MIT Joint Program on the Science and Policy of Global Change

A Strategy for a Global Observing System for Verification of National Greenhouse Gas Emissions

R. Prinn, P. Heimbach, M. Rigby, S. Dutkiewicz, J.M. Melillo, J.M. Reilly, D.W. Kicklighter and C. Waugh

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This report is one of a series intended to communicate research results and improve public understanding of climate issues, thereby contributing to informed debate about the climate issue, the uncertainties, and the economic and social implications of policy alternatives. Titles in the Report Series to date are listed on the inside back cover.

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A Strategy for a Global Observing System for Verification of National Greenhouse Gas Emissions [#]

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Abstract

With the risks of climate change becoming increasingly evident, there is growing discussion regarding international treaties and national regulations to lower greenhouse gas (GHG) emissions. Enforcement of such agreements is likely to depend formally upon national and sectoral emission reporting procedures (sometimes referred to as "bottom-up" methods). However, for these procedures to be credible and effective, it is essential that these reports or claims be independently verified. In particular, any disagreements between these "bottom-up" emission estimates, and independent emission estimates inferred from global GHG measurements (so-called "top-down" methods) need to be resolved. Because emissions control legislation is national or regional in nature, not global, it is also essential that "top-down" emission estimates be determined at these same geographic scales. This report lays out a strategy for quantifying and reducing uncertainties in greenhouse gas emissions, based on a comprehensive synthesis of global observations of various types with models of the global cycles of carbon dioxide and other greenhouse gases that include both the natural and human influences on these cycles. The overall goal is to establish a global observing and estimation system that incorporates all relevant available knowledge (physical, biogeochemical, technological and economic) in order to verify greenhouse gas emissions, as a key component of any global GHG treaty.

Contents

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EXECUTIVE SUMMARY

For treaties or legislation to control greenhouse gas (GHG) emissions to be effective, and considering that enforcement is likely to be practical only by national emission reporting or "bottom-up" methods, it is essential that these reports or claims be independently verified. In particular, any disagreements between these bottom-up emission estimates and independent emission estimates inferred from global GHG measurements ("top-down" methods) need to be resolved. Because emissions control legislation is national or regional in nature, not global, it is also essential that "top-down" emission estimates be determined at these same geographic scales.

This report lays out a strategy for quantifying and reducing uncertainties in greenhouse gas emissions, based on a comprehensive synthesis of global observations of various types with a model of the global cycles of carbon dioxide and other greenhouse gases that includes the natural and human influences.

The goal is to establish a system that incorporates all available knowledge (physical, biogeochemical, and economic) to verify greenhouse gas emissions, as a key component of a global greenhouse gas treaty. The needed model consists of four sub-models:

(1) A model of the global transport and chemical processes affecting GHGs in the atmosphere;

(2) A model of the air-sea exchange of GHGs and the subsequent relevant transport, chemical, and biological processes affecting them in the ocean;

(3) A model of the exchange of GHGs with the land vegetation and soils and subsequent relevant biological and chemical processes in the land (terrestrial) system;

(4) A model that calculates emissions based on reliable national economic data regarding sectoral activities (agriculture, energy, production, transport) and trade among nations.

These sub-models each consist of numerical calculations, encapsulated in complex software or code. The overall global model requires that these sub-models be "coupled" to one another, so that the fate of GHGs (both natural and anthropogenic) is followed through the four systems, and fluxes or flows from one to the other are coordinated so that the full system is consistent, meaning that at any time the total budget of gases is fully accounted for. This fully-coupled system model we refer to as the "forward model".

The "forward model" would be a complex system that would produce estimates of GHG distributions in the terrestrial, ocean, atmosphere and human systems from some initial time (say the beginning of 1990, which is the reference year for the U.N. Framework Convention on Climate Change) forward to the present. This is referred to as the "forward model integration". Model results of, for example, global maps of CO_2 levels could be provided at any interval (*e.g.,* every hour, day or year).

However, there will be significant deviations between the forward model and real world "observations" of GHGs (and other components that influence the distribution of GHGs, for example human activity and the amount of carbon that temporally resides in land plants and the ocean). These deviations will be a result of several factors:

• uncertainties in the observations,

• uncertainties in the GHG emissions,

- uncertainties within the model components (the sub-models are not completely faithful representations of the real world and they also need to make assumptions about the "initial conditions" for the integration).

Fortunately, there are advanced methodologies that can significantly decrease the discrepancies between model results and the observations (and which still encapsulate knowledge of the observational uncertainties). This is true even if there is a suite of observations that are on very different spatial and time scales. The application of an "adjoint" model that follows the "forward model" through its integration can in retrospect provide quantitative information on how changes in model outputs are linked to the inputs, that is, it very efficiently calculates the sensitivities of model outputs to any model input. This "adjoint model" which is as complex as its "parent" forward model, is produced using computer software that systematically works through the forward model code (so called automatic differentiation tools).

The information that the adjoint model gives can be used in several ways:
- it can suggest the value that the model parameters should be for the forward model to produce GHG values that are in closer consistency with the real world observations;
- it can suggest how first-guess (or reported) GHG emissions should be corrected such as to obtain a better fit between observed and simulated GHG concentrations everywhere;
- it can suggest what the initial values of GHG concentrations need to be at the start of the integration (*e.g.,* January 1990, as in our example above) so that the GHG model values are most consistent with the observations.

In short, the adjoint model weighs all available ingredients (model, observations, and prior uncertainties) to provide quantitative information on how a very large set of uncertain variables (parameters, first-guess emissions, initial conditions) ought to be modified such as to produce optimal consistency among all ingredients. In this way the forward model can be "constrained" by the observations to produce an "optimal estimate" in terms of consistency between the model and the real world. Importantly, the adjustment of uncertain parameters is performed within their expected or prior error bounds, and the optimal estimate comes with posterior uncertainties that quantify the remaining uncertainties after all ingredients have been used.

Other estimation techniques are available (some of which are subsumed under the category of ensemble or Monte Carlo methods), but many of these suffer from the "curse of dimensionality"; that is they are not suitable for dealing with a very large set of uncertain variables such as encountered in the problem at hand. The adjoint method is among the most powerful methods to tackle the dimensionality problem. In the framework suggested here, each sub-model (atmosphere, ocean, terrestrial, and economics) would have to be adjoined. The fully-coupled system (all components linked together) would then be adjoined, so that sensitivity and error propagation among the components could be quantified and corrected.

We argue that an accurate estimation system can only be successful in a fully-coupled context that can account for the significant variability in background fluxes (both emissions and sinks) as a result of internal climate variability in the atmosphere, ocean, and land systems, and variability in biological activity on land and in the ocean. Comprehensive verification efforts such as the one proposed are looking to the relevant agencies (notably NASA, NOAA, and their international

counterparts) to ensure the sustained provision and improvement of optimal flow fields, suitable for accurate tracer transport purposes. A long-term vision would be the combined inversion of both the trace gas evolution and physical flow field used to advect them.

With this "fully-coupled and adjoined" estimation system we could address the critical questions: what are the errors in the national emission reports; how can we correct the reports in order to bring the forward model into optimal consistency with the observations of GHGs and other components of the coupled system that influence the GHG distributions; and, how large are the residual uncertainties in the emissions reports?

In this way the estimation system provides an extremely powerful tool to verify national greenhouse gas emissions. There are however many challenges in developing such a tool and producing such estimates:

(a) the uncertainties in, and scarcity of, the current observations of GHG distributions in the Earth system (land, ocean, atmosphere);

(b) the uncertainty, scarcity or lack of observations of components that have substantial influence on GHG distributions (*e.g.,* carbon stored in plants or in the deep ocean);

(c) the fidelity of our model components and our parameterization of key features (*e.g.,* transport of carbon from the surface ocean to the deep ocean);

(d) continued access to best-possible estimates of atmospheric and oceanic flow fields of ever increasing quality through sustained estimation efforts supported by the relevant agencies.

The Global Emissions Estimation System

The proposed research path involves merging the above fully-coupled and adjoined model with a rigorous application of advanced optimal estimation and control methods that are well known in engineering. The merger comprises several steps:

(1) All available observations (satellite and *in situ*) would be brought into consistency with the above fully-coupled model through a weighted least-squares optimization, based on the adjoint method. The coupled model is driven by best-possible estimates of the actual atmospheric and oceanic circulation fields provided by so-called reanalysis or state estimation procedures. These are not altered in the estimation procedure and are referred to as "passive" variables. "Control" variables, that are uncertain and adjusted as a part of the inversion process, include model parameters, initial conditions in GHG concentrations, as well as first-guess distributions of surface fluxes of greenhouse gases (including anthropogenic emissions from economic modeling and reported bottom-up emissions). Any variable (*e.g.,* atmospheric CO_2 levels) that can be affected by changes in any of the control variables is referred to as "active" and is generally observable.

(2) The adjusted control variables then provide information on the extent to which prior information is consistent with the observations and the known dynamics. Large adjustments in the surface fluxes point to inconsistencies between prior (or bottom-up) values and what is estimated from observation and model synthesis (posterior or top-down values);

(3) The second-derivative information obtained at the minimum of the least-squares misfit function provides information about output (posterior) uncertainties of the controls in the context of all the observations used. The calculation of such posterior uncertainties is a crucial step in the process as it provides error bounds on the adjusted surface fluxes;

(4) The inferred surface fluxes along with their error bounds are used as best estimates in an inversion of an economic model that links emissions reports and cross-sectoral economic activity (agriculture, energy, transportation) with surface fluxes. The result is an estimate of corrected economic parameters, and the correction of reported (bottom-up) emissions in particular, together with residual (posterior) error bounds.

The **Figure** below illustrates the coupled-model framework or system for estimation of GHG fluxes of the three major GHGs with both anthropogenic and natural influences on their global cycles (CO_2, CH_4, N_2O). Model names represent models available at MIT and are for illustration only. More simplified frameworks are applicable to purely anthropogenic greenhouse gases (chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), *etc*.). The availability of such a formal estimation system also provides a powerful quantitative basis for informing observing-system design. Specifically, in the design phase of the needed new global system, application of this coupled model to so-called "Observing System Simulation Experiments (OSSEs)" will be a critical contribution as discussed below. The success of the application phase of the system will furthermore depend on taking maximum advantage of all available observations of the diverse relevant variables of the various components, and accurate knowledge of their uncertainties. Design studies can address questions such as: which existing or proposed observations contribute most to constraining greenhouse gas emissions?; what does an optimal observing system that minimizes uncertainties in estimated emissions look like (*i.e.* which variables to measure, where to measure them and at what resolutions, precisions and accuracies)?; and, which new sensors would best serve the targeted purposes?
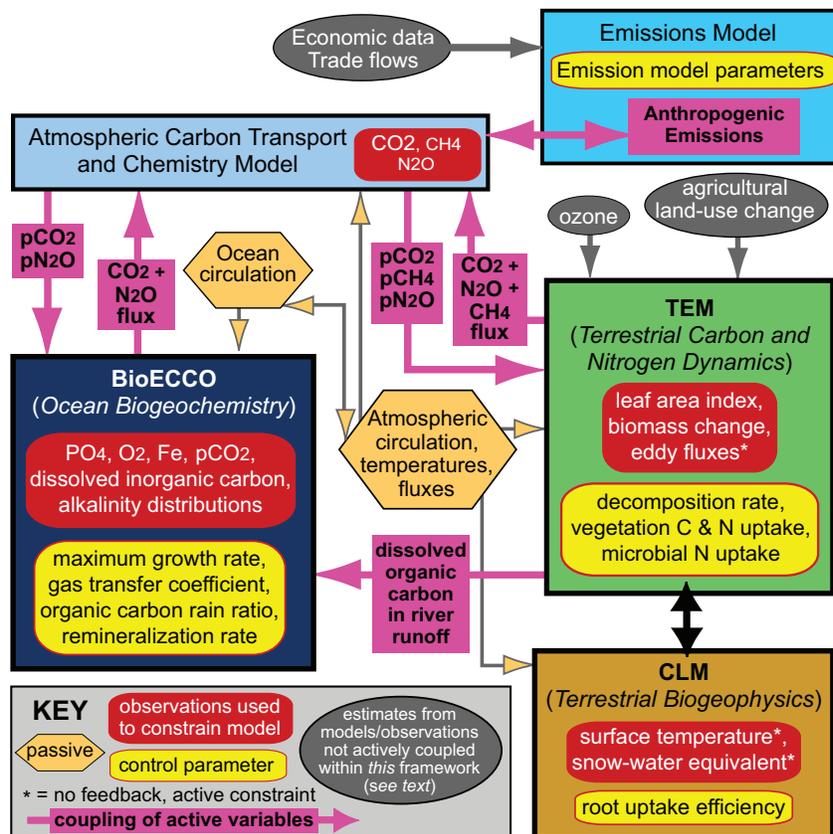
No framework currently exists that attempts to account for all the tasks described above. Yet, various reports, including the recent study by the National Research Council (NRC) on "*Verifying Greenhouse Gas Emissions: Methods to Support International Climate Agreements*" make strong calls for the need of such a system. Conceptually, the system we propose is not unlike those used in operational numerical weather prediction, although our emphasis is on quantifying and reducing uncertainties, rather than prediction. While there are substantial technical challenges to be overcome, studies in more limited settings (atmosphere-only, ocean-only, land-only inversions) are showing promising results. Given the societal and economic implications, tackling the rigorous coupled end-to-end problem is a worthwhile and timely endeavor.

The Global Observing System: Present and Future

The current Global Observing System is measuring various aspects of the evolving composition of Earth's atmosphere, oceans and land ecosystems and is providing the fundamental understanding needed to construct accurate process models. These measurements include:

- Surface-based *in situ* measurements of all major GHGs at high-frequency stations augmented by flask sampling;
- Remote sensing of mole fractions of atmospheric CO_2, CH_4 and N_2O, and other GHGs both from the surface and from space;
- Vertical profiles of GHGs using aircraft and balloons;
- Land GHG flux measurements, using eddy covariance and smoke-stack monitoring;
- *In situ* and satellite observations of land vegetation, soil moisture and other relevant biogeochemical and hydrologic variables for land GHG flux determination;
- Oceanic measurements of partial pressures of CO_2, N_2O (pCO_2, pN_2O in the Figure above) and other GHGs for flux determination;
- *In situ* and satellite measurements of biologically and biogeochemically important oceanic tracers, and relevant material fluxes;
- Economic data on production and trade flows associated with industrial and agricultural activities that generate GHGs.

The combination of all of these complementary data with state-of-the-art global models of atmospheric chemistry and circulation, land ecosystems, oceanic circulation and biogeochemistry models is already providing a significant advance in our understanding of the global sources, chemistry, transport and sinks of the trace substances determining atmospheric composition and air quality, and the radiative forcing of climate change.

However, while it is essential that this system continue to operate, in order to address the challenge of accurate GHG emissions verification it will need significant improvements:

(a) For the current atmospheric GHG monitoring systems, future treaty verification will require significant improvements in the precision and accuracy of the remote sensing measurements, new approaches for inverting satellite radiance measurements over partially clouded regions, and order of magnitude increases in the spatial coverage of the high-frequency *in situ* measurements.

(b) For the current oceanic monitoring systems, future treaty verification will require continued and consistent remote sensing of ocean color properties, significant increases in the spatial coverage of the *in situ* measurements of carbon, pCO_2 (partial pressure of CO_2, which is the typical measure of CO_2 content in the ocean, whereas mole fractions tend to be used in the atmosphere) and other important biogeochemical properties, both at the surface and deeper in the water column of the oceans. New networks (perhaps vertical profiling floats) will need to be established as ship-board measurements alone will not provide the needed spatial and temporal coverage.

(c) For the current land monitoring systems, future treaty verification will require: significant improvements in remotely-sensed measurements of changes in vegetation cover, above-ground plant biomass and soil moisture; tracking of major ecosystem disturbances (*e.g.,* insect outbreaks, fire, wind damage); increases in the number of *in situ* measurements of CO_2, N_2O and CH_4 fluxes along climatic gradients within major vegetation types (biomes) and for various management regimes (*e.g.,* fertilization, irrigation, tillage) in agro-ecosystems; and increases in the number of *in situ* measurements of nitrogen deposition, which can affect net fluxes of CO_2, N_2O and CH_4.

For the future Global Observing System, new measurement technologies are beginning to emerge that have the potential to dramatically reduce the uncertainty of GHG emissions estimates. Also, further advances in the knowledge of source and sink processes and oceanic and atmospheric circulations, and the resultant improvements in the accuracy of process models will lower uncertainties in the significant background fluxes of GHGs, which are due to intrinsic climate variability in the atmosphere, ocean, and land. Finally, the inclusion of reliable economic, production and trade flow data along with the GHG measurement data could also improve emission estimates. Some examples of these potential breakthroughs are briefly outlined below.

(i) High-frequency carbon dioxide, methane and nitrous oxide isotopologue observations

For GHGs that have natural, anthropogenic, industrial and biogenic emissions, such as CO_2, CH_4 and N_2O, measurements of atmospheric abundances alone are often inadequate to differentiate precisely among these different sources. High frequency *in situ* measurements of not just the total mole fractions of these gases, but also their isotopic compositions (^{12}C, ^{13}C, ^{14}C, ^{14}N, ^{15}N, ^{16}O, ^{18}O, H, D) are a new frontier in global monitoring and hold the promise of revolutionizing understanding of the natural cycles of these gases and verifying claims of emission reductions. High-frequency *in situ* isotopic measurements are now becoming feasible using optical (laser) detection. Recent improvements in mid-infrared quantum cascade lasers (QCL) enable continuous wave (CW) operation near room temperature with higher power, narrower line-widths, and higher spectral mode purity than previously possible. For CH_4 and N_2O, automated cryogenic pre-concentration will be necessary to measure their isotopic compositions with the precision necessary to differentiate their various surface fluxes (biogenic, anthropogenic) and photochemical sinks.

(ii) Space-Based Differential Absorption Lidar (DIAL)

Current space-based GHG observations rely on spectral measurements of backscattered or reflected sunlight (particularly in the near-infrared). This limits these observations to the daytime and at low-latitude, and therefore could induce a bias in the derived emissions. Plans are

underway for active systems in which space-based instruments detect CO_2 concentrations using lidar. Such potential missions are NASA's Ascends and ESA's A-SCOPE. The use of lidar will allow measurements throughout the day at all latitudes. Furthermore, a measurement of the atmospheric path is obtained, providing information about scattering by aerosols.

(iii) Enhanced coupled Forward Models and their Adjoints

In this report we recommend a modeling framework that will:

• Contain a detailed economics model that will provide initial estimates of release rates of anthropogenic GHGs to the atmosphere, and will help attribute emissions to the nations responsible through use of trade-flow information on fuels, agricultural products and energy-intensive goods;

• Simulate atmospheric and oceanic trace gas transport and chemistry using the highest resolution meteorological and oceanic analyzed flow fields available;

• Simulate terrestrial sources and sinks of CO_2, CH_4 and N_2O using a natural and managed ecosystem model, constrained offline by meteorological data and hydrological measurements;

• Simulate natural oceanic sources and sinks of CO_2, CH_4 and N_2O using a physical-biogeochemical-ecosystem model;

• Be fully coupled between each model component such that global budgets of all GHGs are fully accounted for at all times and change strictly, in addition to emissions, according to known physical and biogeochemical conservation laws;

• Be fully adjoined in order to quantify the sensitivity of all of the described measurements throughout the model environment, to changes in each uncertain model parameter. This adjoined system will allow the incorporation of the current measurements, and desired future observations, to improve the accuracy of estimates of both emissions and uncertain model parameters. The simultaneous determination of uncertain anthropogenic and natural model parameters is crucial, since this will allow covariance information between various model components and residual uncertainties in emissions estimates to be quantified.

(iv) Incorporation of Reliable Economic Data

The accuracy of emission estimates is expected to be significantly improved by inclusion of a reliable data-based economics model that will provide initial estimates of release rates of anthropogenic GHGs to the atmosphere, and will help attribute emissions to the nations responsible through use of trade-flow information on fuels, agricultural products and energy-intensive goods. The most efficient way to incorporate economic data is to develop an accounting framework that in the first step takes advantage of available data. The required model could follow the IPCC three-tier methodology with the tier level being determined based on data availability, the level of detail needed to adequately constrain emissions estimates, and the degrees of freedom in the inverse approach. Within the model, the trade of emission-containing goods between countries will be accounted for using trade data so that measured emissions from *in situ* stations and satellite networks will match the emissions of country consumption, not production. Although the methodology is laid out, additional work will need to be done to construct a system for mapping the economic data to a global grid.

1. INTRODUCTION

1.1 The Scientific, Technological and Policy Challenge

The uncertainties of current regional emission estimates either by top-down or bottom-up approaches are commonly greater than 10-20% – sometimes much greater – and thus are grossly inadequate for verifying claims of emission reductions by nations. Looking to the future, it is clear that the spatial density of precise high-frequency atmospheric trace gas measurements, whether using *in situ* or remotely sensed methods, needs to be increased by an order of magnitude or more. Equally important, the knowledge (theory, observations) embedded in models of industrial and ecosystem fluxes should be incorporated into the model and estimation system to enable estimation of uncertain parameters in these flux models as opposed to simply the fluxes themselves. In essence, this approach combines the best features of the bottom-up and top-down methods in flux estimation.

1.2 Previous Work

Interest in this area has increased substantially in the past two years spurred by a number of meetings and reports. Some ones of significance to our study are discussed briefly below.

(a) **DOE/NASA/NOAA Greenhouse Gas Information System Workshop, Sandia National Lab., May 2009:** This workshop was the first significant meeting devoted specifically to assessing the potential requirements and completing a gap analysis for an operational Global Greenhouse Gas Monitoring and Information System. While international cooperation was an important consideration, this workshop was focused on U.S. national capabilities. The goal was to identify key requirements that need to be addressed in developing a scientifically and operationally robust system for verifying compliance with potential climate agreements. The workshop was conducted as a series of plenary and breakout working sessions by topic. The desired outcome of the meeting was to stimulate a community consensus regarding the specific requirements for a scientifically and operationally robust global greenhouse gas information system, an integrated assessment of the gaps between those requirements and current capabilities, and options for closing the gaps.

(b) **8th Quadrennial International Carbon Dioxide Conference (ICDC8), Jena, Germany, September 2009:** In what has become an authoritative scientific platform on carbon dioxide, the conference in Jena highlighted the multi-disciplinary nature of the carbon cycle problem, from basic science to operational monitoring and economic mitigation approaches. Crucial questions addressed at the conference are summarized by Heimann (2010), and a collection of latest findings was published in a special issue of *Tellus B*, Vol. 62(5), November 2010.

(c) **Royal Society, London meeting on "Greenhouse Gases in the Earth System", February 2010:** This meeting discussed the use of long-term monitoring to understand greenhouse gases in the Earth system. The papers presented showed overall that new scientific advances promise regional audit of emissions, assessment of uptakes, and better understanding of controlling and feedback processes. The participants assessed these issues that are shaping the agenda for the next 20 years. This meeting was held as a part of 350th Anniversary of the Society. The papers will be published in a special issue of the *Philosophical Transactions of the Royal Society A*.

(d) **NRC 2010 Report, "Verifying Greenhouse Gas Emissions: Methods to Support International Climate Agreements":** This report by the National Research Council (Pacala *et al.*, 2010) reviewed national inventories of greenhouse gas emissions, measuring fluxes from land-use sources and sinks, emissions estimated from atmospheric and oceanic measurements, and provided a set of recommendations for future research. Very relevant to our study here was their recommendation for CO_2: "Develop a state-of-the-art carbon data assimilation system that is coupled and/or synergistic with meteorological, land, and oceanographic data assimilation systems for the United States. This would require new approaches for coupling circulation and biogeochemical models and for deriving biogeochemical properties (and hence surface fluxes) from the observations. It would also require enhanced collaboration among federal agencies with carbon observations, especially between NASA and NOAA, so that the best estimates and the uncertainties in the meteorology become integral components of emission estimation from a replacement OCO".

