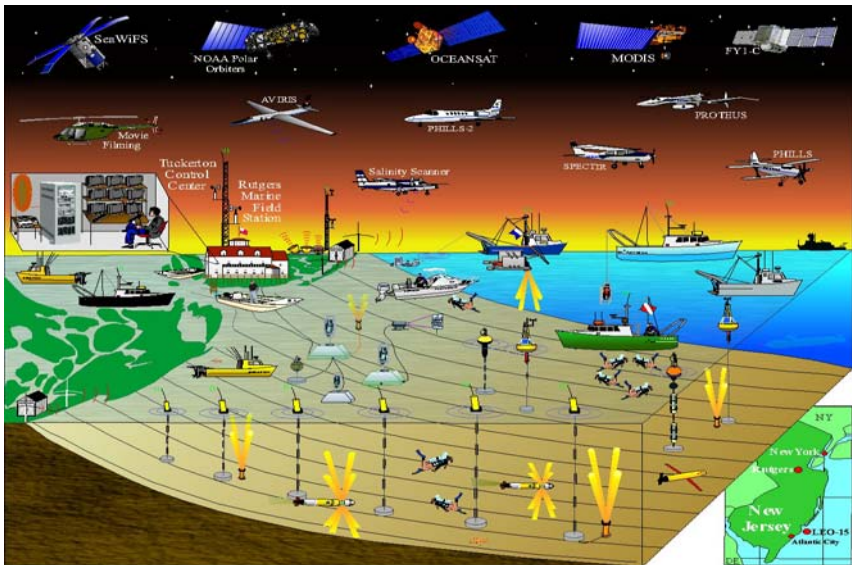

Figure 25: The Long term Ecosystem Observatory (LEO) was an early prototype of the ocean observatories that will be deployed by the United States.

The scientific successes of the ocean observatories throughout the globe in last decade, for example Rutgers University Long-term Ecological Observatory (LEO) shown in Figure 25, has led the National Science Foundation to propose to build a suite of ocean observatories. These observatories will be constructed as part of the ocean Observatory Initiative (OOI) which has recently undergone its conceptual design review. Currently implementation is to begin in late 2008 and early 2009. While the OOI will serve a diverse array of science interests spanning tectonics to microbial ecology, some specific assets will be extremely useful for SOLAS. The coastal components of the OOI include infrastructure will enable long-term time series (Endurance Array) as well as interactive process studies (Pioneer Array). The assets will be powerful in providing subsurface measurements of the physics, chemistry, and biology and coupling those measurements of air-sea fluxes.

The Pioneer Arrays: The OOI will build the Pioneer Array providing the oceanographic community for the first time an integrated network capable of resolving multiple spatial scales with sufficient fidelity to resolve critical processes in the coastal ocean. The network will allow researchers to adaptively sample the environment using a variety of mooring and AUV systems that will be operated as a network. The moorings will have surface expression to facilitate air-sea studies. The subsurface mooring and mobile assets will provide comprehensive pictures of the subsurface physical, chemical, and biological processes. The initial application of the Pioneer Array is currently recommended for the Mid-Atlantic Bight which is characterized by a relatively broad shelf, a persistent equatorward current originating well north of the United States, a well defined shelf-slope front, variable wind forcing, distributed buoyancy inputs by a number of rivers, and off-shore forcing by intermittent rings shed by an energetic western boundary current (the Gulf Stream). The proposed initial application of the Pioneer Array focuses on transport processes and

ecosystem dynamics within the shelf-slope front, a region of complex nonlinear dynamics, intense mesoscale variability, and greatly enhanced biological productivity relative to the adjacent shelf and slope. The scientific questions center on processes controlling the transport of heat, salt, nutrient and carbon fluxes across the shelfbreak front; the relationship between variability in the shelfbreak frontal jet and the along-front structure in phytoplankton distributions; and the aspects of interannual variability that are most important for modulating shelf-slope exchange.

The Endurance Arrays: The OOI proposes to build two Endurance arrays which will provide long term time series measurements on the scale of a large marine ecosystem. The time series will be anchored by cross shore arrays of highly capable profiling moorings or large towers powered by electro-optical cables. The time series sites will provide vertically resolved measurements in the water column and provide sufficient surface expression to allow for air-sea flux experiments. The fixed point mooring arrays will be complemented with langragian long duration gliders providing sustained spatial time series to complement the high frequency sampling of at the moorings and towers. The spatial time series will enable research on coastal biogeochemistry, climate, and ecosystem dynamics. The Endurance arrays are proposed to be located in the Pacific northwest and in the South Atlantic Bight. The proposed component in the South Atlantic Bight (SAB) array may be of particular interest to SOLAS (Figure 26). The proposed SAB observatory will: characterize Gulf Stream variability; quantify atmospheric forcing and air-sea exchange processes; lead to improved knowledge of the carbon cycle; quantify the importance of episodic events in oceanic forcing, circulation, sediment transport, fisheries, and cycling of biogeochemically important materials. The SAB network will be anchored by high powered towers providing excellent platforms for both the ocean and the atmosphere research.