(e) **NIST Greenhouse Gas Emissions Quantification and Verification Strategies Workshop, May, 2010:** The purpose of this 2010 workshop was to better understand the constraints and uncertainties incurrent "bottom-up" emissions quantification methods, and then to define a path that will reduce these uncertainties. It is one of a series sponsored by the National Institute of Standards and Technology (NIST) to identify the key technology and measurement areas related to issues of national and global importance. Emissions of primary interest will be those defined by regulation and legislation: carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, and fluorinated gases. NIST's interest was stimulated by the Energy Policy Act of 2005, Title XVI, Sec. 1610 (H), that includes a mandate for the Department of Energy to collaborate with NIST to develop standards and best practices for calculating, monitoring, and analyzing GHG intensity.

(f) **NASA Carbon Monitoring Scoping Study Workshop, Boulder, July, 2010:** The primary objective of this workshop was to provide background, context, and input for NASA's Carbon Monitoring System strategic development, both in the near and long term. A particular focus was to report on information that will integrate the agency's efforts related to carbon decision support. This study was intentionally focused on potential roles for NASA in supporting GHG/carbon monitoring efforts by the U.S. and/or international community. Topics covered included GHG emissions from area sources and urban "domes", carbon stocks and stock changes, ocean carbon fluxes, observations, modeling and data assimilation, and decision-support issues. A Final Report on the workshop is available online (NASA, 2010).

(g) This general subject has also been a focus of research over the past decades resulting for example in a number of books (*e.g.,* Kasibhatla *et al.,* 2000; Enting, 2006). Papers that have appeared in the scientific literature on this subject so far have focused on quantifying the benefits of various measurement systems for flux estimation in single aspects of the Earth system (*e.g.,* carbon dioxide flux estimates from satellite observations; Kaminski *et al.,* 2010; Chevallier *et al.,* 2007, 2009).

1.3 Goals and Scope of This Report

This report outlines our current ability to estimate global greenhouse gas (GHG) emissions and examines how we might move towards an Earth observation system that can accurately verify emissions on national and regional scales, as will likely be required by future climate treaties.

The greenhouse gases that will be the major focus of this report are broadly defined by the gases regulated under the Kyoto protocol:

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide (N_2O)
- Chlorofluorocarbons (CFCs)
- Hydrofluorocarbons (HFCs)
- Perfluorocarbons (PFCs)
- Sulfur hexafluoride (SF_6)

Although CO_2 will be the major focus of future verification systems since it is the major contributor to anthropogenic long-lived greenhouse gas (LLGHG) radiative forcing, it is highly important to also consider the non-CO_2 GHGs since, they collectively contribute one third of the LLGHG radiative forcing (Forster *et al.,* 2007) and many have extremely large global warming potentials (GWP), making them likely first targets of emissions reduction strategies. It should be noted that additional compounds that strongly absorb infrared radiation might also fall under future climate treaties (*e.g.,* nitrogen trifluoride, NF_3).

At the center of this discussion will be an outline for the development of the needed comprehensive coupled atmosphere-ocean-biosphere-economics modeling and optimal estimation framework and its application to defining the structure and observational assets of the desired emissions verification system. Specific goals for this subsequent development will be:

- To create a modeling and estimation framework that is capable of performing the most accurate emissions verification and Earth system model parameter optimization possible using diverse types of existing observations, and that will be in place to refine these estimates as new measurements become available.

- To perform extensive Observing System Simulation Experiments (OSSEs) for greenhouse gas emissions verification and GHG cycle dynamics. These OSSEs will rigorously test the ability of the current observing systems to resolve surface fluxes and emissions model parameters. More important, they will also allow us to explore where gaps exist in our current measurement capabilities, and quantitatively determine the specifications for future observing systems.

In this report we propose a modeling and optimal estimation framework that will be able to fulfill these aims. The proposed system will:

- Simulate atmospheric and oceanic trace gas transport and chemistry using the highest resolution and best-possible meteorological and oceanic physical flow fields available from the existing major reanalysis and estimation projects.

- Contain a detailed economics model that provides first-guess estimates of release rates of anthropogenic GHGs to the atmosphere, and helps attribute emissions to the nations responsible through use of trade-flow information on fuels, agricultural products and energy-intensive goods.

- Simulate terrestrial sources and sinks of CO_2, CH_4 and N_2O using a natural and managed ecosystem model, constrained offline by meteorological data and hydrological measurements.

- Simulate natural oceanic sources and sinks of CO_2, CH_4 and N_2O using a physical-biogeochemical-ecosystem model.

- Be fully coupled between each model component such that global budgets of all GHGs are fully accounted for at all times and change strictly, in addition to emissions, according to known physical and biogeochemical conservation laws.

- Be fully adjoined so that extremely large quantities of data can be used to constrain surfaces fluxes and model parameters using a variational assimilation technique, and provide residual (posterior) error bounds.

To frame this discussion, we will outline the current state-of-the-art models that could be used in such a coupled framework (Section 2). We will then go on to discuss the current observations relevant to trace gas emissions verification (Section 3). A key feature of the proposed collection of models is that the system should be fully adjoined. This will allow us to quantify the sensitivity of all of the described measurements throughout the model environment, to changes in each model parameter. Ultimately this adjoint system will allow the incorporation of the measurements described above, and future observations, to improve uncertain parameters. The theoretical framework for such a coupled adjoint-based optimal estimation system is outlined in Section 4.

The initial step after the creation of the framework will be to perform a series of OSSEs where emission outputs from a simulation will be used as "truth", and "pseudo-datasets" will be constructed using "measureable" outputs from the model (*e.g.,* atmospheric concentrations). Realistic pseudo-data are created by adding random noise to the simulated measurements, the magnitude of which can informed by specifications of existing and future observations. These experiments will determine the level of model parameter uncertainty reduction (compared to prior estimates) that can be obtained by existing observations. They will then allow us to quantify the additional error reduction that may be achievable by future monitoring systems. These OSSEs will inform observation system design, by highlighting areas of the world which require increased measurement coverage, by identifying new variables that should be measured, and by determining precisions that are required in order for maximum error reduction to be achieved using the fewest additional observations. Future directions and potential OSSEs are discussed in Section 5.

2. FORWARD MODEL FRAMEWORK AND COMPONENTS

In reviewing the state of knowledge in Section 1, a compelling case has been made for the strongly coupled nature of the carbon cycle problem, and the significance of background fluxes of CO_2 within and across the components due to natural fluctuations in the climate system, such as ENSO or volcanic eruptions. Section 2 describes in detail the component models used to simulate the coupled carbon cycle. Corresponding observations available to constrain each of these components will be described in Section 3.

2.1 Ocean circulation and biogeochemistry

Ocean biogeochemical models are designed to capture the cycling of bio- and geochemically important elements (*e.g.,* nitrogen, phosphorus, carbon) within the surface and deep waters of the global oceans and their fluxes to and from the atmosphere (although recent developments are underway to also include riverine fluxes to the ocean, *e.g.,* Manizza *et al.,* 2009). These models typically capture the transformation of elements between inorganic and organic compounds as well as their repositioning within the oceans by ocean currents and mixing. It is only over the last two decades that such global three-dimensional (3-D) models have become feasible due both to the computational cost and to prior lack of knowledge on how to parameterize the processes involved. The ocean carbon modeling intercomparison project (OCMIP) produced some of the first comprehensive studies of ocean biogeochemical cycles, and many of the chemical protocols developed in that project are employed in most current, more sophisticated models. One of the findings of OCMIP was that the integrity of the physical environment was crucial to obtain reasonable biogeochemical fluxes (Doney *et al.,* 2004).

In this section we review some of the key features needed to capture the cycling of key greenhouse gases in the oceans. For the purposes of the coupled Earth system model framework described in this report, the ocean biogeochemical model needs to provide the global patterns and timings of the flux of greenhouse gases to and from the ocean surface. This pattern requires knowledge of the redistribution of that gas by the physical circulation and mixing within the ocean, and through chemical and biological interactions within the water column. First we review the needs of the physical environment and the recent developments of ocean state estimates (sometimes somewhat inadequately referred to as "reanalysis" products) that we believe are essential. We then discuss how to parameterize the fluxes of gases between the ocean and the atmosphere. We provide a rationale for the biogeochemical parameterizations we believe are important for capturing the cycling of carbon (and therefore CO_2) in the ocean, and highlight a few of the many models that are available.

2.1.1 Ocean circulation

Knowledge of the physical state of the ocean (temperature, salinity, flow field) and its evolution in time through advection and diffusion is a crucial ingredient to modeling biogeochemical cycles in the ocean. Oceanic variability on seasonal to inter-annual to (multi-) decadal time scales and associated oceanic teleconnections (*e.g.,* Liu and Alexander, 2007) strongly influence the air-sea fluxes of trace gases and are thus responsible for a significant part

of the background tracer concentration variability in the atmosphere. Examples are the El Niño/Southern Oscillation (ENSO), the North Atlantic Oscillation (NAO), or the Atlantic Meridional Overturning Circulation (AMOC).

An optimal way to provide a complete time-evolving state is through synthesis of all available observations (satellite and *in situ*) with the best-possible physics and dynamics as encapsulated in a general circulation model. The result is a product that optimally fits all observations within prior errors, that is consistent with the dynamics and physics that will drive tracer simulations, and that fulfills known physical conservation laws at any moment in time. Several groups have produced such state estimates for the global ocean over the past few decades. A compilation of these efforts is summarized in the Community Whitepaper for OceanObs'09 (Lee *et al.,* 2009). An important distinction between available products is in the estimation (or data assimilation) scheme used in the inversion. Research indicates that the requirement of dynamical consistency over the entire estimation period considered seriously limits the number of suitable estimation products for driving biogeochemical models (*e.g.,* McKinley *et al.*, 2004). Artificial sources or sinks that are incurred at analysis times in sequential estimation (or filter-based) schemes (*e.g.,* optimal interpolation or Kalman filtering) prohibit faithful representation of tracer advection and diffusion processes over time scales relevant to the carbon cycle modeling.

One of the few products that is fully variational (or smoother-based) in that it fulfills the known conservation laws exactly is the one produced by the "Estimating the Circulation and Climate of the Ocean" (ECCO) consortium which has been developed in part to support the Global Ocean Data Assimilation Experiment (GODAE). The so-called ECCO-GODAE model is a 1° horizontal resolution, 23-layer configuration with a KPP mixed-layer (Large *et al.*, 1994), Gent and McWilliams (1990) eddy mixing scheme and dynamic sea-ice. ECCO is applying a technique known as the adjoint or Lagrange multiplier method (similar, but in important ways different to 4DVar in meteorology) to determine the global, time-dependent ocean circulation. It uses the MIT ocean general circulation model (Marshall *et al.*, 1997a,b), a state-of-the-art general circulation model, as dynamical interpolator, and almost the entirety of the oceanic observations available from 1992 to present (Stammer *et al.*, 2002; Wunsch and Heimbach, 2006, 2007). The results (http://www.ecco-group.org) involve about 410 million data constraints, each of which is weighted by an estimate of the observational error. The backbone of the data constraints is formed by the quasi-global satellite altimetric data, the mean dynamic topography derived from a satellite gravity-derived geoid, the *in situ* observations collected during WOCE, and the recent global Argo profiling program. The NCEP/NCAR reanalysis serves as atmospheric forcing (Kalnay *et al.*, 1997), and is modified by the fitting procedure. The adjoint model used in the gradient-based optimization procedure has been derived using automatic/ algorithmic differentiation (AD; see Giering and Kaminksi, 1998; Marotzke *et al.*, 1999; Heimbach *et al.*, 2005; Heimbach, 2008) permitting the use of constrained least-squares. The ECCO-GODAE results are believed to be "best" estimates of the ocean circulation for 1992-2008. The same ocean model and estimation procedures have been used in an offline mode to study transient tracers (tritium, CFCs, *etc*.; Li and Wunsch, 2003, 2004; Khatiwala, 2007),

simple biogeochemical model to look at CO_2 and O_2 fluxes (Verdy *et al.,* 2007) and for a more sophisticated ecosystem model (Follows *et al.,* 2007; Dutkiewicz *et al.,* 2009).

The use of the state estimates in the context of a global carbon cycle estimation system will be in so-called "passive mode", in the same way as atmospheric flow fields taken from reanalysis products will be used to drive atmospheric transport models. What this means is that neither of these physical states will be modified in trying to match observed and simulated trace gas concentrations, and they are not an active part of the underlying control problem (see Section 4). It is believed that the determination of optimal flow fields for the atmosphere and ocean is, for the time being, best pursued separately from the determination of time-varying passive tracer concentrations such as pursued here. We emphasize, however, that optimal estimation of such flow fields and their provision through sustained efforts are essential. The passive nature of the physical states is reflected in Figure 2.5.1.

2.1.2 Ocean biogeochemistry

For the purposes of the coupled model framework described in this report, the ocean biogeochemical model needs to provide the global patterns and timings of the flux of greenhouse gases to and from the ocean surface. In this section we review the parameterization of fluxes of greenhouse gases between air and ocean, and between land and ocean. We also expand on the elements needed to capture the cycling of carbon dioxide through the system.

The standard air-sea gas transfer formulation for a gas A is:

$$F = k_w \rho([A] - [A]_{sat}) \tag{2.1.1}$$

where F is upward flux of A, k_w is the gas transfer coefficient specific for gas A, ρ is the density of the surface water, $[A]$ is ocean surface concentration of gas A and $[A]_{sat}$ is the concentration of the gas if the gas was in equilibrium with atmosphere (the saturated concentration). The gas transfer coefficient k_w is a function of sea surface temperature and wind speed, though the exact formulation remains an uncertainty in models. k_w is usually expressed as a power function of the wind speed, but the value of the exponent has been estimated to be anywhere from 1 to 3 (Liss and Merlivat, 1986; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Nightingale *et al*., 2000; Ho *et al*., 2006; Wanninkof *et al*., 2004), and the estimates of the scaling factor for carbon dioxide of the power function (usually derived from ocean bomb ^{14}C inventories) ranges from 0.26 to 0.39 (Wanninkhof, 1992; Sweeney *et al*., 2007). This and other coefficients are however in general specific for the individual gases. Usually not parameterized is the impact of bubble injection, which may be important (see for instance Stanley *et al*., 2010). Surface seawater density is calculated from the sea surface temperature and salinity. For gases that do not chemically interact in seawater and are not consumed or produced during biological activity (*e.g.,* CFC's) $[A]$ is straightforward, and is set by the advection and diffusion of the gas within the ocean. However for more complex gases (*e.g.,* CO_2) finding $[A]$ is more complicated (see below). $[A]_{sat}$ is a function of the atmospheric concentration of A, atmospheric pressure, ocean surface temperature and salinity and the coefficients of the function are specific for the type of gas.

2.1.2.1 The Carbon Cycle

The ocean stores more than 50 times the inorganic carbon as the atmosphere and at least 15% of the atmospheric inventory of carbon passed through the ocean every year: there is a dynamic and crucial interaction between the two systems that will be essential to parameterize well for any attempt to follow the pathway of emissions. The oceans take up about 20 to 35% of anthropogenic CO_2 emissions, though the capacity of the ocean to continue this uptake is changing (Khatiwala *et al*., 2009; LeQuere *et al*., 2009). The growth of atmospheric CO_2 varies considerably more than the estimated anthropogenic emissions (Conway *et al*., 1994; Peylin *et al*., 2005) suggesting that there is large variability in terrestrial and ocean CO_2 uptake. While the atmospheric carbon inventory is mostly in the form of CO_2 gas, in the ocean dissolved inorganic carbon (DIC) is composed of $[CO_2]$, $[HCO_3]$ and $[CO_3]$. The amount of $[CO_2]$ at any place and time is a function of the total DIC, but also temperature, salinity, alkalinity, boron, silicate and phosphate concentrations. Since the individual patterns of these variables are quite different and can vary significantly over the seasons, the pattern of $[CO_2]$ (or pCO_2) varies over a range of about 200 ppmv spatially and temporally (see **Figure 2.1.1**). Since it is assumed that the three chemical forms of inorganic carbon are influenced by physical and biological redistribution in the same
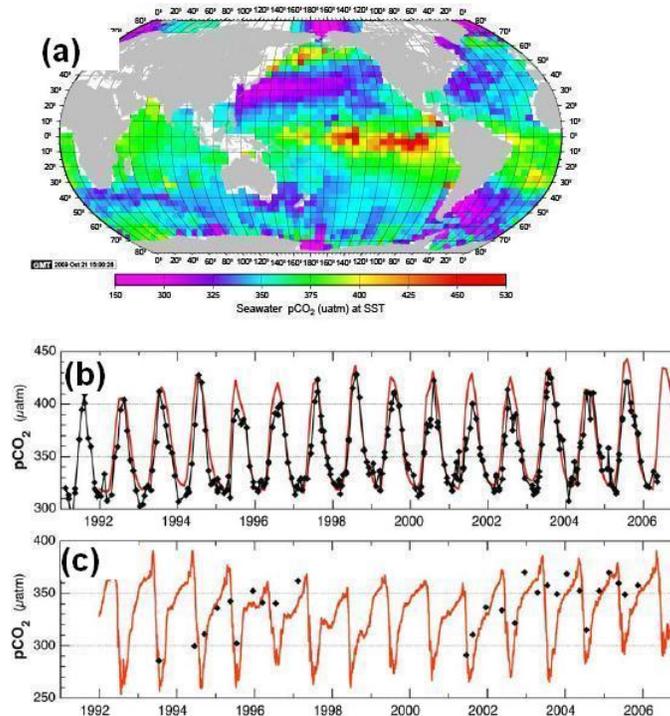

Figure 2.1.1. Spatial and temporal variability in ocean surface pCO_2. (a) Global map interpolated from ship board observations for January 2000 (from Takahashi *et al.,*2009); (b) Timeseries at location of Bermuda Atlantic Timeseries Station (BATS), black from *in situ* observations (Bates, 2007), red from biogeochemical model of Ullman *et al.* (2009); (c) Timeseries from northwest Atlantic ocean, black from *in situ* observations (Corbiere *et al.,*2007), red from biogeochemical model of Ullman *et al.* (2009). pCO_2 varies widely as a function of (mainly) temperature and dissolved inorganic carbon (DIC) concentrations in the water: warmer water has higher pCO_2 and upwelling water rich in DIC has higher DIC. Where pCO_2 is higher than the air concentration there will be outgassing of CO_2 from the ocean to the atmosphere.

way, ocean biogeochemical models usually consider the fate of total dissolved inorganic carbon and determine the local pCO_2 only for the purpose of the air-sea flux calculations ([*A*] in Eq. 2.1.1).

The seasonal cycle of pCO_2 seen in Figure 2.1.1b,c is to a large part determined by the seasonal cycle of sea surface temperature, upwelling of carbon rich waters and uptake of carbon (DIC) due to photosynthesis. It is essential to capture all these processes in a model of the ocean carbon cycle. Thus a biogeochemical model which hopes to accurately capture the pattern global air-sea fluxes of carbon requires a parameterization of the biological uptake of inorganic carbon during photosynthesis and the sinking of the organic matter to depths where it undergoes remineralization back to an inorganic form. This "biological" pump stores as much as 200 ppmv of carbon in the deep ocean (**Figure 2.1.2**). The combination of temperature and DIC patterns drive patterns of pCO_2 (Figure 2.1.1a) that are regionally greater than or less than the atmospheric saturated value. Following from Equation 2.1.1, this leads to some regions where there is a flux of carbon dioxide into the ocean and others where carbon dioxide comes out of the ocean (**Figure 2.1.3**).

Relatively simple formulations of the biological processes, which do not explicitly represent the organisms (phytoplankton) that photosynthesize, have been widely used (*e.g.,* OCMIP (Matsumoto *et al.*, 2004; Orr *et al.*, 2001; Dutkiewicz *et al.*, 2006; Galbraith *et al.*, 2010) and have been successful in capturing the large temporal (annual) and spatial scale patterns of air-sea fluxes of carbon dioxide. The 3-D ocean component of the MIT Integrated Global Systems Model (IGSM2.3) uses such a formulation (Dutkiewicz *et al.*, 2005; Table 2.1.1, Figure 2.1.2). However the timing of pCO_2 cycle (Figure 2.1.1b,c) in these models can never be accurate as the biological draw-down is over-simplified and does not capture, for instance, the intense spring blooms of phytoplankton in the higher latitudes. A framework to verify CO_2 emissions will need an explicit
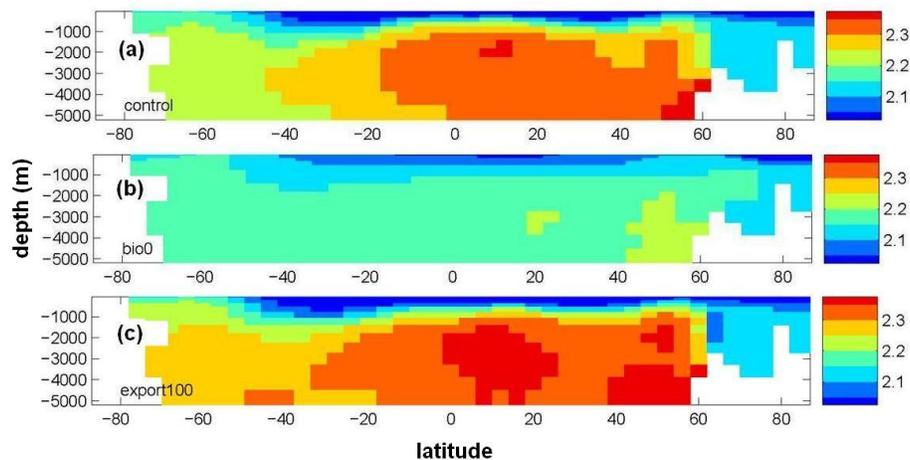

Figure 2.1.2. Impact of biological pump on ocean inventory of carbon. Latitudinal averaged dissolved inorganic carbon (DIC) with depth of the oceans from simulations with the MIT IGSM2.3 (Dutkiewicz *et al.*, 2005). (a) Current-day ocean with parameterization of biological pump adapted to match observations of DIC (GLODAP, Key *et al.*, 2004); (b) Simulation where ocean biology has been removed; (c) Simulation where all phytoplankton are assumed to be large species which export all of their organic carbon to depth. The no-biology ocean (b) has released almost 200 ppmv to the atmosphere and the surface patterns of carbon are set by the temperature-driven exchange of carbon dioxide ("solubility pump") only. In the simulation with higher export of organic carbon (c) 30 ppmv more carbon is removed from the atmosphere and stored it in the deep ocean than in (a).
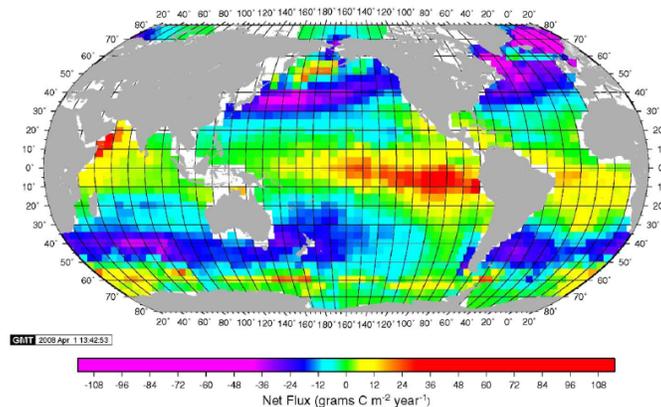
Figure 2.1.3. Spatial patterns of air-sea flux of carbon dioxide as estimated from the data compilation of Takahashi *et al*., 2009. Positive values indicate outgassing of carbon from ocean to atmosphere, while negative indicates the ocean is taking CO_2 out of the atmosphere. In general where pCO_2 (Figure 2.1.1a) is higher than the air concentration there will be flux of CO_2 from the ocean to the atmosphere. The strength of this flux will be determined by the gas transfer coefficient k_w (see Equation 2.1.1).

ocean ecosystem model, including: uptake of carbon by phytoplankton during photosynthesis, passage of carbon to higher trophic levels (*e.g.,* zooplankton) by grazing, formation of organic detrital matter, gravitational sinking of detrital matter to the deep ocean and subsequent degradation of the organic matter through bacterial processes to an inorganic form (DIC). The amount of carbon and the depth to which it is exported is strongly determined by the type of phytoplankton in the sunlight upper ocean. For instance blooms of larger phytoplankton such as diatoms and coccolithophers lead to significantly more export of organic matter to depth (see Figure 2.1.2c) than small phytoplankton that are more tightly linked in a microbial loop where organic matter is recycled in the surface oceans. Additionally, calcium carbonate forming phytoplankton (*e.g.,* coccolithophers) alter the alkalinity of the oceans, which in turn alters the ability of the ocean to take up CO_2. At a minimum an ocean biogeochemical/ecosystem model that will capture the seasonal and complex spatial patterns of CO_2 fluxes (Figure 2.1.3) will need to explicitly resolve several "functional" types of phytoplankton (see Table 2.1.1). Detailed discussions on these and other biogeochemically important plankton functional types can be found in Hood *et al*. (2007) and Le Quere *et al*. (2007). Biogeochemical models must also resolve the cycling of several macro and micro-nutrients which limit the growth of phytoplankton in the world's oceans in order to capture the required patterns of photosynthesis and export of organic carbon to the deep ocean. At a minimum these should include nitrate, silicic acid and iron.

There are many biogeochemical models currently available, most of which capture some level of the complexity of the ocean ecosystems. A few representative models and their features are shown in **Table 2.1.1**. Such models have been validated against existing *in situ* and satellite derived observations of the ocean (see Section 3.1), and their ability to capture interannual variability (such as ENSO) in surface chlorophyll and phytoplankton assemblages (see *e.g.,* Wang *et al*., 2005) is an essential feature of such validation. However as yet the impact of variability on CO_2 fluxes in the ocean remains an open question that models are attempting to address (*e.g.,* McKinley *et al*., 2004; Ullman *et al*., 2009; Bennington *et al*., 2009).

19

Table 2.1.1. Features of some existing ocean biogeochemical models. This is not an exhaustive list and additional well-established models such as PISCES (Aumont *et al*., 2003), TOPAZ (Dunne *et al*., 2005), NEMURO (Kishi *et al*., 2001) also include many of the features listed here.

	MIT-simple DIC[a]	MIT-ecosystem[b]	NOBM[c]	PlankTOM[d]	BEC[e]
nutrient cycling	C,P,Fe,O_2	C,N,P,Si, Fe, O_2	C,N,Si, Fe	C,N,P,Si, Fe	C,N,P,Si, Fe, O_2
alkalinity	yes	yes	no	no	yes
Phyto-plankton functional types	none	Diatom, large and small eukaryotes, *Synecoccous*, *Prochloroccus*, Coccolithopheris, *Trichodesmium*, Unicellular diazotrophs	Diatom, Coccolithophes, Cyanbacteria, Chlorophytes	Diatoms, Coccolithophers, Pico-autotrophs, Diazotrophs, DMS-producers, mixed	Diatom, Coccolithophers, Pico-autotrophs, Diazotroph
zooplankton	none	at least 2	one	pico, proto, meso	one
explicit sinking detritus	no	yes	yes	yes	yes
nitrogen fixation/ denitrification	no	yes	no	yes	yes
air-sea exchange of CO_2	yes	yes	yes	yes	yes
DMS	no	no	no	yes	no
N_2O	no	no	no	yes	no
Methane	no	no	no	no	no
spectral radiation module	no	in development	in development	no	no
adjoined	yes	partly	no	no	no

References: (a) Dutkiewicz *et al*. (2005, 2006); (b) Darwin Project Model (Follows *et al*., 2007; Dutkiewicz *et al*., 2009; Hickman *et al*., 2010); (c) NASA Ocean Biogeochemistry Model (Gregg *et al*., 2003); (d) Green Ocean Model (Le Quere *et al*., 2007); (e) BEC, Coupled Biogeochemistry/Ecosystem/Circulation model (Moore *et al*., 2004).

Although there are significant observations of various aspects of the ocean biogeochemistry (see Section 3.1), there are nevertheless significant gaps in spatial and temporal coverage, and often the measurements that are available do not necessarily match the output of models. One such mismatch is that between satellite observations (upwelling radiation at the sea surface) and model outputs (chlorophyll and primary production). Though satellite derived products (through empirical algorithms) of chlorophylls and primary production are available there is considerable uncertainty in them. In fact biogeochemical model derived primary production captures *in situ* measurements almost as well as satellite derived values (Saba *et al*., 2010). In a proof of concept study, Kettle (2009) showed that backscattering coefficients could be a more useful constraint on a 1-D ecosystem models than chlorophyll alone. The MIT biogeochemical model and NOBM (Gregg *et al*., 2003) are working to incorporate explicit radiative transfer parameterization and phytoplankton specific optical properties. These parameterizations will provide variables (upwelling irradiance) closer to that seen by satellites. Though considerable work is still needed in the implementation of these model derived optical properties, these developments may provide better validation and optimization context than previous model outputs.

2.1.2.2 Methane Cycling

In general global 3-D biogeochemistry models have not included the cycling of methane, and separate model development would have to be undertaken to address this gas. Air sea exchange

parameterization will follow the formula given above, with coefficients specific for methane. Methane is thought to be supersaturated in surface ocean waters. A small percentage of tropospheric CH_4 is of marine origin; however data coverage is rather poor. Contributions from estuaries and shallow coastal shelves are far larger per unit area (*e.g.,* Bange *et al.*, 1994; Upstill-Goddard *et al.*, 2000), implying that such estimates require revision. Marine sources of methane include production by benthic organisms in anoxic sediments, release from deep-sea sediments in geologically active areas, and hydrates. Much of the methane produced deep in the ocean is degraded and transformed into CO_2 before reaching the surface waters. This process is currently not parameterized in models. Methane hydrates (crystalline methane molecules) occur abundantly in marine sediments, especially in the Arctic, are stable and do not enter the marine water or atmosphere except in extreme circumstances (though potentially 2-9 $TgCH_4$/y reaching the atmosphere from hydrates; EPA, 2010). Very little is known on how much marine produced methane reaches the atmosphere, though current isotropic studies may prove useful in this research. Current estimates of the ocean source of methane is small (between 1 and 13.3 $TgCH_4$/y; EPA, 2010), and much of this comes from the coastal ocean with additional input from rivers (Bange *et al.*, 2009) and methane in the ocean appears to have a very strong gradient from shallow waters to deep (Bange *et al.*, 2009). In the past, atmospheric inversion studies have generally neglected the ocean as a source or sink of methane (*e.g.,* Chen and Prinn, 2006; Rigby *et al.*, 2008).

2.1.2.3 Nitrous Oxide

The ocean is one of the largest natural sources of on N_2O (2.3 to 8.7 TgN/y, IPCC 4th assessment; Huang *et al.*, 2008; Hirsh *et al.*, 2006). Sources of N_2O in the ocean include nitrification and denitrification by microbial communities both in the water column and in the sediments. Denitrification occurs mostly in the low oxygen regions of the deep ocean and N_2O production is highly sensitive to oxygen concentrations (*e.g.,* Suntharalingham *et al.*, 2000; Jin and Gruber, 2003). Enhanced emissions to the atmosphere are found in coastal upwelling region where deep water is brought to the surface. Reduced oxygen concentrations in the future warmer ocean will lead to an increase in the natural production (Schmittner *et al.*, 2008). The anthropogenic component of N_2O is large, most reaching the oceans via rivers.

The processes of N_2O production have been represented in some biogeochemical models, leading to much insight into the distributions and emissions (*e.g.,* Suntharalingham and Sarmiento, 2000; Suntharalingham *et al.,* 2000; Jin and Gruber, 2003; Yakushev *et al.*, 2007). Models planning to capture N_2O emissions need to explicitly include the processes of nitrification and denitrification and capture changing oxygen distributions.

2.1.3 Adjoint model

An essential feature of the model framework proposed in this report is that each component, including the ocean biogeochemistry, and the fully-coupled system will be adjoined. This will enable comprehensive sensitivity propagation within each and across the coupled components. Full three dimensional ocean biogeochemical models of simpler complexity than described above have been adjoined in the past. Dutkiewicz *et al.* (2006) used the adjoint of the MIT

simple DIC model (see Table 2.1.1) to explore the sensitivity of air-sea CO_2 exchange on iron supply to the ocean. Kwon and Primeau (2008) used an even simpler biogeochemical model to explore optimizing several key parameters, for instance the remineralization timescale for organic matter, and Tjiputra *et al.* (2007) have used satellite chlorophyll measurements to constrain parameters in a simple ecosystem model, finding that the most sensitive parameters were those controlling the grazing terms. Additionally, Kurado and Kishi (2004), with limited success, used an adjoint of a regional ecosystem model to assimilate information from a single ocean station to constrain several of the ecosystem parameters. In a more formal evaluation, Friedrichs *et al.* (2007) used single water column frameworks (as opposed to 3-D models) with several different ecosystem models and their adjoints to explore parameter optimization. In particular, they found that only a handful of the many model parameters could be optimized with the observations available. The paucity of data is a strong constraint on parameter optimization seen by other authors (*e.g.,* Ward *et al.*, 2010). We should be mindful of the need to be selective in choosing parameters to optimize and we suggest a few key parameters as suggested by Friedrichs *et al.* (2007) and Tjiputra *et al.* (2007) (see **Table 2.1.2**). Friedrichs *et al.* (2007) also found that more complex models (greater number of plankton groups and limiting nutrients) were better optimized between different regions of the ocean than simple models. From a coupling perspective work has also been conducted to propagate adjoint sensitivities through a coupled terrestrial and atmospheric transport model in an attempt to estimate parameters from measured carbon fluxes (*e.g.,* Scholze *et al.*, 2007; Kaminski *et al.*, 2010). These early studies indicate the feasibility and timeliness of the proposed system.

Because of the reverse nature of the adjoint integration, the nonlinearity of the problem, and the non-self-adjointness, in general, of the underlying operators, developing an adjoint is generally as demanding as developing the forward model itself. The adjoint model development can be significantly facilitated through the use of automatic differentiation (AD) tools (Griewank and Walther, 2008) such as TAF (Giering and Kaminski, 1998) or OpenAD (Utke *et al.*, 2008).

Of key importance for the deployment of AD to generate an adjoint of a complex coupled biogeochemical/ecosystem model needed in a project such as described in this report, is that the model and its components should be formulated to be compatible with AD. Within ECCO we have gained substantial experience in the use of AD to state-of-the-art coupled ocean/sea-ice

Table 2.1.2. Potential parameters to be optimized (partial listing). See Dutkiewicz *et al.* (2009) for additional parameters and values.

Parameter	Definition	Prior Range	Units	Reference
μ_P	Phytoplankton growth rate (*Prochlorrocuccus*)	1-1.5	1/d	Shalalpyonok *et al.* (1998), Partensky *et al.* (1999)
μ_D	Phytoplankton growth rate (*Diatoms*)	2-3	1/d	Tang (1995)
r_C	remineralization rate for organic carbon	1/150-1/700	1/d	Hansell *et al.* (1995), Kwon & Primeau (2008)
f_{DOC}	fraction mortality to DOC *vs.* POC	0.2-0.7	unitless	Estimate
G	Zooplankton grazing rates	0.033-0.2	1/d	Estimate
Kp	grazing half saturation	10-50	mmol C/m^3	Estimate
Mz	zooplankton mortality	1/10-1/30	1/d	Estimate

models. Other groups have acquired similar experience in the context of terrestrial carbon cycle modeling. The experiences gained lend confidence to the prospect of successful application of AD to coupled carbon cycle models such as envisioned here.

2.2 Atmospheric Circulation and Chemistry

Atmospheric chemical transport models (CTMs) attempt to calculate realistic dispersion of pollutants throughout the atmosphere, based on surface emissions fields, boundary conditions, chemical reaction schemes and meteorological fields. We will focus here on Eulerian CTMs (in which transport is calculated from the reference frame of some grid) that determine pollutant transport off-line, using reanalyzed meteorology. The term 'off-line' refers to the pollutant transport being determined separately from the estimation of meteorological fields, which have to be calculated in advance. Several 'reanalysis' products are available for this purpose, and need not be developed as part of the proposed work. However, it should be noted that uncertainties in these fields will have a significant influence on derived emissions or model parameters. Quantification of this uncertainty will form a key component of the proposed methodology.

In this section, we will briefly discuss the physical and chemical processes that determine the transport and chemistry of the species of interest, before examining the specific requirements of a CTM that can accurately perform the proposed work and then investigating the current state-of-the-art models available. The following is not intended to be an exhaustive description of transport model development, but rather is intended to highlight key features and frame differences between models.

2.2.1 Atmospheric Chemistry and Transport – Background

2.2.1.1 Transport

Transport of chemicals in the atmosphere is determined by large-scale phenomena such as advection, which largely takes place at the resolution of current reanalysis products, and by sub-grid-scale processes that are parameterized in the models. Tracer advection in the models outlined here is calculated off-line using reanalyzed wind-fields. However, given the discretized nature of these fields, care must be taken to ensure pollutant mass conservation (*e.g.,* Lin and Rood, 1997). Sub-grid-scale transport processes that need to be parameterized include boundary layer turbulence (the boundary layer is the part of the atmosphere closest to the Earth's surface) and convection (*e.g.,* Holtslag and Boville, 1994; Hack, 1995; Zhang and MacFarlane, 1995). Each CTM offers different solutions to these issues, even if the same reanalysis is used, with various advection schemes and convection and boundary layer parameterizations.

2.2.1.2 Chemistry

For the species simulated in the proposed work, simplified chemistry schemes can be implemented with little loss of accuracy. The major GHGs can either be considered to be inert in the atmosphere, become oxidized by one or more oxidants, or in the case of CO_2, be an oxidation product themselves.

Several potent greenhouse gases: SF_6, the PFCs, and CO_2, can be considered to have no chemical 'sink' in the atmosphere. This is because the chemical or photochemical processes responsible for their destruction are relatively weak, or take place in very limited regions of the atmosphere, leading to chemical lifetimes of the order of thousands to tens of thousands of years (*e.g.,* Muhle *et al.,* 2010; Rigby *et al.,* 2010).

The majority of greenhouse gases regulated under the Kyoto protocol are reduced species that exhibit oxidation reactions and have lifetimes of tens to hundreds of years (CH_4, HFCs, HCFCs, CFCs). The main oxidant in the atmosphere for these gases is the hydroxyl radical (OH). OH is formed by the photolysis of ozone in the presence of water vapor, and has a maximum tropospheric concentration in the tropics. With a lifetime of around 1 second, it is hard to scale *in situ* measurements of OH concentration to global scales. Therefore, its global concentration is often inferred through its influence on one or more reduced species. In particular, 1,1,1-trichloroethane (CH_3CCl_3), whose emissions are relatively well known, has been used extensively to 'calibrate' the global OH field (*e.g.,* Prinn, 2001). More minor chemical sinks for these gases include the $O(^1D)$ radical and tropospheric and stratospheric chlorine.

To accurately simulate the global distribution of OH and $O(^1D)$, an extremely detailed and computationally expensive chemical scheme is required (*e.g.,* Emmons, 2010). For the purpose of this modeling framework, however, it is anticipated that OH and $O(^1D)$ fields can be specified off-line, based on the output of full photochemical models. While this approach prevents feedbacks on the OH or $O(^1D)$ field from being accounted for, the changes associated with such feedbacks are small enough for all of the reduced greenhouse gases that little loss of accuracy is anticipated. The OH fields used can be calibrated using measurements of CH_3CCl_3, to ensure that the lifetimes of the reduced species are realistic.

Photolysis of several GHGs in the stratosphere plays a key role in their destruction. In fact, this represents the main sink for atmospheric N_2O. CTMs can generally calculate photolytic destruction either by implementing a reduced photolysis scheme, in which wavelength-dependent cross sections are specified in conjunction with a simple radiative transfer model, or by specifying fields of the pre-calculated photolytic destruction rates (so-called 'J-values'). It is anticipated that the latter will be the most appropriate for the proposed atmospheric modeling, given that it will be more computationally efficient and more straightforward for adjoint coding.

While CO_2 can be considered to exhibit no chemical destruction in the atmosphere, it does have an *in situ* source: as an oxidation product, particularly of carbon monoxide. Similarly to the OH fields and photolysis parameters above, it is anticipated that this source can be included off-line by imposing a time-varying CO field. This field has been estimated in previous studies using satellite observations (*e.g.,* Kopacz, 2009).

2.2.2 Meteorological fields

A vital component of the proposed modeling framework will be the meteorological reanalysis fields used to drive the CTMs. These fields will not be modified in the proposed work, and

therefore their accuracy will be critically important in determining pollutant sources using atmospheric measurements.

Meteorological analysis refers to the assimilation of meteorological observations (from surface sites, radiosondes and satellites) into an atmospheric model to generate a 3-D estimate of the entire state of the atmosphere at a particular instance. They are typically used to generate initial conditions for weather forecasts. A reanalysis product is the re-assimilation of historical observations using a single version of a model, to obtain a consistent estimate of the history of the atmosphere at some frequency (usually 6-hourly) over several decades.

Several meteorological features are embedded in reanalysis products that will be vitally important for the simulation of pollutant transport from sources to receptors. These range from small-scale features such as the passage of fronts and 'weather-systems', to large-scale phenomena such as the movement of the Intertropical Convergence Zone (ITCZ). These features also span timescales from hours, such as the diurnal cycle of the boundary layer height, to decade-long changes such as the influence of the El-Niño 'oscillation'.

Several reanalysis products will be available for the proposed modeling framework. They include reanalysis from the National Center for Environmental Prediction/National Centers for Atmospheric Research (NCEP/NCAR; Kalnay, 1996), the National Oceanic and Atmospheric Administration's Global Forecasting System (NOAA GFS), European Center for Medium Range Weather Forecasts (ECMWF; Uppala, 2005) and the NASA Modern Era Restrospective-Analysis for Research and Applications (NASA-MERRA). Given the critical role of these reanalyses in the proposed framework, it is desirable that a modeling framework be set up that can readily incorporate as many different reanalysis fields as possible, so that an estimate can be made of the influence of structural model uncertainties on the derived emissions fields or model parameters.

2.2.3 Existing Chemical Transport Models

Given the above considerations, and taking computational efficiency into account, the desirable characteristics that a CTM should possess for the proposed modeling framework are:
- The ability to simultaneously model the transport and chemistry of many (~50) chemical species
- The capability to add off-line OH, O(^{1}D), CO and photolysis rates
- A high level of parallelization
- Compatibility with several reanalysis data sets
- The ability to substitute advection, convection and boundary layer schemes
- An adjoint of the transport and chemistry
- A list of several currently available chemical transport models is given in **Table 2.2.1**.

2.2.4 Adjoint Chemical Transport Modeling

In recent years, several studies have used adjoined CTMs to address problems in atmospheric chemistry. For example, global estimates of CO_2 emissions were estimated using NOAA observations (see Section 3.2.1) and the TM3 chemical transport model (Kaminski *et al.*, 1999;

Table 2.2.1 Example chemical transport models.

Model name	Institution	Reference	Meteorology	Adjoint
MOZART	NCAR	Emmons *et al.* (2010)	NCEP/NCAR	N
			NASA GEOS-5	
CAM-CHEM	NCAR	Lamarque *et al.* (2005),	NCEP/NCAR	N
		Pfister *et al.* (2007)	NASA GEOS-5	
GEOS-CHEM	Harvard (and global collaborators)	Bey *et al.* (2001)	NASA GEOS-5	Y
PCTM	NASA-JPL	Kawa *et al.* (2004)	NASA GEOS-5	Y
TM5	Global collaborators	Krol *et al.* (2005)	ECMWF, ERA	Y
IMPACT	Lawrence Livermore National Lab., CA	Rotman *et al.* (2004)	NASA GEOS-4	N
			NCAR MACCM3	N
TOMCAT	University of Leeds, UK	Chipperfield (2006)	ECMWF / UKMO	N

Details are given for meteorological datasets that are currently available for each model. Only global, Eulerian models with offline advection schemes are outlined here.

Kaminski and Heimann, 2001). More recently, adjoined CTMs have been used to extract emissions information from satellite observations of methane (Frankenberg *et al.,* 2005, 2008; Bergamaschi *et al.,* 2009) and carbon monoxide (Kopacz *et al.,* 2010) as well as other species. Adjoined CTMs have also been used to estimate the sensitivity of proposed observations to emissions fields. For example, Chevallier *et al.* (2009) estimated the sensitivity of the space-based Orbiting Carbon Observatory observations to surface CO_2 emissions, while Kaminski *et al.* (2010) performed a similar investigation into the proposed A-Scope measurements, and Zhang *et al.* (2009) conducted an intercontinental source attribution study of ozone pollution based on observation sites located in the western U.S.

2.3 Terrestrial ecosystem biogeophysics and biogeochemistry

Land surface models attempt to simulate the influence of landscape characteristics and ecosystem processes on global energy dynamics. Biogeophysical characteristics (*e.g.,* albedo, surface roughness) and processes (*e.g.,* latent heat exchange associated with evapotranspiration) have a direct influence on the exchange of energy between land ecosystems and the atmosphere, whereas biogeochemical processes associated with the cycling of carbon (*e.g.,* photosynthesis, respiration, decomposition, methanogenesis) and nitrogen (*e.g.*, nitrification, denitrification) affect the uptake and release of greenhouse gases (*e.g.,* CO_2, methane, nitrous oxide) to influence global energy dynamics indirectly. These biogeophysical and biogeochemical characteristics and processes may be influenced by many environmental factors including land-use change (*e.g.,* Houghton *et al.,* 1983; Melillo *et al.,* 1988; McGuire *et al.,* 2001; Strassmann *et al.,* 2008), land management (*e.g.,* fertilizer application (Felzer *et al.,* 2004, 2005; Tian *et al.,*2011), irrigation (Mariko *et al.,*2007; Jabro *et al.,* 2008), tillage (Curtin *et al.,* 2000; Alluvione *et al.,* 2009; Ussiri and Lal, 2009; Galford *et al.,* 2011), natural disturbances (*e.g.,* wildfire (Thonicke *et al.,* 2001; Bond *et al.,* 2005; Balshi *et al.,* 2007, 2009), insect infestations (Kurz and Apps, 1999; Kurz *et al.,* 2008), wind damage (Chambers *et al.,* 2007; Zeng *et al.,* 2009)), climate (Cox *et al.,* 2000; Friedlingstein *et al.,* 2003, 2006), atmospheric CO_2 concentration (Friedlingstein *et al.,* 1995;

Post *et al.,* 1997; Kicklighter *et al.,* 1999; Sokolov *et al.,* 2008), atmospheric nitrogen deposition (Melillo *et al.,* 1983, 1989; Jain *et al.,* 2009, Thornton *et al.,* 2007), air pollution (*e.g.,* ozone (Felzer *et al.,* 2004, 2005, 2007; Sitch *et al.,* 2007), and the redistribution of vegetation (Cramer *et al.,* 2001; Gritti *et al.,* 2006, Euskirchen *et al.,* 2009). The influence of environmental factors on biogeophysics often counteracts simultaneous effects on biogeochemistry (Brovkin *et al.,* 2006) so that the net effect on global energy dynamics is not easily determined.

The influence of these environmental factors on terrestrial biogeophyics and biogeochemistry are not independent of each other. For example, nitrogen limitations on plant productivity reduces the potential benefits of CO_2 fertilization from increasing atmospheric carbon dioxide concentrations (Kicklighter *et al*., 1999; Oren *et al*., 2001; Hungate *et al*., 2003; Thornton *et al*., 2007; Bonan, 2008; Sokolov *et al*., 2008; Zaehle *et al*., 2010a). Improvements in the availability of nitrogen for plant uptake either through the application of nitrogen fertilizers, atmospheric deposition or warming-induced nitrogen mineralization associated with decomposition can enhance the benefits of CO_2 fertilization on terrestrial carbon sequestration (Melillo *et al.,* 1983, 1989; Xiao *et al.,* 1998; Felzer *et al.,* 2004, 2005; Thornton *et al.,* 2007; Bonan, 2008; Sokolov *et al.,* 2008; Jain *et al.,* 2009; Zaehle *et al.,* 2010a; Bonan and Levis, 2010; Tian *et al.,* 2011). In another example, wildfires can change the albedo of landscapes to enhance warming of the soil, which in turn, enhances permafrost degradation and changes the hydrological dynamics in Arctic ecosystems (Yi *et al.,* 2009). Changes in soil thermal and hydrological regimes, either from fires, land-use change or global warming, influence plant phenology and productivity along with decomposition rates to influence the net flux of atmospheric carbon dioxide and methane to the atmosphere (Euskirchen *et al.,* 2006; Wickland *et al.,* 2006; Zhuang *et al.,* 2006, 2007; Balshi *et al.,* 2007, 2009; Hayes *et al*., 2011) and the contribution of water, carbon and nitrogen from land to river networks (McClelland *et al.,* 2004; Frey *et al.,* 2007; McGuire *et al.,* 2010).