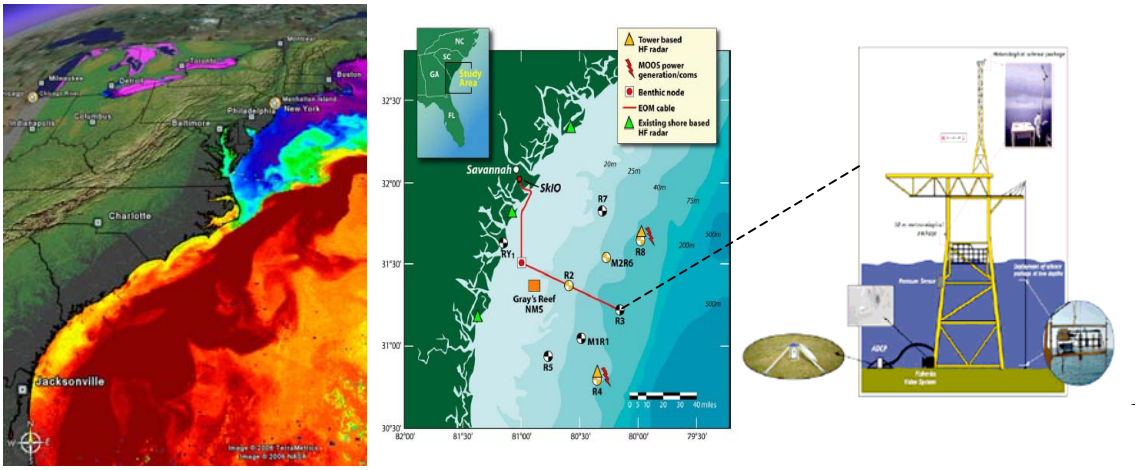

Figure 26: The Endurance array proposed by the OOI for development and deployment. The array is bordered by the energetic Gulf stream in the offshore and consists of a series towers which have ample power for a variety of sensors making measurements both in the ocean and atmosphere.

The OOI will benefit SOLAS by providing and an extensive array of infrastructure and supporting measurements to facilitate research on air-sea dynamics. The OOI will benefit

from SOLAS which will provide a large pool of researchers and sensors to populate and use the ocean observatories which are being constructed to serve the wider scientific community.

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Project

4.4

Data Management for US-SOLAS

Goals

Provide a data management structure for US-SOLAS that integrates with the established data centers and the data management systems of other relevant US programs.

Understanding to Date:

Data management of diverse data sets has undergone tremendous improvements over the last decade with better relational database software, more powerful query routines, and interfaces that are easier to use. Applying these and other new data management principles and techniques are critical to the success of US-SOLAS, as it will obtain multi-disciplinary and diverse data.

Project Description

Target 1: Provide data management support for US SOLAS activities.

A coordinated data management system is critical to the success of the program. One of the top priorities of the US-SOLAS data management office needs to be the open access to all data generated by the US-SOLAS program. This Science Plan and Implementation Strategy identifies data and model management as critical logistical tasks. The implementation will involve the collection of large quantities of environmental data by both nationally and internationally organized projects. The data will include measurement of biological, physical, and chemical parameters collected from process studies and experiments (field and laboratory), time-series studies, and large-scale surveys. Presently, the SOLAS project envisions encompassing significant field activity in approximately nine global regions or Field Campaign Provinces. The data expected to stem from these projects will extend beyond the projects themselves and will be of interest to other investigators. Further, because of the multi-disciplinary aspect of SOLAS, many of the data will be more useful when combined with, or compared against, data from non-SOLAS projects. Scientific findings derived from SOLAS projects should be available for independent scientists to assess. To fulfill this objective, the underlying data and/or models must be readily accessible.

To fully benefit from the data that will be obtained in US-SOLAS activities, data management activities should follow these guidelines. The data should:

- Be documented fully, including the models and the output
- Have undergone standardized quality control procedures
- Be obtainable through query statements and relational functions
- All the data must be available through a single location on a common server accessible by the Internet
- Data should be made available to the scientific community in less than one year after the study

Target 2: Perform data management outreach to link to relevant historical datasets and datasets from other applicable US and international programs

Another function of the US-SOLAS data management office will be to link to relevant historical datasets and improve the availability and documentation of this historical data. Climate impacts and feedbacks are a major focus of the SOLAS project and are often best studied through a historical perspective.

The US-SOLAS data management office will also undertake the task of determining the scales of relevance for both processes that benefit from global climatological datasets and for global assimilation products. In some instances, other programs have already started case global re-analysis projects. If the SOLAS data management system can link to these re-analysis projects, the collaboration could result in value-added SOLAS science projects.

By design, SOLAS is an international program that brings about collaboration among countries and scientific disciplines. The US-SOLAS data management office can work together with the international data management office to help meet the objectives of both offices. Within the US, there are several related programs, such as Ocean Carbon and Biogeochemistry (OCB) program, where close interaction could benefit both programs. The US-SOLAS team should investigate the opportunity for shared infrastructure and personnel.

International Interactions

This open exchange of data advocated by the US-SOLAS team can serve as a positive example for other national SOLAS projects. The projects are listed here with links to the available data management plans:

- Canada SOLAS
  http://csolas.dal.ca/solas_6685.html
- UK-SOLAS
  (in progress)
- Japan Oceanographical Data Center (JODC)
  http://www.jodc.go.jp/aboutJODC_work_data.html

Research Needs

The US-SOLAS team needs to establish a data management sub-group that can do the following:

- Set forth the data management principles
- Select data management software and architecture
- Select which historical data sets should be linked

After the data management office is established, this sub-group could serve as a liaison between the community and the data management office.

The US-SOLAS data management office, possibly in coordination with the OCB program data management enterprise, should be functioning prior to the start of any major US-SOLAS projects. Having this office in place will optimize the scientific return from US-SOLAS projects.

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Appendix

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