Besides interactions, the influence of these environmental factors also occurs over a range of spatial and temporal scales. For example, large regions (many square kilometers), especially away from mountainous areas, may experience similar air temperatures, whereas neighboring small plots of land (few square meters) can experience very different land uses and land management practices. Natural and anthropogenic disturbances cause land ecosystems to rapidly lose carbon and nitrogen to the atmosphere or neighboring river networks, whereas carbon sequestration associated with recovery may take decades to centuries. While the uptake and release of CO_2 by land ecosystems to the atmosphere and the emissions of methane (CH_4) from wetland ecosystems (*e.g.,* Baker-Blocker *et al.,* 1977; Bartlett *et al.,* 1990; Roulet *et al.,* 1992; Segers, 1998; Wickland *et al.,* 1999; Zhuang *et al.,* 2004; Bohn *et al.,* 2007) are rather continuous, these fluxes vary in magnitude with seasonal variations in air temperature. In contrast, nitrous oxide (N_2O) emissions may be very ephemeral and depend on rapidly changing environmental conditions associated with snow melt during the spring, soil drainage following large rain events or fertilizer application events (*e.g.,* Vitousek *et al.,* 1989; Matson *et al.,* 1991; Li *et al.,* 1992; Smith *et al.,* 1997; Wagner-Riddle and Thurtell, 1998; Hall and Matson, 1999; Kiese and Butterbach-Bahl, 2002; Kiese *et al.,* 2003; Butterbach-Bahl *et al.,* 2004; Davidson *et al.,* 2004, 2008; Rees *et al.,* 2006; Werner *et al.,* 2007).

While many land surface models have been used to examine global carbon dynamics in Earth system modeling frameworks (Plattner *et al.,* 2008; Sitch *et al.,* 2008; Qian *et al.,* 2010), most have not considered the influence of carbon/nitrogen interactions on carbon dynamics until recently (Raich *et al.,* 1991; Melillo *et al.,* 1993; Xu-Ri and Prentice, 2008; Thornton *et al.,* 2007; Levis *et al.,* 2009; Bonan and Levis, 2010; Zaehle and Friend, 2010; Zaehle *et al.,* 2010a,b). Although the models that simulate both terrestrial carbon and nitrogen dynamics have many common features, there are still a number of differences in the ecosystem processes and disturbances (both human and natural) considered by the models, and the temporal resolutions used for the simulations (**Table 2.3.1**). In all of these process-based models, work is moving towards a full implementation of N cycle structure, inclusion of natural disturbances beyond fire (*e.g.,* insect infestations, wind damage), better tracking of the effects of land-use change (*e.g.,* conversion of natural ecosystems to agriculture, reversion of agriculture to natural ecosystems with abandonment, urban expansion, wetland drainage), implementation of land management schemes (*e.g.,* nitrogen fertilizer application, irrigation, tillage), and mechanistically-based vegetation community dynamics that include dispersal, establishment, and survival.

In the MIT IGSM, terrestrial ecosystem biogeophysics is simulated using the Community Land Model (CLM) whereas biogeochemistry is simulated using the Terrestrial Ecosystem Model (TEM). The TEM is a process-based biogeochemistry model that simulates the cycling of carbon, nitrogen and water among vegetation, soils and the atmosphere (*e.g.,* Raich *et al.,* 1991; McGuire *et al.,* 1992, 1993, 1995, 1997, 2001, 2010; Melillo *et al.,* 1993, 2009; Tian *et al.,* 1998, 1999, 2003, 2011; Pan *et al.,* 2002; Zhuang *et al.,* 2003, 2004, 2006; Felzer *et al.,* 2004, 2005, 2009; Balshi *et al.,* 2007, 2009; Sokolov *et al.,* 2008, 2009; Euskirchen *et al.,* 2009; Galford *et al.,* 2010, 2011; Hayes *et al.*, 2011) and includes consideration of permafrost effects on soil thermal dynamics (Zhuang *et al.,* 2001; Euskirchen *et al.,* 2006; Yi *et al.,* 2009). The model uses numerous parameters to describe the effects of temperature, soil moisture, photosynthetically active radiation, nitrogen availability, atmospheric CO_2, and atmospheric ozone on the uptake of carbon and nitrogen into plant biomass, the release of carbon from plants biomass and soil organic matter, the release of nitrogen from soil organic matter and the loss of inorganic nitrogen through leaching and trace gas emissions (Raich *et al.,* 1991; Tian *et al.,* 1999, 2003; McGuire *et al.,* 2001, 2010; Felzer *et al.,* 2004; Hayes *et al.,* 2011). Some parameters are assumed to be constant across biomes and are based on literature reviews whereas other parameters are assumed to vary across biomes and are calibrated to data collected at intensively studied field sites. Uncertainty in these model parameters contributes to the uncertainty of the estimates projected by TEM. To date, the importance of parameter uncertainty on TEM estimates have only been examined for a few TEM parameters (*e.g.,* Webster *et al.,* 2003, 2010; Sokolov *et al.,* 2008, 2009). To conduct a more comprehensive analysis of the importance of parameter uncertainty on model estimates, we have been determining the range and distribution of parameter values within different biomes for all the algorithms used in TEM based on a review of the literature (**Table 2.3.2**).

Table 2.3.1. Features and expected improvements of existing terrestrial models.

Features	Models			
	TEM[a]	LPJ/DyN[b]	CLM-CN[c]	O-CN[d]
Carbon dynamics	Carbon storage, primary production (GPP, NPP), plant respiration, plant allocation, litterfall, decomposition, CH_4 consumption, production, diffusion, plant-assisted transport and ebullition, DOC leaching	Carbon storage, primary production (GPP, NPP), plant respiration, plant allocation, reproduction, litterfall, decomposition	Carbon storage, primary production (GPP, NPP), plant respiration, plant allocation, litterfall, decomposition	Carbon storage, primary production (GPP, NPP), plant respiration, plant allocation, litterfall, decomposition
Nitrogen dynamics	Organic and inorganic nitrogen storage, N fixation, plant uptake of DIN, plant allocation, litterfall, mineralization, immobilization, nitrification, denitrification, DON and DIN leaching	Organic & inorganic nitrogen storage, N fixation, plant uptake of DIN, plant allocation, litterfall, mineralization, nitrification, denitrification, diffusion of NO, N_2O and N_2, NH_3 volatilization, DIN leaching	Organic & inorganic nitrogen storage, N fixation, plant uptake of DIN, plant allocation, litterfall, mineralization, immobilization, denitrification, NH_3 volatilization, DIN leaching	Organic & inorganic nitrogen storage, N fixation, plant uptake of DIN, plant allocation, litterfall, mineralization, immobilization, nitrification, denitrification
Water dynamics	Soil water storage, evaporation, transpiration, water yield	Soil water storage, percolation, evaporation, transpiration, surface runoff, drainage	Soil water storage, percolation, evaporation, transpiration, surface runoff, drainage	Soil water storage, percolation, evaporation, transpiration, surface runoff, drainage
Energy exchange	Soil thermal dynamics	Soil thermal dynamics	Soil thermal dynamics, albedo, sensible heat, latent heat	Soil thermal dynamics, albedo, sensible heat, latent heat
Permafrost	Effects on soil temperature, carbon, nitrogen & water dynamics	Effects on soil temperature, carbon and water dynamics	Effects on soil temperature and water dynamics	Effects on soil temperature and water dynamics*
Air pollution	CO_2, ozone, atmos. N deposition	CO_2, atmos. N deposition	CO_2, atmos. N deposition	CO_2, atmos. N deposition
Natural disturbances	Wildfire	Wildfire, extreme temperatures, invasive species	Wildfire	Wildfire, extreme temperatures
Land use and land-use changes	Row-crop agriculture, pastures, timber harvest, land conversion/ abandonment	Row-crop agriculture, pasture, land conversion/ abandonment	Row-crop agriculture, timber harvest, land conversion	Agriculture
Land management	N fertilizer application, irrigation, tillage	Irrigation, treatment of residues, intercropping	N fertilizer application*, irrigation*	N fertilizer application
Land-atmosphere interactions	CO_2 uptake/emissions, CH_4 uptake/emissions, NO, N_2O, and N_2 emissions*, evaporation, transpiration	CO_2 uptake/emissions, NO, N_2O, N_2 and NH_3 emissions, evaporation, transpiration	CO_2 uptake/emissions, NH_3 emissions, evaporation, transpiration	CO_2 uptake/ emissions, NO, N_2O, N_2, NH_3 emissions, evaporation, transpiration
Land-water linkages	Water yield, leaching of DOC, DON and DIN	Water yield, leaching of DIN	Water, yield, leaching of DIN	Water yield, leaching of DIN
Dynamic vegetation modeling	Climatically-favored PFTs compete for light, water and nitrogen	Climatically-favored PFTs compete for light, water and nitrogen*	Specified PFTs compete for water and nitrogen	Climatically-favored PFTs compete for light, water & nitrogen*
Time step	Monthly	Daily	Hourly	Half-hourly

*anticipated

[a] Raich *et al.,* 1991; Melillo *et al.,* 1993; McGuire *et al.,* 2001; Tian *et al.,* 1999, 2003, Felzer *et al.,* 2004; Zhuang *et al.,* 2003, 2004; Galford *et al.,* 2011; McGuire *et al.,* 2010; Hayes *et al.,* 2011.

[b] Sitch *et al.,* 2003; Gritti *et al.,* 2006; Beer *et al.,* 2007; Bondeau *et al.,* 2007; Xu-Ri and Prentice, 2008.

[c] Thornton *et al.,* 2007; Levis *et al.,* 2009; Bonan and Levis, 2010.

[d] Krinner *et al.,* 2005; Zaehle and Friend, 2010; Zaehle *et al.,* 2010a,b.

Table 2.3.2. Uncertainty in TEM parameters for black spruce forests (Tang and Zhuang, 2009).

Parameter	Definition	Prior Range	Units	Reference
Initial Pool Sizes				
C_V	Initial carbon in vegetation	[2000,20,000]	g C m^{-2}	McGuire *et al*. (1992); O'Neill *et al*. (2003)
C_S	Initial reactive organic carbon in soils	[6000, 20,000]	g C m^{-2}	McGuire *et al*. (1992); O'Neill *et al*. (2003)
N_V	Initial nitrogen in vegetation	[10, 40]	g N m^{-2}	McGuire *et al*. (1992); Van Cleve *et al*. (1983)
N_S	Initial reactive organic nitrogen in soil	[250, 1000]	g N m^{-2}	McGuire *et al*. (1992); Van Cleve *et al*. (1983)
N_{AV}	Initial available inorganic nitrogen in soil	[0.1, 0.9]	g N m^{-2}	McGuire *et al*. (1992); Weber & Van Cleve, (1984)
Soil Texture Properties				
Θ	Soil porosity	[30, 60]	cm^3 cm^{-3}	Frolking *et al*. (1996)
FLDCAP	Soil field capacity	[25, 40]	cm^3 cm^{-3}	Frolking *et al*. (1996)
WILTPT	Soil wilting point	[20, 25]	cm^3 cm^{-3}	Frolking *et al*. (1996)
Vegetation Parameters				
VEGC2N	Mean C:N of vegetation	[200, 600]	g C (g N)$^{-1}$	estimate
MINLEAF	Minimum photosynthetic capacity of vegetation	[0.2, 0.8]	none	McGuire *et al*. (1992)
ALEAF	Coefficient to model the relative photosynthetic capacity of vegetation	[0.1, 1.0]	none	McGuire *et al*. (1992)
BLEAF	Coefficient to model the relative photosynthetic capacity of vegetation	[0.1, 1.0]	none	McGuire *et al*. (1992)
CLEAF	Minimum relative photosynthetic capacity of vegetation	[0.0, 0.5]	none	McGuire *et al*. (1992)
ROOTZ	Effective rooting depth	[0.7, 2.5]	m	estimate
CFALL	Proportion of vegetation carbon lost in monthly litterfall	[0.0001, 0.015]	gC (gC)$^{-1}$mo^{-1}	estimate
NFALL	Proportion of vegetation nitrogen lost in monthly litterfall	[0.003, 0.012]	gN (gN)$^{-1}$mo^{-1}	McGuire *et al*. (1992)
CMAX	Maximum carbon uptake by plants from photosynthesis	[50, 1500]	gC m^{-2}mo^{-1}	McGuire *et al*. (1992)
k_C	Half saturation constant for CO$_2$-C uptake by plants	[20, 600]	μL L^{-1}	Raich *et al*. (1991)
k_I	Half saturation constant for PAR use by plants	[20, 600]	μL L^{-1}	Raich *et al*. (1991)
T_{min}	Minimum temperature for CO$_2$ uptake by plants	[-12, -1]	^{o}C	estimate
T_{optmin}	Minimum optimum temperature for CO$_2$ uptake by plants	[0, 15]	^{o}C	estimate
T_{optmax}	Maximum optimum temperature for CO$_2$ uptake by plants	[15, 25]	^{o}C	estimate
T_{max}	Maximum temperature for CO$_2$ uptake by plants	[25, 35]	^{o}C	estimate
KR_C	Logarithm of plant respiration rate at 0°C	[-7.5, -1.5]	none	McGuire *et al*. (1992)
RAQ10A0	Leading coefficient of the Q10 model for plant respiration	[1.3502, 3.3633]	none	estimate
RAQ10A1	First order coefficient of the Q10 model for plant respiration	[-0.054577, -0.051183]	(^{o}C)$^{-1}$	estimate
RAQ10A2	Second order coefficient of the Q10 model for plant respiration	[0.0022902, 0.0024381]	(^{o}C)$^{-2}$	estimate
RAQ10A3	Third order coefficient of the Q10 model for plant respiration	[-0.0000417, -0.0000397]	(^{o}C)$^{-3}$	estimate
NMAX	Maximum nitrogen uptake by plants	[0.05, 0.7]	g N m^{-2} mo^{-1}	McGuire *et al*. (1992)

Parameter	Definition	Prior Range	Units	Reference
k_{n1}	Half saturation constant for N uptake by plants	[0.5, 10]	$g \, N \, m^{-3}$	Raich *et al.* (1991)
Microbial Parameters				
MOISTOPT	Optimum soil moisture content for heterotrophic respiration	[20, 80]	%	McGuire *et al.* (1992)
RHQ10	Change in heterotrophic respiration due to $10^{o}C$ temperature increase	[1,3]	none	Raich *et al.* (1991)
KDC	Heterotrophic respiration rate at $0^{o}C$	[0.0005, 0.0007]	$gC \, m^{-2} \, mo^{-1}$	McGuire *et al.* (1992)
NUP	Ratio between N immobized and C respired by heterotrophs	[0.005, 0.1]	$gN \, (gC)^{-1} mo^{-1}$	McGuire *et al.* (1992)
k_{n2}	Half saturation constant for N uptake by heterotrophic organisms	[0.5, 10]	$gN \, m^{-3}$	Raich *et al.* (1991)

Adjoint methods have already been used with some land surface models, *e.g.,* the CSIRO Biospheric Model (CBM; Wang *et al.,* 2001, 2007), the Carnegie Ames Stanford Approach Model (CASA; Randerson *et al.,* 2002), the Simple Diagnostic Biosphere Model (SDBM; Kaminski *et al.,* 2002), the Biosphere Energy Transfer Hydrology Scheme (BETHY; Rayner *et al.,* 2005; Scholze *et al.,* 2007; Knorr *et al.,* 2010), to infer optimal parameter combinations from observations and to explore parameter sensitivities and the uncertainty in estimated carbon fluxes between the land surface and the atmosphere, particularly net ecosystem exchange (NEE). Although the structure of the models vary, the studies have generally found that parameters associated with photosynthesis are relatively well-constrained by observations. In contrast, most of the uncertainty in NEE appears to be associated with parameter uncertainties associated with storage of soil carbon. One of the key issues with soil carbon storage is the appropriateness of using simple Q_{10} relationships to describe the influence of temperature on the dynamics of soil organic matter decay (Davidson and Janssens, 2006).

2.4 Economics

2.4.1 Introduction

The motivation behind considering economics in a coupled atmosphere-ocean-biosphere modeling framework is that since anthropogenic emissions are associated with economic activity, total emissions resulting from an activity can be estimated if the amount of activity and the emissions corresponding to that activity are known. Fortunately, much of the data needed to construct such a model is available and, when combined with estimates from other top-down and bottom-up methods, the addition of an economic model could play a significant role in reducing overall uncertainty in emissions estimates.

In this section we review the structure of existing economic models that are used to give both historic estimates and future projections of greenhouse gas emissions and address the relevance of the structure of these models for constructing an economic model for climate treaty verification (CTV) purposes. Following discussion on the structure of these models, we address special considerations that must be taken into account in using economic data in a coupled modeling framework. We conclude by identifying areas for additional development as well as next steps towards implementation.

2.4.2 Existing Models and Model Structure

Economic models used to estimate greenhouse gases consist mainly of two kinds: models to predict historic greenhouse gas emissions and models to project future emissions. Most economic models used to project emissions of greenhouse gases are founded on basic microeconomic theory where producers seek to maximize profits while consumers seek to maximize utility. These models include endogenous projections of GDP, energy demand, energy supply, the price of goods, and other industrial activities. Emissions of greenhouse gases are estimated by multiplying a coefficient by the level of economic activity. This coefficient is commonly referred to as the *emissions factor*.

Due to significant computational intensity and data limitations, forecasting models are typically highly aggregated both spatially and in terms of economic activity. In most models the world is spatially aggregated into 12-30 regions while economic activity is usually aggregated among 20-50 sectors. These models typically make estimates over a 100-year horizon in 5 to 15 year time steps. Some of the more prominent models for projecting future GHG emissions based on economic activity are given in **Table 2.4.1**. The resolution of CO_2 emissions from coal, oil, and gas combustion are fairly adequate in these models, but other activities related to non-CO_2 GHG emissions and other sources of CO_2 (*e.g.,* land use change) are probably too highly aggregated to be of use for CTV purposes. More importantly, the principal purpose of these economic models is to simulate future prices and incomes as they affect industrial activities that emit greenhouse gases. For historical estimation there are direct measurements of the industrial and agricultural activities of interest so there is no need to project them.

More relevant for CTV purposes are relatively simple accounting models used to generate bottom-up inventories of greenhouse gas emissions. Emissions estimates are derived by multiplying the level of an emitting economic activity by an emission factor. Some of the more

Table 2.4.1. Greenhouse Gas Emissions Forecasting Models.

Model	Regions	Greenhouse Gases	Timeline; Time Step	Sectors	Source
EPPA	16	CO_2, CH_4, N_2O, PFCs, HFCs, SF_6	2100; 5 year	Energy, Industrial, Agriculture	Paltsev *et al.* (2005)
IMAGE[†]	26	CO_2, CH_4, N_2O, PFCs, HFCs, SF_6	2100; 10 year	Energy, Industrial, Agriculture	PBL (2010)
MESSAGE	11	CO_2, CH_4, N_2O, PFCs, HFCs, SF_6	(Variable); 10 year	Energy	IIASA (1995)
AIM	21	CO_2	2100; 10 year	Energy, Industrial, Agriculture	AIM (2008)
GCAM	14	CO_2, CH_4, N_2O, PFCs, HFCs, SF_6	2095; 15 year	Energy, Agriculture	GCAM (2006)
ReMIND	11	CO_2, CH_4, N_2O	2100; 5 year	Energy	Potsdam (2008)
GEM-E3	21	CO_2	2030, 1 year	Energy, Industry, Agriculture	Leuven (2008)
MERGE	9	CO_2, CH_4, N_2O	2150; 10 year	Energy	MERGE (2004)
WITCH	12	CO_2, CH_4, N_2O, PFCs, HFCs, SF_6	2100; 5 year	Energy	Fondazione (2010)

[†] MAGE consists of multiple sub-models (PHOENIX, TIMER, GTAP, HYDE, FAIR, *etc.*) with various time-steps. The time step recorded here is for HYDE.

notable inventories that use accounting models include the EPA Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990-2020 (EPA, 2006), the GTAP v7 Non-CO_2 GHG Emissions Dataset (Rose *et al.,* 2008), and the Emissions Database for Global Atmospheric Research (EDGAR) version 4.1 (Van Aardenne *et al.,* 2010). Because their focus has been on country-level reporting with the goal of defining activities with a common or default emissions factor, the spatial and sectoral disaggregation is much greater than that of forecast models. In addition to economic data, the models underlying these inventories also depend largely on emissions reporting data that has been compiled by the U.N. Framework Convention on Climate Change (UNFCCC, 2010).

Overall these historical inventories produce relatively consistent predictions in aggregate; however, because of their dependence on emissions reporting data obtained by the UNFCCC, their usefulness for CTV purposes is limited. All of the aforementioned historic models derive some of their estimates directly from the emissions reported by Annex 1 and non-Annex 1 countries in both the Common Reporting Format (CRF) and National Inventory Report (NIR) data. For CTV purposes this is obviously a major concern since any model that is to be used to verify emissions reporting data must be independent of the data it is trying to verify.

Although both historic and forecasting models are inadequate for CTV purposes, the common structure of estimating emissions as a coefficient—*i.e.* emission factor—multiplied by a given amount of economic activity is relevant. This structure underscores the fundamental framework of the Intergovernmental Panel on Climate Change three-tier methodology for emissions reporting (IPCC, 2006). In this approach three tiers or methods are outlined for estimating emissions from economic activity. Each subsequent tier provides improved emissions estimates with less uncertainty but also requires more detailed data and parameters that may be difficult to obtain. In what follows, we present a generalized version of the three-tier framework and discuss how this approach could be used in a coupled atmosphere-ocean-biosphere-economics modeling framework.

Tier one methodology is the simplest of the three and is the least intensive in terms of the data required. It involves multiplying the total amount of activity in a given economic sector by a global emissions factor for activity in that sector. For example, if one wanted to calculate the total amount of CO_2 emissions for the U.S. from electricity production, one would multiply the total output of the electricity sector in the U.S. by the global emissions factor of CO_2 for electricity production. In general, the emissions from gas i in country j for sector k are expressed as:

$$Emissions_{i,j,k}(kg) = EmissionFactor_{i,k}\left(kg/unit\right) \times Activity_{j,k}(unit) \tag{2.4.1}$$

The activity unit varies by activity. For fossil energy the unit is typically the energy content of the fuel (*e.g.,* GJ). For emissions of methane from agriculture, units might include the number of ruminant livestock, tons of manure, or hectares of paddy rice.

Tier two methodology differs from tier one only in that emissions factors are country specific. This is done to account for the fact that inputs to economic activity vary across countries such that the emissions intensity in a given sector of one country may not be the same in the same sector of another country. For example, methane emissions from ruminant livestock may vary

33

depending on the type of livestock and the quality of feed. For tier two methodology, the emissions of gas *i* in country *j* for sector *k* are expressed as:

$$Emissions_{i,j,k}(kg) = EmissionFactor_{i,j,k}\left(kg\big/unit\right) \times Activity_{j,k}(unit) \tag{2.4.2}$$

Tier three methodology is based on either taking direct measurements of emissions from the source—*e.g.,* a CO_2 monitor on a coal-fired power plant—or detailed emissions modeling that takes into account specific technologies or conditions under which an activity is conducted. For example, tier three methods for methane would distinguish different ruminant livestock (sheep, beef cattle, dairy cattle) and consider the typical feeding regime. Or, for N_2O, tier three methods would model different forms of nitrogen applied (anhydrous ammonia, urea, compound nitrate and phosphate), soil types, and weather as it affects the nitrogen cycle. In this case, the emissions factor becomes a technology-specific factor that is equivalent across countries. For tier three methodology the emissions of gas *i* in country *j* for sector *k* using technology *t* is expressed as:

$$Emissions_{i,j,k}(kg) = \sum_{t}\left(EmissionFactor_{i,k,t}\left(kg\big/unit\right) \times Activity_{j,k,t}(unit)\right) \tag{2.4.3}$$

The substantive difference between the different tiers is largely the level of disaggregation. The underlying assumption is that a more precise description of the activity will result in a more precise estimate of the emissions factor and hence less potential error introduced by virtue of the fact that a more grossly determined average emission factor inadequately represents the variation of sub-types of activities in different regions. An economic component of a coupled atmosphere-ocean-biosphere-economic model could be built using this approach based on the availability of data and on requirements for detail. For economic sectors where data is sparse, tier one methods would be used. For other sectors where data is more widely available, tier two or tier three methods could be used. Although tier two and tier three methods may be feasible, they may not necessarily be needed. One goal of the Observing System Simulation Experiments (OSSEs) is to determine the sensitivity of the overall coupled atmosphere-ocean-biosphere-economic model to changes in input parameters. If it were found that a tier three representation of an economic sector provided no advantage over a tier one representation, the tier one representation would be preferred since it would require fewer input parameters.

Also, another purpose of having a coupled atmosphere-ocean-biosphere-economic model is to use observational feedback data to optimize the model input parameters. In theory either the economic activity or the emissions factors could be considered the parameters being optimized in an economics model. However, since we would expect the emissions factors to remain less variable over time, we treat them as the parameters that are optimized and allow economic activity to vary.

2.4.3 Consideration for Using Economic Models in a Coupled Framework

When coupling an economic model with a comprehensive Earth systems model some special considerations must be taken into account. First, the temporal and spatial resolution of the economic data can be vastly different than that of the Earth systems model. Earth-systems data is often allocated in daily/hourly time-scales on a global grid with geographical resolution of 0.1°

latitude by 0.1° longitude. In contrast, most economic data are reported at annual levels, and commonly available data typically has geographical resolution limited to entire countries. Because of this, using an economic model as part of a coupled model framework will require mapping aggregate country economic data to individual grid cells, or aggregating finer spatial and temporal scale data from Earth system models to an annual and country level. For verification purposes, the annual and country level is all that is required since that is the level at which commitments are made, but more detailed spatial data would likely help constrain the inverse methods approach. For example, urban areas near country borders often have suburbs in the neighboring country and attributing emissions accurately to each of the countries would require a finely resolved inverse modeling approach. Economic activity data that, with a fair level of confidence, could distinguish economic activity on one side of the border from the other could be of high value. Given that economic data is collected by political jurisdictions, it is much more likely that it would attribute correctly to the spatial scale that matters for verification—the nation. Although many integrated assessment models have approaches for allocating emissions spatially, these are often based on relatively crude indicators such as population density. Since the data is originally aggregated for an entire country, this could contribute to uncertainty in the spatial allocation within a country, even though the aggregation for the country may be relatively certain.

Although mapping of national aggregate economic data to individual grid cells can give rise to large uncertainty, less uncertain spatial allocation of estimates from economic activity is possible if highly disaggregated regional economic data is used. An example of how this might be done is given by (Ichihara *et al.,* 2009) for the state of São Paulo, Brazil. In their approach, detailed input/output tables for regional economic activity within a country are combined with advanced geographic information systems (GIS) that provide the specific location of various economic activities. This combination reduces uncertainty since the source economic data is already disaggregated within a country to begin with. The main disadvantage is that such data has only been developed for a few countries.

Another important consideration that must be taken into account is the role of regional and global trade-flow when attributing emissions to specific countries. By this we refer to goods that physically contain the emission source—*e.g.,* carbon content in agricultural products—that are transported across regions and countries. This does not refer to energy intensive goods—*e.g.,* cement production—that may have produced a large amount of emissions in the country or region of origin, but that physically do not contain the emission source. The problem arises in the following circumstances: A growing crop of corn in the Midwest U.S. will be detected via inversion methods as a carbon sink. If that crop is harvested, exported, and fed to cattle somewhere else in the world it will be detected via inversion methods as a source of CO_2 from respiration of the livestock and decomposition of waste, and also partly as a methane source. Similarly, forest growth in one region will be detected via inversion methods as a sink, and if timber or paper products are exported these would be attributable as a sink for the exporting region but may show up eventually as a source in the importing region. This is generally not the attribution convention in international agreements. In general, the carbon dioxide emissions from

decomposing waste and sinks due to the harvest of crops and forest products do not enter the carbon budget for policy purposes. The general convention is that stocks in products are rapidly cycling so no one takes credit or is penalized for them. In contrast, changes in stocks on land that are permanent –or at least not part of an annual cycle—can create credits or penalties in national reporting. On the other hand, methane and nitrous oxide from ruminant digestion, manure, *etc.* are penalized where they occur even if the food source was imported. For applicable sectors of the economy, we can incorporate this attribution convention by adding imports and subtracting exports from the original production of a particular sector. In general, the net economic activity in country *j* for sector *k* is a country's own production minus exports to countries *l* plus imports from countries *m*. Mathematically this is represented as:

$$Activity_{j,k} = Output_{j,k} - \sum_l Exports_k + \sum_m Imports_k \qquad (2.4.4)$$

where *j* is not contained in *l* or *m*.

The activities and products where this phenomenon is important are those products that absorb carbon as they grow, and then re-emit it when they are used. Mostly these are food, feed, forest, and fiber products and perhaps more important in the future, biomass energy products (for further discussion see Reilly and Asadoorian, 2007). A related issue is the attribution of emissions from international transportation or from defense operations. Here the treatment of "bunker fuels" in international negotiations remains unresolved. Possible conventions are to attribute them to the nation where the fuels are sold or to the nation with which the carrier that purchased the fuels is registered. Inverse methods will detect the source of these emissions as flight, shipping, trucking, and rail paths that may cross international waters and third party countries unrelated to either the source of the bunker fuel or the nation with which the carrier is registered. Inverse methods will need to be able to attribute these emissions following the legal conventions established for them if they are to contribute to the verification process.

2.4.4 Adjoint models

Compared to transport and (biogeo)chemical models of the atmosphere, ocean, and land, economic models rely mainly on linear response functions which relate economic activity to regional emissions estimates. While potentially complex in terms of book-keeping, the derivation of adjoint expressions which provide sensitivities of emissions to changes in economic activity are conceptually simple since these are essentially just the emissions factors. We thus expect straightforward implementation within a coupled adjoint framework. We note, that optimal emissions strategies have also been investigated in which an adjoint of a coupled integral climate response and macro-economic model was used to "optimize" a CO_2 emissions path with respect to climate change mitigation *vs.* adaptation costs (Hasselmann, 1997; Hasselmann *et al.,* 1997).

2.4.5 Economics Summary

In summary, the most efficient way to incorporate economic data is to develop a simple accounting framework that in the first step takes advantage of available data (as discussed in Section 3.4). The proposed model could follows the IPCC three-tier methodology with the tier

level being determined based on data availability, the level of detail needed to adequately constrain emissions estimates, and the degrees of freedom in the inverse approach. Within the model, the trade of emission-containing goods between countries will be accounted for using trade data so that measured emissions from *in situ* stations and satellite networks will match the emissions of country consumption, not production. Although the methodology is laid out, additional work will need to be done to construct a system for mapping the economic data to a global grid.

2.5 Driver and Couplings

The overall framework for a coupled forward and inverse model is presented in **Figure 2.5.1** and **Figure 2.5.2**. Fluxes of the main GHGs between components will link the different models. In general the different components (ocean, terrestrial, economics) will be connected through the atmosphere component. However, it is likely that a link between the terrestrial component and the ocean will also need to be developed to account for riverine sources of some of the greenhouse gases to the ocean. In order to couple the different model components, a coupler program that serves as a driver for the whole system will need to be built. All the component models and the coupler will need to be made to run on the same computer platform.

The coupled system consists of several layers, which are summarized as follows:

- The core layer consists of a set of prognostic component models which simulate the space and time evolution of trace gas concentrations and associated biogeochemical tracer cycles. These components are:
    - an atmospheric transport and chemistry model (ATM),
    - an ocean biogeochemical and ecology model (BioECCO),
    - a terrestrial carbon cycle and nitrogen model (TEM/CLM),
    - an economy/emissions model linking human trade to emissions.

    The combined set of variables simulated by this coupled system constitutes **the prognostic coupled model state of active variables**;

- Corresponding to each element of the coupled state are **observations of active variables** which can be used for formal misfit evaluation and which are indicated in red in each component;

- **Inter-component fluxes of active variables** (mostly air/sea and air/land) are indicted in purple; of particular importance are the anthropogenic emissions whose sensitivities are propagated through the coupled system;

- **Active parameters,** indicated in yellow; these are uncertain parameters which are adjusted as part of the estimation/optimization process, along with the anthropogenic emissions;

- **Passive time-varying flow fields** of the atmosphere and the ocean which "drive" the atmospheric and oceanic transports, as well as the land hydrology; the "passive" attributes indicates that these fields are not adjusted as part of the optimization, but are assumed to be already optimized; these fields are indicated by the orange cycle in Figure 2.5.1;

- **Passive boundary conditions,** such as ozone levels, trade flows, and land use change, which are not modified in the estimation, and are represented in dark grey.

37
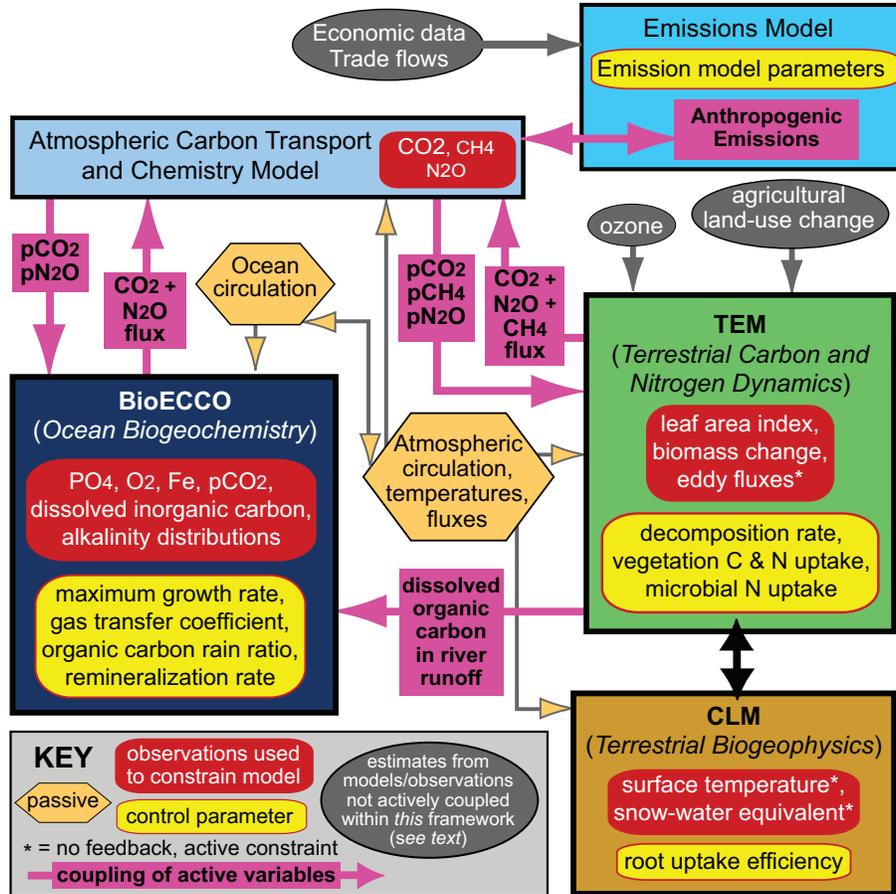
Figure 2.5.1. Coupled framework for estimation of the cycling of GHGs that have significant natural sources and sinks such as carbon (CO_2), nitrous oxide (N_2O) and methane (CH_4) through the full Earth system. There are four sub-models to this system (names are based on those used at MIT and are for illustration only): an atmospheric transport and chemistry mode ("atmosphere", lightest blue box); and ocean transport and biogeochemical mode ("ocean", dark blue box), a "terrestrial" model composed of both land vegetation (green box) and land hydrology (brown box); emissions model ("economics", bright blue box). The two components of the terrestrial system are significantly linked already (indicated by dark black arrow between green and brown box), and they will be treated as one sub-model in this framework. The four sub-models will be linked to each other by the fluxes of the GHG from one to another (illustrated by the purple boxes and arrows). It is assumed that the best possible ocean and atmospheric circulation and mixing will be available for the transport of GHG (and other necessary elements) through these systems. As such these will be treated as "passive" in our system and the adjoint machinery will not examine them. Certain datasets that are inputs to some of the sub-models (*e.g.*, ozone concentrations, land use changes) are not actively predicted by the model and will be instead also treated as "passive" parts of the system (grey ovals). A subset of the observations that are available for each sub-model are indicated in red and full sets are provided in Tables 3.1.1, 3.2.1, 3.3.1, 3.4.1. These are also variables that each sub-model will carry as a "state variable" (*e.g.*, CO_2, N_2O) or quantities that the model will calculate (*e.g.*, biomass change). The models have a significant number of parameter values (*e.g.*, maximum growth rates of phytoplankton and plants) that are based often on observed quantities, but that have uncertainties associated with them. Subsets of these are given in the yellow boxes in the figure, and more are given in Tables 2.1.2 and 2.3.2. In the adjoint these are called "control" parameters and simulations including the adjoint will be able to "optimize" these values so that the model system will be brought closer to observed system.
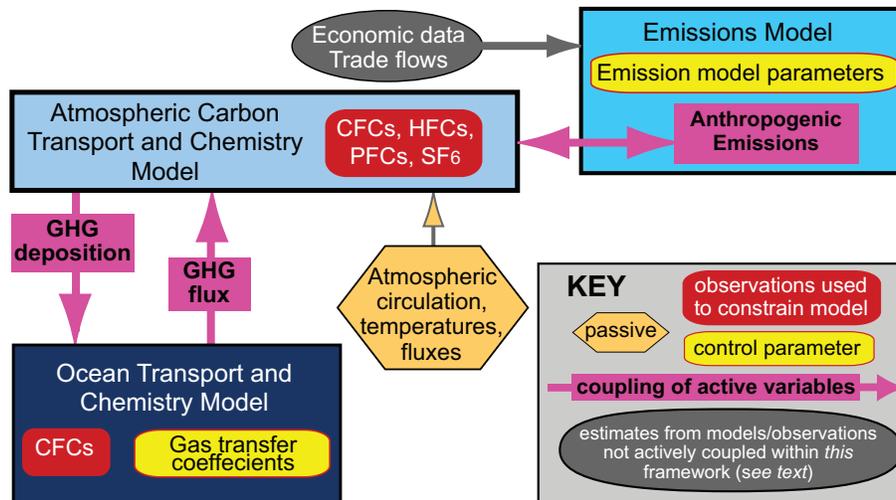
Figure 2.5.2. Coupled framework for estimation of cycling of purely anthropogenic greenhouse gases (that do not have significant natural sources and sinks). These gases can be treated much more simply than those shown in Figure 2.5.1. Emitted gases enter the atmosphere from the ocean or the economics model, and are then transported and chemically transformed. Some of these gases are transferred back into ocean, where they are simply transported. Observations (red) of these gases in the ocean and atmosphere will be used to constrain the full system, and control parameters (shown in yellow in the figure, such as solubility of these gases) can be optimized by the framework.

The various component models have different temporal and spatial scales. The coupler will bring the models together and integrate them forward by adopting a time-splitting scheme. The atmospheric component will have the shortest temporal scale and thus likely produces the fastest changes in fluxes over interfaces with the ocean and land. The coupler will therefore need to be built with the atmospheric component temporal scale as the base scale. The fluxes into oceans and land from the atmosphere will be accumulated and then averaged before being supplied to their respective components. The fluxes to the atmospheric module from the slower component models will be kept constant during the integration time step. The model components will also likely have different spatial resolutions and the coupler will also be required to re-grid greenhouse gas fluxes between components. Several flux interpolation/extrapolation methods will need to be examined to find an optimal solution.

Models linking some of these components in a forward configuration are in existence (*e.g.,* see the coupled model intercomparison project, CMIP, http://www-pcmdi.llnl.gov/projects/cmip/). However, these models have not generally included an economic/human driven component. There is significant experience at MIT in the coupling of complex atmospheric, oceanic, land biogeophysical and land ecosystem models together with economic modules through the construction of the MIT Integrated Global System Model (IGSM; Prinn *et al*., 1999; Sokolov *et al*., 2005, 2009), which includes in its latest version TEM/CLM (McGuire *et al.,* 2010; Bonan and Levis, 2010) and the MIT ocean general circulation model (Marshall *et al*., 1997a,b) with simple biogeochemistry (Dutkiewicz *et al*., 2005). A significant difference in the framework needed for the assessment and validation of the emissions to the fully-coupled models described above, is that each component and the driver will need to be adjoined. This will require

considerable development in each component and new and innovative ideas when approaching the coupled system. These issues are discussed further in Section 4.

3. DATA AND OBSERVATIONS

3.1 Oceans

In this section we briefly review the types of observations that are available to constrain the ocean biogeochemical model. These observations include nutrients, organic pools, and estimations of the phytoplankton (in terms of chlorophyll) as well as pCO_2 and air-sea fluxes. We focus here on datasets that have been already produced and quality controlled. These are summarized in **Table 3.1.1**. Acronyms and relevant websites for the different datasets are provided in the glossary. Once again we stress the importance of observations of the physical flow fields, but whose use in constraining the *dynamical* models is regarded as a separate, albeit crucial, effort.

3.1.1 Satellite derived products

The datasets with the most coverage globally and temporally are those derived from satellite imagery. Several satellites have missions that include the investigation of ocean biota. The NASA Sea-viewing Wide Field-of-view Sensor (SeaWiFS) was launched in August 1998 and has since then, with only a few short interruptions, been providing images of the Earth. The sensor detects visible light in 6 wavebands. Additional NASA satellites Aqua (launched 1999) and Terra (launched 2002) have the Moderate-resolution Imaging Spectroradiometer (MODIS) instrument on board. MODIS has 9 wavebands in the visible spectrum. These satellites cover the Earth surface in 8-day intervals with resolution of 1 to 9 km. There are several additional satellite observing systems (*e.g.,* OCTS, POLDER) that capture ocean color relevant properties, but useable and widely disseminated products from these are less available. The satellite retrieval from MODIS and SeaWiFS is reflectance in several specific wavebands. The sea surface upwelling irradiance must be corrected for the atmospheric contamination. The most commonly used products from these measurements are chlorophyll and primary production. However both these products use empirical formulas (models) to calculate values from these irradiance values. There has been considerable effort put into evaluating these output (*e.g.,* the "Primary Production Algorithm Round Robin" PPARR projects; Carr *et al.,* 2006; Friedrichs *et al.,* 2009; Saba *et al.,* 2010), but there is still much (possible 50%) uncertainty in these values. Thus, although the temporal and spatial coverage is good, care will be needed when assimilating these data. The uncertainties are even larger in coastal (Case II) waters where turbidity can mask the chlorophyll signal.

Additional newer products have been deduced from the satellite waveband retrieval. Though there are still large uncertainties in these products, they may be useful for constraining aspects of the ecosystem model. These products include estimates of surface particulate organic carbon (*e.g.,* Stramski *et al*., 1999), particulate inorganic carbon (*e.g.,* Balch *et al.,* 1999), plankton size (Ciotti and Bricaud, 2006; Uitz *et al.,* 2006; Hirata *et al.,* 2008; Kostadinov *et al.,* 2009; Mouw and Yoder, 2010) and phytoplankton functional types (Alvain *et al.,* 2009; Bracher *et al.,* 2009; Raitsos *et al.,* 2008). A useful discussion of the protocols used in ocean color products is provided by Mueller *et al.* (2003).

3.1.2 In situ datasets

Collecting data directly from the oceans is a costly and difficult. Though "ships of opportunity" (merchant vessels that offer to take scientific measurements while underway) may sample the surface ocean along certain transects frequently, deep-sea measurement require a dedicated research ships. Casts to many 100 m even 1000 m depth in the ocean to collect water are time consuming and often only a few such casts (10's) can be achieved on a single cruise. The water collected must then be analyzed (usually separately) for properties such as various nutrients, carbon content, phytoplankton and organic matter. International co-operations have led to several repeat transects of the oceans during the last 20 years as part of WOCE, JGOFS and CLIVAR programs leading to a large influx of biogeochemical data. These data along with others collected on other cruises have been collected, quality controlled and interpolation to data sparse regions have been undertaken. Nutrient (PO_4, NO_3, silicic acid) and oxygen monthly climatologies are available (World Ocean Atlas, Garcia *et al.,* 2009a,b). GLODAP has provided an annual climatology of ocean carbon and alkalinity (see **Figure 3.1.1**). While these provide essential climatologies that will be needed for this project, there are uncertainties that are derived from the interpolation and extrapolation schemes involved. Dataset specific for the North Atlantic, in particular additional data for the Arctic (CARINA; Tanhua *et al.,* 2009) has recently become available. More sparse, but extremely important are the observations of iron an important micro-nutrient that limits primary production in large sections of the ocean. An ad hoc collations of iron is available (Moore and Braucher, 2008), though should be updated.

Particularly important datasets are those from long timeseries such as the Bermuda Atlantic Timeseries (BATS) and Hawaii Ocean Timeseries (HOTS). Here shipboard measurements of physical, chemical inorganic and organic properties are taken regularly (often monthly) at the same location. At Bermuda such measurements have been taken since 1955 (Hydrostation "S") and since 1997 at BATS itself. These stations provide unprecedented temporal view of the ocean biogeochemistry which will be essential for data assimilation, in particular for capturing interannual variability. Several other shorter timeseries data are also available (see **Table 3.1.1**).
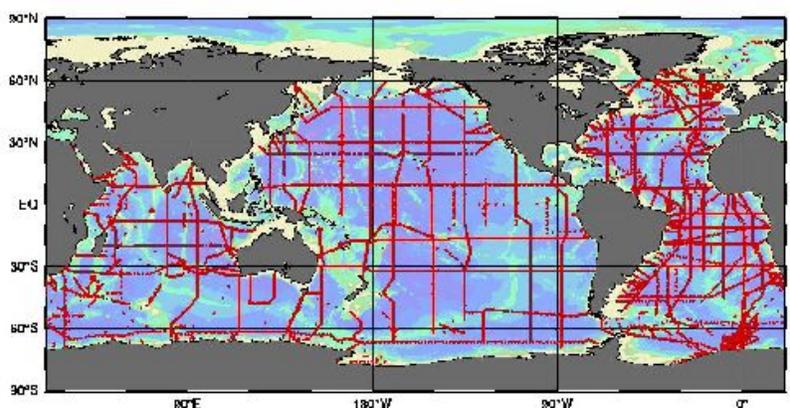
Figure 3.1.1. Location of data samples on the transects in the GLODAP database, and used in the GLODAP gridded climatologies.

The most comprehensive compilation of pCO_2 measurement is that of Takahashi *et al.* (2009) and includes 3 million measurement and have been averaged onto 4º x 5º grid, though there are significantly areas of the global ocean with sparse or no coverage (**Figure 3.1.2**). CO_2 fluxes cannot be measured directly, but must be derived from measurements of seawater pCO2 and estimate of the gas transfer coefficient (a function of sea surface temperature and salinity, and wind speeds). CO_2 fluxes cannot be measured directly, but must be derived from measurements of seawater pCO_2 and estimate of the gas transfer coefficient (a function of sea surface temperature and salinity, and wind speeds). Takahashi *et al.* (2009) also have compiled estimates of CO_2 fluxes from these data. Though uncertainties from the scarcity of pCO_2 measurements are amplified in the flux calculations by the assumptions that must be made about the gas transfer coefficient (see Section 2.1.2) and could be as much as 50%.

Table 3.1.1. Datasets of ocean biogeochemistry observations. For abbreviation and websites see below.

Extent/type	Variable	Measurement type	Frequency	Period	Reference
global gridded (9 km)	upwelling radiation	Satellite, Level 3	8-day	1998 to present	SeaWiFs, MODIS-Aqua, MODIS-Terra OCTS
global gridded (9 km)	Chl, PAR, POC, PIC, primary production	Satellite+empirical model	8-day	1998 to present	SeaWiFs, MODIS-Aqua, MODIS-Terra OCTS
global gridded (1° x 1°)	DIC, alkalinity	*in situ* (from WOCE, JGOFS, TTO, GeoSecs), interpolated	annual climatology	1980s and 1990s	GLODAP (Key *et al*. 2010)
	PO_4, NO_3, SiO_2	*In situ*, interpolated	monthly climatology	1950s-2000s	WOA09 (Garcia *et al.* 2009a)
	Oxygen	*in situ*, interpolated	monthly climatology	1950s-2000s	WOA09 (Garcia *et al.,* 2009b)
global gridded (4^ox5^o)	pCO_2, CO_2 fluxes	*in situ*, interpolation	monthly climatology	1968-2006	(Takahashi *et al.,* 2009)
site specific (bottle)	DIC, alkalinity, CFC	*in situ*	periodic	1978-2006	CARINA (Tanhua *et al.,* 2009)
site specific (bottle)	DIC, alkalinity, pH, CFC, C^{14}, C^{13}	*in situ*	periodic	1980s and 1990s	GLODAP (Sabine *et al*, 2005)
site specific (bottle)	HPLC pigments	*in situ*	periodic	1975 to present	SeaBASS (Werdell *et al.,* 2005)
repeat transects (bottle)	DIC, PO_4, O_2, NO_3, Fe, SiO_2, Chl, TOC, TON, pCO_2	*in situ*	periodic	2003-2012 1989-1993 1990-1998	CLIVAR JGOFS WOCE
ocean time series stations	DIC, PO_4, Chl, NO_3, O_2, pCO_2, alkalinity, DOC, DON, POC, PON, primary production, particle fluxes	*in situ* time-series	mostly monthly	1980s to present	BATS, HOT, PAPA, OWS-M, OWS-I, Kerfix, CARIACO (Kleypas & Doney 2001)
repeat transect	Chl, PO_4, NO_3, DIC, DOC, DON, DOP, pCO_2, N_2O, O_2, primary production, HPLC pigments	*in situ*	once or twice yearly	1995 to present	AMT
transects	zooplankton and large phytoplankton species	*in situ*	periodic	1931 to present	CPR (Richardson *et al.,* 2006)
sparse	particle fluxes	sediment traps	infrequent	1980s to present	(Dunne *et al.,*2007)
sparse	Fe	*in situ*	infrequent	1980s to present	(Moore and Braucher, 2008)

*Abbreviations and acronyms are provided in the glossary.
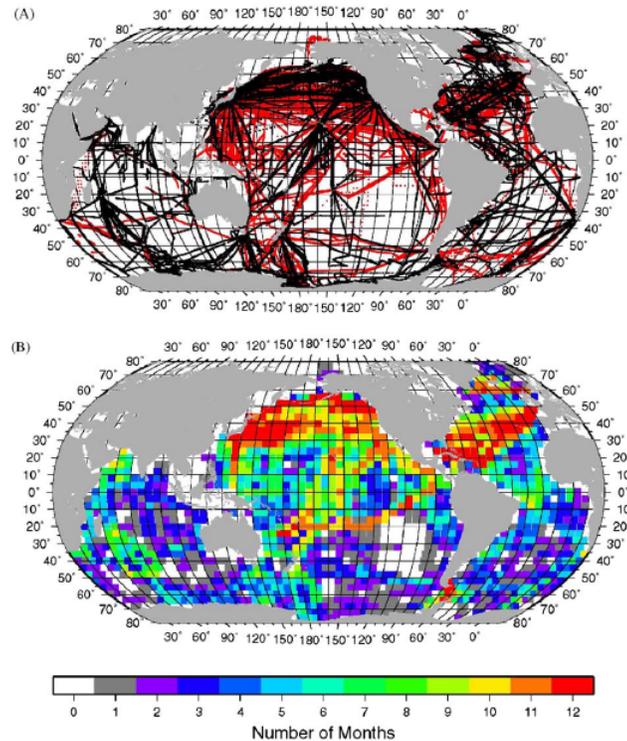
Figure 3.1.2. Sample location and coverage used in Takahashi *et al*. (2009) estimates of pCO$_2$ (see Figure 2.1.1a) and air-sea fluxes. (a) Dots indicate measurement sites (black pre 2002, red post 2002). (b) Number of months since 1970 where at least one surface water p$_{CO2}$ measurement was made in 4º x 5º boxes.

Direct observational data of the ecosystem itself are even sparser. Research cruises have occasionally (though with more regularity) obtained fluorescence data and chlorophyll measurements. High-performance liquid chromatography (HPLC) is a technique to separate mixtures of compounds and has provided pigment data that can help validate satellite products. Many of these data have been collected by SeaBASS (Werdell *et al.*, 2005) and could be useful for model optimization. The Atlantic Meridional Transect (AMT) program has conducted over 19 cruises from the UK to either the Falklands Islands or Cape Town, South Africa over the last 15 years. These cruises have obtained unparalleled data on the optical, phytoplankton size distribution as well as species specifics. Though only covering a slice of the ocean, these data will be useful for establishing the fidelity of an ecosystem model in capturing phytoplankton species distributions. Additional data of zooplankton, and some larger phytoplankton types comes from the 40 year collections in the North Atlantic from the Sir Alistair Hardy Foundation in the form of the continuous plankton recorder (CPR; Richardson *et al.*, 2006).

Measurements of fluxes of organic matter through the water column are essential for understanding and capturing the strength of the biological pump (the amount carbon exported as organic matter to depth in the ocean and therefore "stored"). These measurements are often done with instruments that float or are moored deep in the water column and "catch" particles as they sink out ("sediment traps"). However more sophisticated techniques using radioactive isotopes (*e.g.,* thorium) in organic matter captured in the water column provides a means to determine how

43

fast particles sinking (Buessler *et al.,* 1992). Ad hoc organic flux measurements are available and hopefully more will be available soon through projects such as VERTIGO (Buessler *et al.,* 2007).

3.1.3 Upcoming datasets

Several currently activities will produce data products that will also be useful for this project. The MOMENTO (Bange *et al.,* 2009) program, jointly funded by SOLAS and the European Cooperation in the Field of Scientific and Technical Research, will pull together available N_2O and methane measurements in the oceans into a single dataset. Cruises have just begun on the multi-national GEOTRACES study which will provide much more comprehensive global datasets on trace element (*e.g.,* iron) and their isotopes.

A significant step forward in the monitoring the temperature of the oceans was the development of Argo floats (Roemmich and Owens, 2000). These instruments drift at depth in the ocean, and occasionally profiling up to surface. At regular intervals at depth and more frequently during a profile these instruments measure the temperature, salinity and pressure of the water. Once at the surface the float transmits the collected data (and the location) via satellite. These floats are relatively inexpensive and have mission lengths of 4-5 years. An international collaboration has led to over 3000 of these floats deployed worldwide. Recently developments have been undertaken for "Bio-Argo", Argo floats with biological relevant sensors attached. In particular the U.S. Argo program has decided to equip 25% of the future floats with chlorophyll and back-scattering sensors. These will be a great importance to the observing system needed for projects such as described here.

3.2 Atmospheric Greenhouse Gas Observations

In this section we will briefly examine the major existing GHG monitoring networks. The networks and measurement techniques will be discussed individually, and are summarized in **Table 3.2.1**. We will only discuss networks with a global extent here. Several regional networks exist that are beyond the scope of this report.

3.2.1 The National Oceanic and Atmospheric Administration, Earth System Research Laboratory (NOAA-ESRL)

NOAA-ESRL Global Monitoring Division (GMD) carries out measurements of GHGs and ozone depleting species through the Carbon Cycle Greenhouse Gases group (CCGG) and the Halocarbons and other Atmospheric Trace Species program (HATS). These programs measure several species using flasks, *in situ* stations, tall towers and aircraft. Standards for a very large range of species are prepared by the various groups at NOAA-ESRL and are often adopted by measurement networks worldwide (*e.g.,* Montzka, 1993; Hall *et al.,* 2007).

The CCGG collects flasks at approximately weekly intervals through a collaborative air-sampling network of over 80 surface sites worldwide (Dlugokencky *et al.,* 1994; **Figure 3.2.1**). Flasks are analyzed at Boulder, Colorado for CO_2, CH_4, CO, SF_6, H_2 and N_2O. A subset of flasks is also analyzed for stable isotopologues of CO_2 and CH_4 under the NSTARR program (Trolier, 1996). CCGG flasks are collected at a number of tall tower sites across the U.S. at approximately daily intervals (*e.g.,* Zhao *et al.,* 2009), and from a network of aircraft sites. Aircraft profiles are

also taken at a frequency of approximately one profile per week, with each flight sampling at 12 heights.

The HATS *in situ* monitoring network consists of six stations chosen to be in remote locations (see Figure 3.2.1). Measurements are performed using gas chromatographs (GC) with electron capture detectors (ECD) and mass spectrometric (MS) instruments (Geller *et al.,* 1997; Hall *et al.,* 2007). Using this setup, measurements of N_2O, SF_6, CFC-11, CFC-12 and CFC-113, CCl_4, CH_3Cl, CH_3CCl_3, bromochlorodifluoromethane (halon-1211) and HCFC-22 and -142b are measured at hourly time resolution.

In addition to the baseline *in situ* program, the HATS group also makes measurements of a larger number of gases from flask samples collected at approximately weekly frequency from 12 sites (*e.g.,* Montzka, 1993; 1994). The gases measured include several CFCs, HCFCs and HFCs, chlorinated hydrocarbons, methyl halides, halons, benzene, bromoform ($CHBr_3$) and COS.
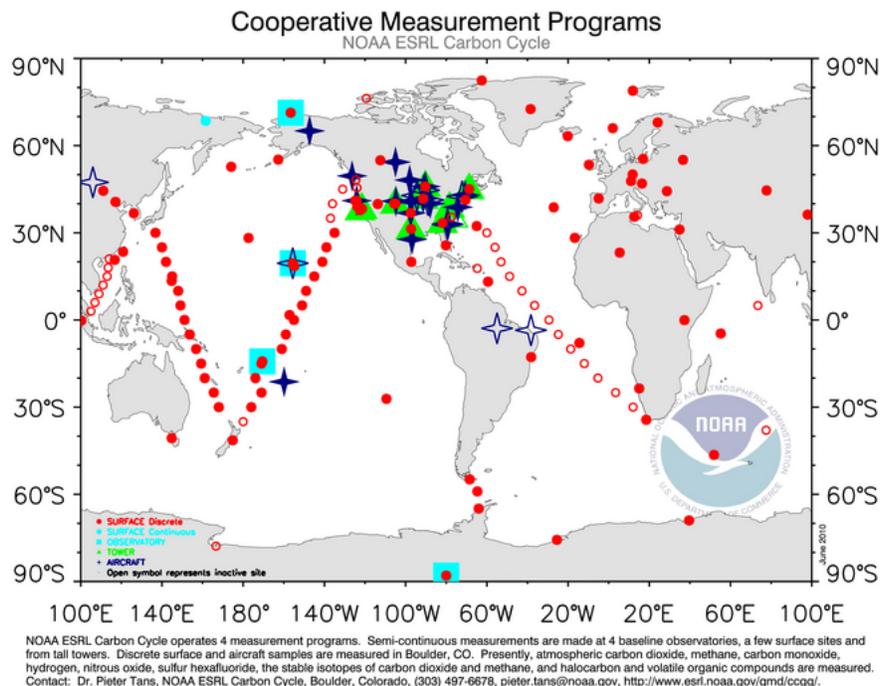
Figure 3.2.1. NOAA sampling locations. Red dots indicate surface flask sampling sites, red dots within blue squares show high-frequency *in situ* monitoring stations, crosses are aircraft profile locations and green triangles show tall-tower sites. (http://www.esrl.noaa.gov/gmd/ccgg/)

3.2.2 The Advanced Global Atmospheric Gases Experiment (AGAGE)

The Advanced Global Atmospheric Gases Experiment (AGAGE: 1993-2010), and its predecessors (Atmospheric Lifetime Experiment, ALE: 1978-1981; Global Atmospheric Gases Experiment, GAGE: 1981-1993) have measured the composition of the global atmosphere continuously since 1978 (Prinn *et al.*, 2000). The case for real-time high-frequency measurement networks like AGAGE is very strong and the observations and their interpretation are widely recognized for their importance to ozone depletion and climate change studies. AGAGE is distinguished by its capability to measure globally, at high frequency, 51 trace gases including all

of the important species (except CO_2) in the Montreal and Kyoto Protocols. The scientific objectives of AGAGE are of considerable importance in furthering our understanding of important global chemical and climatic phenomena.

The current ALE/GAGE/AGAGE stations are coastal or mountain sites located around the world (**Figure 3.2.2**): (a) on Ireland's west coast at Mace Head (53ºN, 10ºW); (b) on the U.S. west coast at Trinidad Head, California (41ºN, 124ºW); (c) at Ragged Point, Barbados (13ºN, 59ºW); (d) at Cape Matatula, American Samoa (14ºS, 171ºW); (e) at Cape Grim, Tasmania, Australia (41ºS, 145ºE); (f) on the Jungfraujoch, Switzerland (47°N, 8°E; 3.57 km), (g) on Zeppelinfjellet, Ny-Alesund, Svalbard, Norway (79°N, 12°E; 0.47 km); (h) at Gosan, Jeju Island, Korea (33ºN, 126ºE); (i) at Shangdianzi, China (40.7ºN, 117.1ºE, 0.29 km); (j) at Hateruma Island, Japan (24ºN, 123ºE); and (k) on Monte Cimone, Italy (44°N, 11°E, 2.17 km).

AGAGE uses *in situ* gas chromatography with mass spectrometry (the "Medusa" GC-MS system) to measure hydrochlorofluorocarbons (*e.g.,* HCFC-22) and hydrofluorocarbons (*e.g.,* HFC-134a), which are interim or long-term alternatives to CFCs now restricted by the Montreal Protocol, other hydrohalocarbons (*e.g.,* CH_3Cl), halons (*e.g.,* H-1211), perfluorocarbons (*e.g.,* CF_4), and trace CFCs, all of which (except CH_3Cl) are involved in the Montreal or Kyoto Protocols. At its 5 original stations, AGAGE also uses *in situ* gas chromatographs (GC) with electron-capture detection (ECD), flame-ionization detection (FID), and (at two of the stations) mercuric oxide reduction detection (MRD) to measure five biogenic/anthropogenic gases (CH_4, N_2O, and $CHCl_3$ at all sites; CO and H_2 at Ireland and Tasmania only), and five anthropogenic gases at all sites (CFCs-11, -12, -113, CH_3CCl_3, and CCl_4) 36 times per day. The list of gases measured with these 'GC-multidetector' or GC-MD systems includes the major chlorofluorocarbons (CFCs) restricted by the Montreal Protocol and the major long-lived non-CO_2 greenhouse gases. Each instrument system is under computer control. The data are calibrated against on-site air standards, calibrated relative to off-site parent standards before and after use at each station. AGAGE depends upon well-defined absolute gravimetric calibration procedures that are repeated periodically to assure the accuracy of the long-term measured trends.

Figure 3.2.2. Locations of the original 5 AGAGE stations (red boxes), and the 6 more recent AGAGE sampling stations. AGAGE and the other major global air-sampling network, NOAA-ESRL-GMD, are independent, but closely cooperating, including frequent inter-comparisons, especially at the Samoa shared site.

Notation: SOGE=System for Observation of Halogenated Greenhouse Gases in Europe, CMA= Chinese Meteorological Administration, NIES=National Institute for Environmental Studies, Japan, SNU=Seoul National University, Korea.

(http://agage.eas.gatech.edu/)
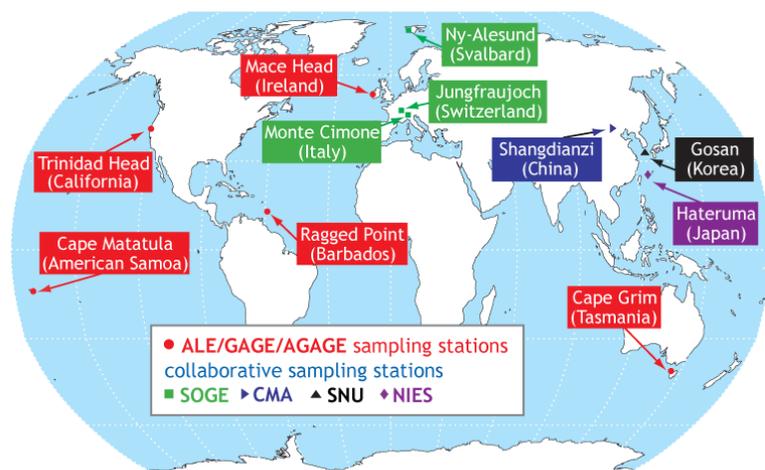
3.2.3 Network for the Detection of Atmospheric Composition and Change (NDACC)

Using a variety of ground-based remote sensing instruments, NDACC aims to monitor stratospheric and upper-tropospheric composition. Relevant to this report are several solar absorption Fourier transform infrared spectrometers (FTIR) that can obtain tropospheric- and column-averaged CH_4 and N_2O at 22 locations (Warneke *et al.,* 2006).

3.2.4 Total Carbon Column Observing Network (TCCON)

The NASA-run TCCON network obtains Fourier transform near-infrared spectra from which CO_2, CH_4, and N_2O columns can be retrieved (*e.g.,* Wunsch *et al.,* 2010). The ground-based network consists of 19 sites across the globe.

3.2.5 Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY)

Aboard the Envisat satellite, SCIAMACHY measures atmospheric trace species from transmitted, backscattered and reflected solar radiation in a range of spectral regions (Burrows *et al.,* 2005). Using the nadir-viewed near infrared channel, observations of reflected sunlight allow SCIAMACHY to retrieve column abundances of CO_2, CH_4 and N_2O (along with other species not directly relevant to this report). The typical spatial resolution of these observations is of the order of 30km North-South and 60 km East-West, with global coverage every 6 days. Pixels with a high cloud fraction and aerosol loading are generally removed, since high sensitivity to the surface is desired for inverse modeling purposes. Further, many ocean observations must be discarded, due to the low reflectance of the ocean surface. The CH_4 product has been used in inverse estimates of surface emission rates, and has an estimated absolute uncertainty of 2% (Meirink *et al.,* 2006; Frankenberg *et al.,* 2008; Bergamaschi *et al.,* 2009).

3.2.6 The Greenhouse Gases Observing Satellite (GOSAT)

Launched in 2009, the Japanese Aerospace Exploration Agency (JAXA) GOSAT satellite aims to produce global measurements of CO_2 and CH_4 from space (Yokota *et al.,* 2009). The satellite follows a sun-synchronous orbit at 666km above the surface, with a return time of 3 days. The main instrument onboard is the Thermal and Near-infrared Sensor for Carbon Observation–Fourier Transform Spectrometer (TANSO-FTS), which has a circular field of view of 10 km at nadir, and has an across-track scanning capability to extend the scanning range between orbital tracks. Over the ocean the instrument tracks the solar glint to overcome the low reflectivity of the ocean surface. The simulated density of measurements over a three-day period is shown in **Figure 3.2.3**. Work to characterize biases and accuracy of the GOSAT-TANSO-FTS instrument is ongoing, although for CO_2, the overall uncertainty is expected to be between 1.2 and 3.2 ppm, depending on solar zenith angle (Chevallier *et al.,* 2009).

3.2.7 The Orbiting Carbon Observatory (OCO)

The original OCO satellite failed to launch in February 2009. However, a follow-up mission is expected to fly in the next few years (OCO-2). The OCO was designed to follow a sun-
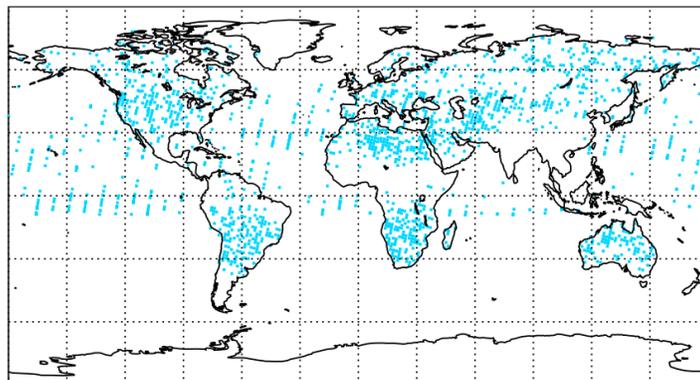
Figure 3.2.3. Simulated GOSAT retrieval locations during a 3-day period in July (Chevallier *et al*., 2009).

synchronous orbit with a return period of 16 days (Crisp *et al.,* 2004). By measuring reflected sunlight in the near infrared, the instrument was designed to have maximum sensitivity close to the boundary layer. The anticipated precision, and spatial resolution are expected to be somewhat higher than GOSAT, at ~1 ppm (for CO_2) and 1 x 1.5 km respectively (Connor *et al.,* 2008). The specified accuracy and anticipated spatial coverage of the OCO instrument (taking into account rejection of pixels due to cloud and aerosol contamination) has been shown to lead to significant error reduction in surface CO_2 flux estimates (Chevallier *et al.,* 2007). However, potential regional biases (related to *e.g.,* aerosol scattering) have been shown to lead to significant uncertainty in the derived emissions fields (see below).

3.2.8 NASA Atmospheric Infrared Sounder (AIRS)

The AIRS instrument, flying on the NASA Aqua satellite, follows a near-pole, sun-synchronous orbit and allows CO_2 and CH_4 to be retrieved throughout the day and with global coverage (Chahine *et al.,* 2008; Xiong *et al.,* 2008). The peak sensitivity of the instrument lies in the mid- to upper troposphere. However, some sensitivity has been found to surface emissions (Chahine *et al.,* 2008, Xiong *et al.,* 2009). The spatial resolution of the observations is around 90km x 90km, with an accuracy of around 0.5% for CO_2 and 2% for CH_4.

3.2.9 Civil aircraft for the regular investigation of the atmosphere based on an instrumented container (CARIBIC)

The CARIBIC system uses commercial aircraft to carry an instrumented container that can make measurements of a number of species in the upper troposphere (Brenninkmeijer *et al.,* 2007). CO_2 measurements are made *in situ* at high frequency and 28 flask samples are collected per flight, for laboratory measurement of CH_4, N_2O, SF_6 and halocarbons. Flights from Frankfurt to South America or South-East Asia are flown approximately once per month.

3.2.10 Other atmospheric observations

In addition to the global monitoring networks outlined above, there are regional networks that submit their data to the World Meteorological Organization's Global Atmosphere Watch program (WMO-GAW, http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html).

Table 3.2.1. Existing atmospheric measurements of Kyoto protocol greenhouse gases.

Pollutant	Type		Network	Spatial Coverage	Temporal Resolution	Approximate Uncertainty
CO_2	Surface	Flask sampling	NOAA-ESRL	84 sites	~weekly	0.1 ppm
		Ships	NOAA-ESRL	3 ship tracks	~monthly	0.1 ppm
		In situ	NOAA-ESRL	6 sites	hourly	0.1 ppm
		Flask/*in situ*	Other WMO-GAW contributors	~100 sites	hourly - monthly	0.1 ppm
		Tall tower	NOAA-ESRL	9 sites, N. America only	~daily	0.1 ppm
		Isotopologue	NSTARR	20 sites	~monthly	
	Aircraft	Flask	NOAA-ESRL	31 sites	~ weekly	0.1 ppm
			NASA-CONTRAIL	W. Pacific	~monthly	0.1 ppm
		High frequency	HIPPO	Pole-to-pole	6-monthly	0.1 ppm
	Remote sensing	Satellite	GOSAT	~60S-60N	~3-day return time	3 ppm
			AIRS	30S to 90N, 90km x 90km, mid-troposphere	~3 day return time	1.5-2ppm
			OCO	~60S-60N	6-day return time	1ppm
		Surface column FTIR	TCCON	21 sites	high frequency	1ppm
CH_4	Surface	*In situ*	AGAGE	11 sites	hourly	2ppb
		Flask sampling	NOAA-ESRL	84 sites	~weekly	2 ppb
		Ships	NOAA-ESRL	3 ship tracks	~monthly	2 ppb
		In situ	NOAA-ESRL	6 sites	hourly	2 ppb
		Flask/*in situ*	Other WMO-GAW contributors	~100 sites	hourly - monthly	1-4 ppb
		Tall tower	NOAA-ESRL	9 sites, N. America only	~daily	2 ppb
	Aircraft	Flask	NOAA-ESRL	31 sites	~weekly	2 ppb
	Remote sensing	Satellite	SCIAMACHY	60S-60N		15-30 ppb
			AIRS	30S to 90N, 90km x 90km, upper troposphere	~3 day return time	30 ppb
		Surface column FTIR	TCCON	21 sites	high frequency	4ppb
N_2O	Surface	*In situ*	AGAGE	11 sites	hourly	0.4ppb
		Flask sampling	NOAA-ESRL	~ 20 sites?	~monthly	0.4ppb
		In situ	NOAA-ESRL	6 sites	hourly	0.4ppb
	Remote sensing	Surface column FTIR	TCCON	21 sites	high frequency	1.5ppm
HFCs	Surface	*In situ*	AGAGE	9 sites	hourly	<1%
		Flask sampling	NOAA-ESRL	~ 20 sites	~monthly	<1%
CFCs	Surface	*In situ*	AGAGE	11 sites	hourly	<1%
		Flask sampling	NOAA-ESRL	~ 20 sites?	~monthly	<1%
		In situ	NOAA-ESRL	6 sites	hourly	<1%
PFCs	Surface	*In situ*	AGAGE	9 sites	hourly	<1%
		Flask sampling	NOAA-ESRL	~ 20 sites (C_2F_6 only)	~monthly	<1%
SF_6	Surface	*In situ*	AGAGE	11 sites	hourly	1-2%
		Flask sampling	NOAA-ESRL	~ 40 sites	~weekly	1-2%
		Ships	NOAA-ESRL	1 ship track	~monthly	1-2%
		In situ	NOAA-ESRL	6 sites	hourly	1-2%
		Flask	Other (*e.g.,* U. Heidelberg)	~10 sites	~monthly	1-2%
		Tall tower	NOAA-ESRL	6 sites, N. America only	~daily	1-2%
	Aircraft	Flask	NOAA-ESRL	31 sites	~weekly	1-2%

Many other atmospheric measurements exist which will be useful to incorporate into a global trace gas observing system. For example, estimates of CO_2 fluxes (and many other GHGs) at the scale of urban areas can be measured using eddy covariance techniques (*e.g.,* Helfter *et al.,* 2010). These measurements must be made at elevated locations well above the urban canopy layer (*e.g.,* communications towers). Similarly, small-scale flux estimates can be made through measurement of the vertical profile of atmospheric gases, combined with observations of boundary layer turbulence. At even smaller scales, the outflow from chimneys at individual industrial facilities can be monitored and included in very detailed emissions estimation schemes.

3.3 Natural and Managed Land Ecosystems

A variety of data at site, regional and continental-to-global scales have been used to parameterize and evaluate land surface models (**Table 3.3.1**). Information from intensively studied field sites are normally used to calibrate the models; and data from other field sites or times other than the calibration period are used to evaluate the models (Raich *et al.,* 1991; McGuire *et al.,* 1992, 2002; Melillo *et al.,* 1993; Kicklighter *et al.,* 1994; Tian *et al.,* 1998; Amthor *et al.,* 2001; Clein *et al.,* 2002; Zhuang *et al.,* 2001, 2002, 2003; Hayes *et al.,* 2011).

Site-specific data have included field-based estimates of standing vegetation biomass, stocks of soil organic carbon and nitrogen, stocks of inorganic nitrogen, litterfall, net primary production (NPP), net nitrogen mineralization, net ecosystem exchange (NEE) from eddy covariance studies, soil respiration, evapotranspiration, soil temperatures, soil moisture, soil methane emissions and uptake, and soil nitrous oxide emissions.

Model estimates have also been evaluated through comparisons with site-specific experimental responses to warming, nitrogen fertilization, and increased atmospheric CO_2 concentration (Clein *et al.,* 2000). In addition, the results of chronosequence studies have been used to evaluate the ability of models to simulate the recovery of ecosystems after a disturbance (Pan *et al.,* 2002; Zhuang *et al.,* 2002). At the regional scale, model estimates of carbon storage have been compared to inventory-based estimates of NPP (Jenkins *et al.,* 2001), vegetation biomass (Jenkins *et al.,* 2001; Zhuang *et al.,* 2003; Balshi *et al.,* 2007; Hayes *et al.,* 2011) and soil carbon (Tian *et al.,* 2011). In addition, model estimates of water yield have been evaluated against river discharge for watersheds across the United States (Gordon *et al.,* 2004; Felzer *et al.,* 2009).

At continental-to-global scales, model "bottom-up" estimates for carbon exchange have been evaluated with comparisons to "top-down" inverse modeling results based on atmospheric CO_2 data at seasonal (Heimann *et al.,* 1998; McGuire *et al.,* 2000; Dargaville *et al.,* 2002; Zhuang *et al.,* 2003), inter-annual (McGuire *et al.,* 2001; Dargaville *et al.,* 2002; Hayes *et al.,* 2011; Tian *et al.,* 2011), and longer term (Balshi *et al.,* 2007) scales. Model estimates have also been compared with remote-sensing estimates for gross and net primary production (Kimball *et al.,* 2007; Tian *et al.,* 2011), snow cover (Euskirchen *et al.,* 2006), soil freeze thaw (Euskirchen *et al.,* 2006), and growing season length (Euskirchen *et al.,* 2006).

Table 3.3.1. Terrestrial ecosystems and biogeophysical data sets.

Extent	Variable	Measurement type	Frequency	Period	Sources
global	leaf area index, biomass and biomass increment	satellite (NDVI, EVI): modeling	once every 8 to 15 days	1980s to present	AVHRR[a], MODIS[b]
	Net primary production	satellite: modeling	Annual	2001 to present	MODIS[b]
	Gross primary production	satellite: modeling	once every 8 days	2001 to present	MODIS[b]
	Snow water equivalent	satellite: modeling	Monthly	1978-2003	NSIDC[c]
	surface temperature	satellite	4 times per day	1980s to present	AVHRR[a]/SSMI[d]
subglobal/ large areas	biomass and biomass increment	field measurements from long-term plots	once every 5 to 10 years	1920s to present	Forest Inventories[e]
	Water yield, water chemistry	gaged watersheds	Periodic	1960s to present	USGS reports[f]
Site	Latent heat exchange, net ecosystem exchange	Eddy covariance tower measurements	Hourly	1992 to present	FLUXNET[g]
	biomass and biomass increment	field measurements	Periodic	1960s to present	FLUXNET[g], ILTER[h], IBP[i]
	litterfall, leaf area index, net N mineralization	field measurements	Periodic	1960s to present	ILTER[h], IBP[i]
	Net primary production	field measurements	periodic	1960s to present	FLUXNET[g], ILTER[h], IBP[i]
	methane, nitrous oxide	field measurements	periodic	1990s to present	ILTER[h], TRAGNET[j], DNDC[k], CarboEurope[l], literature[m]

[a] Advanced Very High-Resolution Radiometer (AVHRR) 8-km data (Chen and Cihlar, 1997; Myneni *et al*., 2001).

[b] Moderate Resolution Imaging Spectroradiometer (MODIS) 1 km data (http://modis.gsfc.nasa.gov).

[c] Available from National Snow and Ice Data Center (NSIDC) as described by Armstrong *et al*. (2005).

[d] Spatial resolutions of retrievals are 3 km for AVHRR and 25 km for Special Sensing Microwave Imager (SSMI).

[e] Data available from forest inventories conducted in the USA, Canada, Russia, Finland, Norway and Sweden (Birdsey and Heath, 1995; Penner *et al*., 1997; Caspersen *et al*., 2001; Myneni *et al*., 2001; Janssens *et al*., 2003; Zhuang *et al*., 2003; Smith *et al*., 2001, 2004; Smith and Heath, 2005).

[f] Water discharge and quality data from ~1.5 million sites in the USA & Puerto Rico (http://waterdata.usgs.gov/nwis).

[g] Data from over 300 tower sites from the global FLUXNET network (http://www-eosdis.ornl.gov/FLUXNET) are potentially available after obtaining agreements with the corresponding PIs at each site. TEM estimates have been compared to FLUXNET data (Clein *et al*., 2002; Amthor *et al*., 2001; Potter *et al*., 2001; Felzer *et al*., 2006).

[h] Data from the International Long Term Ecological Research (ILTER, http://www.ilternet.edu) network, which consists of a series of research networks of intensively studied field sites within 28 countries.

[i] International Biological Programme predates the LTER. Data collected at IBP sites, along with other less intensively studied sites (NPP, biomass, LAI, soil characteristics), are freely available (http://www-eosdis.ornl.gov).

[j] Data from 29 sites of the Trace Gas Network (Ojima *et al*., 2000; http://www.nrel.colostate.edu/projects/tragnet/).

[k] Global DNDC Network (http://www.globaldndc.net) reports field measurements of nitrous oxide and methane emissions used to evaluate the DNDC model.

[l] Soil observation network of CarboEurope (Schulze *et al*., 2009)

[m] Surveys include 143 sites reported in Xu *et al*. (2008) and Schulze *et al*. (2009)

3.4 Economics Datasets

The data needed for an economic model consists primarily of two kinds: data on the economic output of greenhouse gas emitting sectors, and emission factors that give the ratio of emissions per unit of economic activity. In addition, trade-flow information will also be needed. For an initial model, much of the economic activity data is readily available from international organizations such as the International Energy Association (IEA) and the Food and Agriculture Organization (FOA). The IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006) and scientific literature provide estimates of emissions factors. An overview of data identified to construct an economic model for GHG producing economic sectors is given in **Table 3.4.1**.

Although the data identified covers the majority of GHG emissions, additional data will need to be identified for certain specific industrial processes that are largely related to HFC, PFC, and SF_6 emissions.

As part of a coupled atmosphere-ocean-biosphere-economics model, estimates of the uncertainty surrounding this data must also be available. Uncertainty in emissions factor estimates is thoroughly considered in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories as well as in scientific literature. In their guidelines, the IPCC provides upper and lower limits for the 95% confidence interval for emissions factors across all major greenhouse gas emitting sectors. The uncertainty in these estimates varies widely depending on the specific technology being considered. Emissions factors for fuels are tightly bound since the carbon content of each fuel is precisely known. In crude oil for example, the emission factor for carbon is 20.0±0.6 (kg C GJ^{-1}). In contrast, emissions factors for enteric fermentation in cattle can range from 27-128 (kg CH$_4$ head^{-1} year^{-1}) depending on the kind of cow—*i.e.* dairy or beef—and the livestock's environment.

As mentioned in Section 2.4.3, having higher geographical resolution of the economic data within each country would be useful in decreasing uncertainty when mapping emissions

Table 3.4.1. Source Data for Economic Activity and Emissions Factors.

Description	IPCC Code	Economic Activity Data	Emissions Factor Data
Mobile and Stationary Combustion	1A, 1C	IEA, FAO	IPCC (2006)
Fugitive Emissions: Coal, Oil, Gas	1B	IEA, CDIAC, EIA, FAO	IPCC (2006), CIAB (1994), EURACOAL (2008), Kirchgessner *et al.* (1993)
Industrial Processes and Solvents	2, 3	USGS, IEA, UN Industrial Commodity Statistics, IFA, AFEAS, McCulloch *et al.* (2000), ESIA, Chemical Week (1999)	IPCC (2006)
Livestock	4A, 4B, 4D2	FAO	IPCC (2006)
Rice cultivation	4C	FAO, IRRI	IPCC (2006)
Agricultural soils	4D	IFA	IPCC (2006), Bouwman *et al.* (2002), Van Drecht *et al.* (2003)
Large scale biomass burning	4E, 4F, 5A, 5C, 5D, 5F	FAO, GFED	Andreae and Merlet (2001)
Soild waste and waste incineration	6A, 6C	CRF/UNFCCC	IPCC (2006)
Wastewater handling	6B	U.N. Industrial Commodity Statistics	IPCC (2006), Doorn and Liles (1999), Doorn *et al.* (1997)

estimated from economic activity to a global grid. As was explained earlier, this can be achieved through the use of detailed input/output (I/O) data of each country combined with geographical information systems (GIS). In this approach the emissions factors provided by the IPCC and scientific literature would still be used, but the more aggregate economic activity data presented in Table 3.4.1 would be replaced with the more detailed I/O data. Although the process of collecting extensive I/O data for the world would require significant effort, examples of some I/O data that could be used are given in **Table 3.4.2**.

Table 3.4.2. Input/Output Databases.

I/O Database	Regions	Source
EXIOPOL	EU25	EXIPOL (2010)
WIOD	All major countries	WIOD (2010)
IDE	Asia, Middle East, Africa, Latin America	IDE (2010)
OECD	OECD countries	OECD (2005)

4. ESTIMATION METHODS, UNCERTAINTY QUANTIICATION, AND OBSERVING SYSTEMS

4.1 Introduction

A comprehensive framework which combines the two main knowledge reservoirs, observations (+ errors) and models (+ errors), is essential for quantifying global and regional CO_2 concentrations and fluxes, along with their uncertainties. The framework serves several goals:

- Combine diverse types (in terms of variables measured) of (mostly) disparate (in terms of spatial and temporal sampling) observations,
- Use best-possible knowledge of the dynamics and physics encapsulated in a model as dynamical interpolator between all available observations, and which fulfills known conservation laws,
- Combine all sources of prior uncertainty estimates for model parameters, observation errors, and representation errors,
- Inverse uncertainty propagation: use inverse methods to infer optimal parameter estimates along with posterior parameter uncertainties, in the context of the available observations, their errors, and prior parameter uncertainties,
- Forward uncertainty propagation: use optimal parameter estimates and their posterior uncertainties to calculate prognostic fields and derived target variables (*e.g.,* regional or country-based CO_2 emissions, atmospheric concentrations and their changes, fluxes between different components, *etc.*).

The framework enables optimality studies of various types:

- Optimal estimation: infer best estimates of emissions and their posterior uncertainties,
- Optimal control: determine target CO_2 emissions, which optimize (usually minimize) a pre-defined target quantity (objective function), such as global or regional CO_2 emissions or derived physical properties (global-mean surface air temperature, sea level, *etc.*),
- Optimal observing systems: assess, which observations (types, spatial and/or regional sampling, required accuracy) have the most impact on reducing uncertainties in target quantities.

Without such a quantitative framework, no rigorous data-synthesis is available, no systematic use of basic conservation laws or knowledge of transport processes is made, and no connection can be made between observation and sampling errors on the one hand and parameter and target uncertainty on the other hand. Thus, what appears as an added-on effort is in fact a central ingredient to any comprehensive observation/verification system strategy.

In the following we lay out the different steps required for end-to-end uncertainty quantification (from observations to estimated or projected target quantities). These steps are (1) the definition of target quantities (emission rates), (2) the formulation of a control problem which involves a model that relates uncertain control variables (also called active variables) to the target quantity, subject to passive boundary conditions, (3) the formulation of an inverse/optimization problem, in which the model is fit to the observations through adjustment of the uncertain control variables, (4) an inventory of the sources of error in the observations, model parameters, structural model error, and estimation procedure, (5) inverse propagation of prior observation uncertainties to posterior control variable uncertainties as part of the solution of the inversion/optimization, (5) forward propagation of control uncertainties to target or projection uncertainties.

We realize that the described pipeline is fairly specific and discards alternative UQ methods available (in general, ensemble-based or Monte Carlo methods). Justification for the proposed route is what has been termed "the curse of dimensionality", *i.e.* the need to deploy methods that can handle high-dimensional uncertain parameter (control) spaces (see *e.g.,* the Department of Energy 2009 report on "*Scientific Grand Challenges in National Security: The Role of Computing at the Extreme Scale*"; Bishop *et al.*, 2009). This requirement precludes many of the mathematically elegant methods as unfeasible in practice.

4.2 The coupled forward model

The overall model-coupling framework was presented in Figure 2.5.1. We re-iterate that the coupled approach is essential to better constrain the significant background fluxes and to isolate anthropogenic contributions. The generic components of such a system consist of an atmospheric chemical transport model (A-CTM), an ocean biogeochemical transport model (O-BioTM), a land biogeophysical, hydrology, and ecosystem model (L-BPHEM), and an economics model (E). Each of these models is driven by physical flow fields (atmospheric circulation, ocean circulation, land surface fluxes), which are obtained from state-of-the-art "reanalysis" or state estimation projects (*e.g.,* http://ecco-group.org/). We re-emphasize the crucial role of such flow fields, whose availability and improvement is critical, but not pursued as part of this proposal. Instead, we are looking to the relevant agencies to ensure the sustained production of fields of ever-increasing quality. A long-term perspective would envision the joint treatment of both dynamical and tracer fields in a comprehensive Earth-system model inversion.

For the sake of clarity, we describe in the following a specific coupled framework which is composed of a concrete set of model components, all of which have either been directly developed at MIT, with significant MIT contributions, or which are considered as well-suited for

use in a formal estimation framework such as described here. The key models considered are (i) for the ocean: the MIT ecosystem model driven by the ECCO state estimates (BioECCO), (ii) for the atmosphere: MOZART driven by atmospheric reanalyses, and (iii) for the land: TEM/CLM. Critical coupling interfaces are those between BioECCO and MOZART, as well as between MOZART and TEM/CLM. The coupling procedures are well established, and have been implemented in part in the context of the specific framework through construction of the MIT Integrated Global System Model (Prinn *et al*., 1999; Sokolov *et al*., 2005), which includes in its latest version TEM/CLM (McGuire *et al.,* 2010; Bonan and Levis, 2010) and a simplified version of the MIT ocean general circulation model (Marshall *et al*., 1997a,b) including biogeochemistry (Dutkiewicz *et al*., 2005). We also have significant experience in coupling an atmospheric dynamics model with the above MIT ocean model through the MIT Climate Modeling Initiative (http://paoc.mit.edu/cmi).

Following essentially the notation of Wunsch (2006) we write the basic structure of the equations for the coupled system. We first consider separately the atmospheric component (subscript *A*), and the combined ocean and terrestrial system (subscript *TO*):

$$
\begin{aligned}
L_A &: x_A(i) &\longmapsto x_A(i+1) &= L_A\big(x_A(i), Bq_A(i), \Gamma u_A, t\big) \\
L_{TO} &: x_{TO}(i) &\longmapsto x_{TO}(i+1) &= L_{TO}\big(x_{TO}(i), Bq_{TO}(i), \Gamma u_{TO}, t\big)
\end{aligned}
\tag{4.2.1}
$$

where L_A is the atmospheric transport model, and L_{TO} refers to the Terrestrial Ecosystem Model (*T*) and ocean (*O*) biogeochemistry model. L_A carries forward in time the model state of atmospheric CO_2 concentrations, x_A, and is modified by boundary fluxes Bq_{TO} of CO_2 (from the terrestrial and the oceanic components). Although very different in nature, they can be conceptually described by the same operators and, therefore, are combined here. Both components *T, O*, are forced by atmospheric partial pressure $q_A = pCO_2$, plus other passive fluxes.

For our system, the required time steps for atmospheric (Dt_A), ocean (Dt_O), and land terrestrial (Dt_T) component models are: $Dt_A < Dt_O < Dt_T$. The whole system synchronizes at the end of every time step of TEM/CLM. The commonly used data, such as atmospheric ozone concentration and reanalysis meteorological data, will be distributed by the coupler to each of the component models when needed.

In addition to the equations for the separate models we have available equations, linking the state of one component to fluxes required by the other component, which establishes the coupling:

$$
\begin{aligned}
M_{A2TO} &: x_A(i) &\longmapsto q_{TO} = M_{A2TO}\big(x_A(i)\big) \\
M_{TO2A} &: x_{TO}(i) &\longmapsto q_A = M_{TO2A}\big(x_{TO}(i)\big)
\end{aligned}
\tag{4.2.2}
$$

In the present case, the coupler *MA2TO* converts partial pressures pCO_2 into mean concentrations $q_{TO} = c(CO_2)$ needed by the BioECCO and TEM models. *MTO2A* converts terrestrial and oceanic CO_2 concentrations into CO_2 fluxes required by the atmosphere. In the coupled system q_A and q_{TO} are no longer boundary values, but part of the coupled model state:

$$
x_C(i) = \big[x_A(i), q_A(i), x_{TO}(i), q_{TO}(i)\big]^T
\tag{4.2.3}
$$

and one full timestep of the coupled system may be written, as a composition (we assume synchronous coupling, the asynchronous case is just a matter of index bookkeeping):

$$L_C \; : \; x_C(i) \; \longmapsto \; x_C(i+1) \; = \; L_C\left(x_C(i), Bq_{DYN}, \Gamma u_C, t\right) \tag{4.2.4}$$

with composition:

$$L_C \; = \; M_{TO2A} \circ L_{TO} \circ M_{A2TO} \circ L_A \tag{4.2.5}$$

The flow through the active coupled system then has the following structure:

$$
\begin{array}{ccc}
\left(x_A(i), q_A(i)\right) & \overset{L_A}{\longrightarrow} & x_A(i+1) \\
\uparrow & & \downarrow \\
q_A(i+1) & & q_{TO}(i) \\
\uparrow & & \downarrow \\
x_{TO}(i+1) & \overset{L_{TO}}{\longleftarrow} & \left(x_{TO}(i), q_{TO}(i)\right)
\end{array}
\tag{4.2.6}
$$

Forward integration of the coupled model will first be performed with the initial or reference values for all state vector elements (*x*), control parameters (*u*), *etc.*, followed by a series of integrations and use of the tangent linear versions of the models to examine key sensitivities of carbon fluxes, *etc.*, to oceanic, land ecosystem, land hydrology and human activity. **Table 4.2.1** lists potential state vector elements and Tables 2.1.2 and 2.2.3 list potential controls. Tables 3.1.1, 3.2.1, 3.3.1 and 3.4.1 list potential observations to compare with the state vectors.

Table 4.2.1. State vectors (partial list); see Tables 3.1.1, 3.2.1, 3.3.1, 3.4.1 for other potential candidates.

Atmosphere	greenhouse gas mole fraction, column CO_2, CH_4, *etc.*, flux CO_2
Ocean Biogeochemistry	tracer distributions (PO_4, alkalinity, DIC, O_2), ocean surface pCO_2, air-sea flux, biological export through 100 m, surface chlorophyll
Terrestrial	Vegetation C, vegetation structural N, vegetation labile N, reactive soil organic C and N, soil inorganic N

4.3 Inverse method and inverse uncertainty propagation

4.3.1 Gradient-based solution of the least-squares model-data misfit problem

The first step in the uncertainty quantification framework consists in the model *vs.* data synthesis or state estimation procedure, *i.e.* the optimal fit of the coupled model to all available observations, as well as its associated *inverse* uncertainty propagation from observation uncertainties to control variable uncertainties. Using the notation of control theory, we formulate the state estimation system as an *objective function*, *J*, which maps a set of so-called *independent* variables, or *controls*, *u*, which can be varied/tuned to a scalar-valued *dependent* variable that is a diagnostic (*i.e.* function) of the *model state* variables, *x*. Here, the *model L* refers to a mapping that carries a set of model state variables forward in time from t_i to t_{i+1} (note that the model is thus a partial function of the full objective function).

Any variable that can be affected by changes in any of the control variables is referred to as active, variables that remain unaffected are passive. For the coupled problem we distinguish two branches. In the first branch, the coupling of the active components is considered, in the present case the carbon fluxes between the components. This branch is the one that will be modified as part of the estimation problem to minimize the objective function. In a second branch, all remaining aspects of the system are considered that will not change during the optimization. This branch includes the atmospheric and oceanic dynamics, which we assume as given.

Through variation of the controls u_C (and initial conditions $x_C(t=0)$) of the coupled system we seek a solution of the coupled state $x_C(t)$, which minimizes J. A schematic of the iterative method is given in **Figure 4.3.1**. The general structure of J consists of four sums measuring: (1) the departure of the initial state $x_X(0)$ from a first guess x_{X0}; (2) the misfit between observations $y_X(t)$ at time t and the model projected onto the observation $E(t)x_X(t)$; (3) the deviation of the controls $u_X(t)$ from a prior; and (4) imposing that $x_C(t)$ satisfy the model equations L_C through the introduction of Lagrange multipliers $\mu_C(t)$.

$$J = \sum_{\Xi}^{A,T,O} \left[x_\Xi(0) - x_{\Xi_0} \right]^T P(0)^{-1} \left[x_\Xi(0) - x_{\Xi_0} \right]$$

$$+ \sum_{\Xi}^{A,T,O} \sum_{t=0}^{t_f} \left[E(t)x_\Xi(t) - y_\Xi(t) \right]^T R(t)^{-1} \left[E(t)x_\Xi(t) - y_\Xi(t) \right]$$

$$+ \sum_{\Xi}^{A,T,O} \sum_{t=0}^{t_f-1} u_\Xi(t)^T Q(t)^{-1} u_\Xi(t)$$

$$- 2 \sum_{\Xi}^{A,T,O} \sum_{t=0}^{t_f} \mu_\Xi(t) \left[x_\Xi(t) - L_\Xi[...] \right]$$

$$- 2 \sum_{t=0}^{t_f} \mu_{A2TO}(t) \left[q_{TO}(t) - M_{A2TO}[x_A(t+1)] \right]$$

$$- 2 \sum_{t=0}^{t_f} \mu_{TO2A}(t) \left[q_A(t+1) - M_{TO2A}[x_{TO}(t+1)] \right]$$

$$(4.3.1)$$

Instead of absorbing all three model components under the subscript C we have written them out here as sum over $X = \{A,T,O\}$ in order to show that each component is constrained by its own set of observations y_X, and is endowed with its own set of controls u_X. We have also separated L_C, μ_C into the contributions from the individual models L_X, μ_X and the coupling functions M_{A2TO}, μ_{A2TO} and M_{A2TO}, μ_{TO2A}.

A crucial element of the system are the weight matrices $P(0)$, $R(t)$, $Q(t)$, which for weighted least-squares can be interpreted as inverse error covariances, or prior uncertainties. The solution will depend on the availability of estimates of the uncertainties for the initial state vector values, observations to be compared with the state vector, and the model control parameters as discussed in Section 2. In general, the full covariances are not available, and are approximated by diagonal matrices representing estimated variances, potentially augmented by a Laplacian operator as an approximation to the covariance structure and acting de facto as a smoothness constraint.

From a control theory point of view, J is a scalar-valued function of control space:

$$J : u_C \longrightarrow J(u_C) \tag{4.3.2}$$

The model constraints impose equations that lead to the composite mapping:

$$J : u_C \longrightarrow x_C = L_C(u_C) \longrightarrow J(L_C(u_C)) \tag{4.3.3}$$
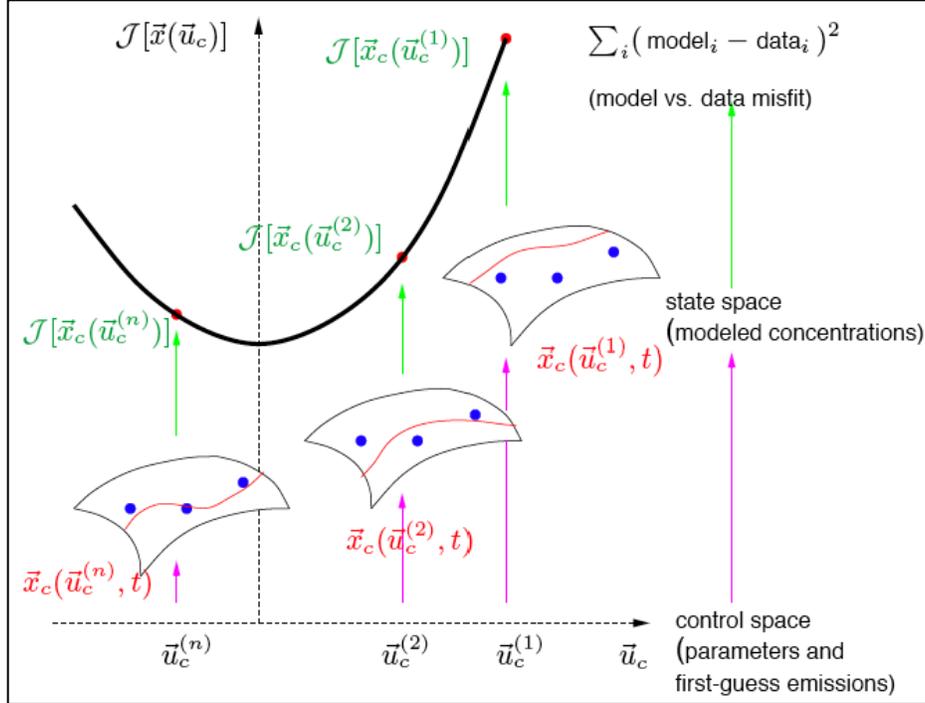
Figure 4.3.1 Schematic of the iterative minimization of the modeled (red trajectory) *vs.* observed (blue dots) concentration misfit J, through variation of the control variables. The optimal fit is achieved for adjusted controls (parameters and emissions) $u = u_c(n)$, which leads to best-estimate concentrations $x = x_c(n)$.

We seek to vary u_C such as to minimize J via gradient-based optimization algorithms (steepest descent, conjugate gradient, Newton method). The gradient is obtained by applying the chain rule to the composite mapping. We obtain the general structure:

$$\nabla_{u_C} J = \left(\frac{\partial x_C}{\partial u_C}\right)^T \left(\frac{\partial x_J}{\partial x_C}\right)^T \delta J^T \tag{4.3.4}$$

The terrestrial and the oceanic components are influenced, not only by the control parameters for each model (see Tables 2.1.2 and 2.3.2), but also by variables that relate to the passive coupling branch (*e.g.,* shortwave radiation for the ocean, hydrological quantities for the terrestrial system). These variables cannot be made control variables. If they were, the dynamical state of the system, *i.e.* the atmospheric and oceanic transport, would become active and change as a consequence of changes to these controls. This control problem is much more complex, and is not attempted here. We will instead explore methods to capture aspects of these sensitivities without altering the dynamic state, or violating energy, momentum or water budgets.

The global carbon adjoint system depicted in Figure 2.5.1 consists of four main components: (i) MOZART (CTM), (ii) TEM, and (iii) BioECCO (iv) ECONOMICS. The Community Land Model (CLM) will be regarded, in the context of a coupled control problem, as a sub-component of TEM. The coupled dynamical cycle consists of: (1) the momentum cycle, (2) the hydrological cycle (precipitation, freshwater, runoff, moisture, *etc.*), and (3) the energy cycle (temperature, radiation, *etc.*).

The set of all relevant variables could be termed the *dynamical state*: $d_C(t) = [d_A(t), d_{TM}(t)]^T$. This state is fully prescribed by the combined NCEP, ECCO, and CLM-derived fields (in short NEC), and is not altered as a consequence of the state estimation. All associated variables are thus passive. A flow diagram might look as follows:

$$
\begin{array}{ccccc}
(d_A, f_A, f_{NEC})(i) & \xrightarrow{MOZART} & & & d_A(i+1) \\
\uparrow & \nwarrow & & & \downarrow \\
f_A(i+1) & & NCEP/ECCO/CLM & & f_{TO}(i) \\
\uparrow & & & \searrow & \downarrow \\
d_{TO}(i+1) & \xleftarrow{TEM/OBGC} & & & (d_{TO}, f_{TO}, f_{NEC})(i)
\end{array}
\tag{4.3.5}
$$
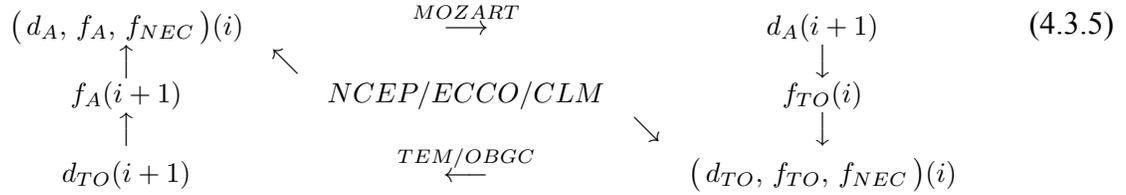
Besides its key role in the state vector and model parameter estimations, the global adjoint system will be used to analyze the origin of observed anomalies in terms of specific model properties and initial conditions. This linking of effects to causes will be invaluable in addressing our scientific objectives.

4.3.2 Hessian-based inverse uncertainty propagation

The solution to the statistical least-squares problem results in a set of control variables, which, applied to the model, minimize the model *vs.* data misfit. In a similar way that the first derivative of the misfit function with respect to the controls (the gradient) provides a powerful tool in the optimization, the second derivative (the Hessian) evaluated at the minimum yields important information regarding the uncertainties. A general expression of our least-squares misfit function formulated earlier, and its approximate form is (see **Figure 4.3.2**):

► Consider linear approx. of cost function

$$J(\vec{u}_c) = \frac{1}{2} (L(\vec{u}_c) - \vec{y})^T R_{prior}^{-1} (L(\vec{u}_c) - \vec{y})^T$$

$$\approx \frac{1}{2} (\vec{u}_c - \vec{u}_{c_0})^T \left(\frac{\partial L}{\partial u}\right)^T R_{prior}^{-1} \left(\frac{\partial L}{\partial u}\right) (\vec{u}_c - \vec{u}_{c_0})$$

► Compare to multivariate Gaussian distribution

$$\mathcal{N}(\vec{u}, R) \propto \exp\left[(\vec{u}_c - \vec{u}_{c_0})^T R_{prior}^{-1} (\vec{u}_c - \vec{u}_{c_0})\right]$$

► posterior error covariance matrix R_{post}^{-1} is inverse of Hessian H of $J(\vec{u}_c)$:

$$H = d_u^2 J(\vec{u}_{c_{opt}})$$

$$\approx \left(\frac{\partial L}{\partial u_c}\right)^T R_{prior}^{-1} \left(\frac{\partial L}{\partial u_c}\right)$$

$$= R_{post}^{-1}$$

► Eigenvalues of H: principal curvatures r_i
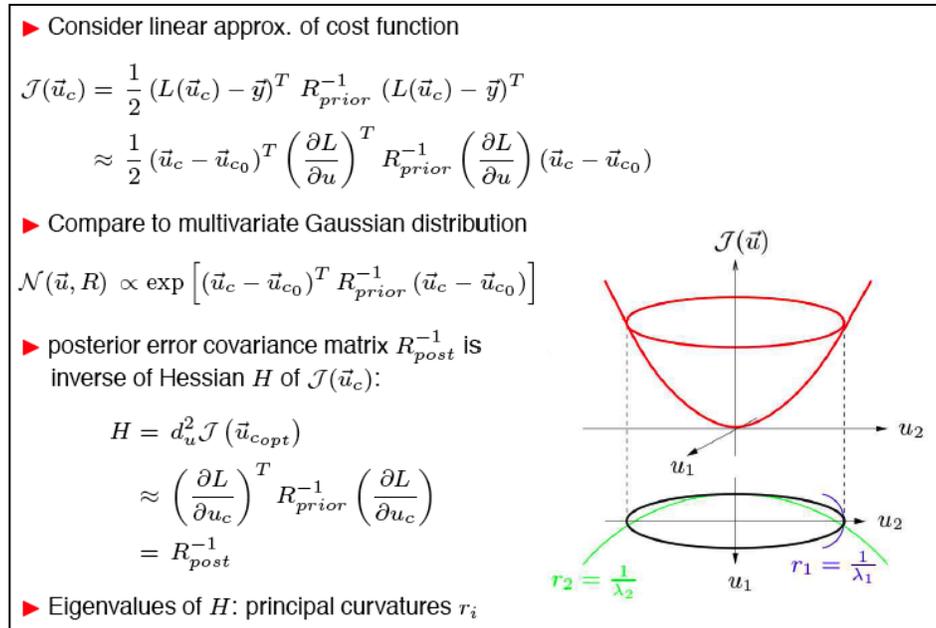
Figure 4.3.2 Schematic of relationship between the misfit function at the minimum, its local curvatures, r_1, r_2, and its prior (R_{prior}) and posterior (R_{post}) uncertainty/error covariances. For large curvatures, the posterior errors are small, for small curvatures, the posterior errors are large. Note that the posterior errors depend on the prior errors, as well as the sensitivities of the model with respect to the controls. Large sensitivities contribute to small posterior uncertainties.

$$J = (L(\mathbf{x}) - \mathbf{y})^T \cdot R_{prior}^{-1} \cdot (L(\mathbf{x}) - \mathbf{y}) \tag{4.3.6}$$

$$\approx \delta \mathbf{x}^T \left(\frac{\partial L}{\partial \mathbf{x}} \right) \cdot R_{prior}^{-1} \cdot \left(\frac{\partial L}{\partial \mathbf{x}} \right) \delta \mathbf{x}$$

Compare this to the general form of a multi-variate Gaussian distribution:

$$\mathcal{N}(\mathbf{x}_0, R) \sim \exp \left\{ -(\mathbf{x} - \mathbf{x}_0)^T \cdot R^{-1} \cdot (\mathbf{x} - \mathbf{x}_0) \right\} \tag{4.3.7}$$

We identify the approximate form of Eqn. 4.3.) as linear transformation of the prior error covariance R_{prior} into the posterior error covariance R_{post} or via the second derivative of J:

$$R_{post}^{-1} = \left(\frac{\partial L}{\partial \mathbf{x}} \right)^T \cdot R_{prior}^{-1} \cdot \left(\frac{\partial L}{\partial \mathbf{x}} \right) = \left[\frac{\partial^2 J_0}{\partial x_i \partial x_j} \right] \tag{4.3.8}$$

The eigenvalues of the inverse Hessian are the posterior control variable uncertainties, *based on the observations used, their uncertainties, and the model sensitivity*, all of which are ingredients in the estimation process (*e.g.,* Tarantola, 1987).

4.4 Target/objective functions and forward uncertainty propagation

In a last step, the posterior uncertainties of the control variables can be used as inputs in conjunction with the model, its linearized version (the model Jacobian), and the optimized control variables to infer uncertainties in any model diagnostic or target quantity considered. Note that in doing so, several crucial things have been achieved:

(1) the forward propagation is with respect to an optimized model trajectory (*i.e.* one which fits the observations used in the previous inversion),

(2) the uncertainties used as inputs are based on the available observations used and their prior uncertainties (use of different or more observations would result in different uncertainty inputs),

(3) the uncertainties are propagated based on the "known" sensitivities encapsulated in the model formulation.

A full end-to-end system of the sort described here does not currently exist. It has nevertheless been achieved using simpler models and in the more limited context of a marine ecosystem model (Fennel *et al.,* 2001) and a terrestrial carbon cycle model (Kaminski *et al.,* 2010). Our proposed system is in many ways a concrete implementation of a generic formal UQ chain as suggested by Oden *et al.* (2010a,b). The ECCO group is working toward enabling such an end-to-end system for quantifying oceanic indices on climate time scales (Wunsch *et al.,* 2009). All studies rely on automatic differentiation to derive 1st and 2nd derivative models required for the optimization and uncertainty propagation. The need to bring these methods to bear in a fully-coupled system and taking advantage of all available observations from all components has clearly been identified by the recent study of the National Research Council (NRC) on "*Verifying Greenhouse Gas Emissions: Methods to Support International Climate Agreements*" (Pacala *et al*., 2011). Specifically, the NRC report envisions the requirement "to reduce errors in the transport models and to overcome the noise from natural climate variability", and the vision that

"information derived from all sources could be synthesized in a data assimilation system to produce accurate estimates of anthropogenic CO_2 emissions and trends at national scales".

4.5 Quantitative observing system design

Observing system design addresses several questions related to the optimal use of existing observations or the potential use of future observations:

(1) For a given mix of observing systems consisting of different types of observations, how does each type contribute to the overall constraint, which locations contribute most, and are there significant redundancies or complementing elements?

(2) For a proposed variable to be monitored or a planned network or instrument to be deployed, which type of observation would contribute optimally to constrain the target quantity, where should observations best be taken, what are required accuracies and sampling rates, and what would be an optimal combination of different instruments?

The assessment of the relative contribution of existing observations in an inversion (item 1) is called Observing System Experiment (OSE), whereas the simulation of observations in a planned observational network (item 2) is called Observing System Simulation Experiment (OSSE). A third category, termed Sensitivity Observing System Experiment (SOSE) is mentioned here, but not further discussed (see, *e.g.,* Langland and Baker, 2004). Several Community Whitepapers (CWPs) on the subject in the context of climate monitoring were published as part of the OceanObs'09 symposium (see, *e.g.,* Heimbach *et al.,* 2009; Lee *et al.,* 2009; Wunsch, 2009).

We anticipate that the coupled, adjoined system described in this report will require significant resources and time to establish. The initial version of this framework will be relatively simple and considerable further development will be required to enhance and improve it. This will be a time consuming process. However, the initial version could be extremely valuable as an aid to understanding the sensitivity of the system to choices made and as a tool to guide further monitoring systems. The initial system can used to perform a series of OSSEs.

The idea behind an OSSE is to assume that the model re-creates a "reality" that can be used to systematically explore how sensitive (important) different parameters and different data sets are in recreating the "truth" as seen by the model. An initial forward simulation with the fully-coupled system will produce output. It will be assumed that this output is the "truth". This output can then be degraded to produce "pseudo-datasets". For instance, ocean surface chlorophyll output from the model can be mapped onto coarser temporal scales to resemble the type of data provided by satellites. This "pseudo-dataset" can then be further downgraded by addition of random noise to capture the uncertainty present in the satellite data. Pseudo-datasets will be reproduced for all the observations described in Section 3 and provided in the tables in that section. Experiment with adjoined version of the model will attempt to uncover how much information these "pseudo-datasets" actually provide.

5. RECOMMENDATIONS

5.1 Maintaining and Improving the Existing System

The current greenhouse gas observing system is measuring various aspects of the evolving composition of Earth's atmosphere, oceans and land ecosystems and is providing the fundamental understanding needed to construct accurate process models. These measurements include:

- Surface-based *in situ* measurements of all major greenhouse gases at high-frequency stations augmented by flask sampling;
- Remote sensing of CO_2, CH_4 and N_2O, and other greenhouse gases both from the surface and from space;
- Vertical profiles of greenhouse gases using aircraft and balloons;
- Land greenhouse gas flux measurements, using eddy covariance and smoke-stack monitoring;
- *In situ* and satellite observations of land vegetation, soil moisture and other relevant; biogeochemical and hydrologic variables for land greenhouse gas flux determination;
- Oceanic measurements of pCO_2, pN_2O and other greenhouse gases for flux determination;
- *In situ* and satellite measurements of biologically and biogeochemically important oceanic tracers, and relevant material fluxes;
- Economic data on production and trade flows associated with industrial and agricultural activities that generate greenhouse gases.

The combination of all of these complementary data with state-of-the-art global models of atmospheric chemistry and circulation, land ecosystems, oceanic circulation and biogeochemistry models is providing a significant advance in our understanding of the global sources, chemistry, transport and sinks of the trace substances determining atmospheric composition and air quality, and the radiative forcing of climate change.

While it is essential that this system continue to operate, to address the challenge of accurate GHG emissions verification it will need significant improvements as summarized below.

5.1.1 Improvements needed to current atmospheric GHG monitoring systems

The three leading greenhouse gases (CO_2, CH_4 and N_2O) are generally measured by a variety of systems (surface *in situ*, surface flask, and surface, aircraft and satellite remote sensing), whereas the lesser GHGs, which have a significant aggregated radiative forcing (*e.g.,* PFCs, SF_6, HFCs, *etc*.), are generally only measured at the surface. For example, AGAGE is the only network that currently makes regular, high-frequency measurements of the major PFCs and all the major HFCs. While the AGAGE network is expanding, there is a great deal of the Earth's surface that is not currently covered by the observations. For example, Stohl *et al.* (2009) find very low sensitivity of the AGAGE network to tropical regions. Satellite observations go some way to addressing the lack of *in situ* measurements of CO_2 and CH_4 in the tropics, and other under-sampled areas of the world. However, the accuracy of current space-based measurements of these gases is much less than can be achieved *in situ* even in cloud-free regions. Further, as

pointed out by Chevallier *et al.* (2007), while even significant uncertainties in individual retrievals can lead to large error reduction in surface flux estimates, regional biases in the satellite observations (due, for example, to scattering by aerosols) could produce errors in the derived emissions fields large enough to prevent them from being useful for treaty verification. Therefore future treaty verification will require significant improvements in the precision and accuracy of the remote sensing measurements, new approaches for inverting satellite radiance measurements over partially clouded regions, and order of magnitude increases in the spatial coverage of the high-frequency *in situ* measurements.

5.1.2 Improvements needed to current oceanic monitoring systems

For the purpose of a greenhouse gas observing system, there is a major lack of *in situ* pCO_2 measurement in the ocean from which to infer air-sea exchange of CO_2 (see Figure 3.1.2). Systematic and regular measurement of pCO_2, particularly in very under sampled Southern latitudes, which cover important parts of the world ocean and are among the most active players of oceanic variability, will be essential. Additional long ocean time series (such as BATS, HOTS, see Section 3.1.2) are also needed. Stations such as these in higher latitude regions are particularly essential. The largest sink of anthropogenic carbon is the Southern Ocean, yet this region has some of the least measurements.

One of the hardest issues in ocean biogeochemistry models is to achieve the correct flux of carbon from the surface ocean to depths. This process effectively "stores" carbon away from the atmosphere. The processes that govern this flux though are extremely complex and involve the types and abundances of organisms in the sunlight layers as well as the sinking and decomposing timescales of the organic matter that they produce. Yet there is very little measurement of these fluxes (see discussion in Section 3.1.1). A network of consistent measurements, possibly both sediment traps and isotopic, needs to be established.

The data with the most global and temporal coverage are those provided by satellite measurements. Though these measurements (chlorophyll, primary production) have large errors, long records provide a means to see (and hopefully understand) the inter-annual variability and trends of the ocean biological pump of carbon. Continued and consistent satellite missions measuring ocean color are essential. Consistency of waveband intervals would greatly aid in maintaining a useful long record.

Measurements of other greenhouse gases such as methane and N_2O are currently not wide spread. More regular and wider coverage of these gases in the ocean needs to be undertaken.

5.1.3 Improvements needed to current land monitoring systems

While the use of land surface models with spatially explicit time series data sets has improved the ability to capture spatial and temporal variations in greenhouse gas emissions from land ecosystems based primarily on associated variations in climate, the lack of information on relatively fine-scale distribution of environmental factors and carbon, nitrogen and water stocks across the land surface has limited the ability of these models to predict GHG fluxes more accurately. Traditionally, these models are parameterized with limited observational data

sampled at relatively small spatial (0.1 m^2 to 1 ha) and temporal (minutes to years) resolutions and are then applied over extended spatial (0.5º latitude x 0.5º longitude) and temporal (decades to centuries) scales. Thus, regional estimates by these models may be biased by their scaling assumptions to represent plot scale dynamics at larger scales (Rastetter *et al.,* 1992, 2003; Kicklighter *et al.,* 1994; Rastetter, 1996; Williams *et al.,* 2002).

Fine-scale spatial variations in GHG emissions from land ecosystems are primarily influenced by topography, variations in soil characteristics, and human and natural disturbances. As described earlier, while some land surface models consider the influence of some major disturbances (*e.g.,* deforestation, row-crop agriculture and wildfires), the influence of other major disturbances (*e.g.,* insect outbreaks, urbanization/suburbanization) are not currently considered. These models also do not consider more subtle changes to ecosystem dynamics imposed by ice storms, wind damage, floods, selective logging, fuel-wood gathering, or land management practices (*e.g.,* fertilizer application, irrigation, tillage) that may have a large influence on the storage of carbon in land ecosystems and GHG emissions.

The recent availability of new, fine-resolution data sets and development of some new measurement approaches will allow improvements in the characterization of environmental factors and carbon stocks across the Earth's land surface, which in turn, will help to improve the parameterization and evaluation of land surface models. For topography, the recent availability of fine resolution (30 m x 30 m) topography developed from imagery collected by the Shuttle Radar Topography Mission (SRTM3; Farr *et al.*, 2007) for about 80% of the Earth's surface potentially allows modeling groups to improve their consideration of drainage and small land depressions on storage of soil moisture in the landscape and its influence on GHG emissions. Because the spatial resolution of existing soil maps for most parts of the world are too coarse to help with practical land management, considerable effort is going into the development of a better digital soil map of the world (Sanchez *et al.,* 2009) based on information of soil properties determined from soil pit analyses, SRTM3 topography, local climate, land cover and remote sensing imagery from a number of satellites including QuickBird, LANDSAT, MODIS and AVHRR. The digital map is being organized to provide information at a variety of spatial scales with a basic product for small-holder farmers having a resolution of 30 m x 30 m. For aboveground carbon stocks, Baccini *et al*. (2008) recently used MODIS data to describe spatial variations in forest carbon density in sub-Saharan Africa at a resolution of 1 km^2. The results matched well with comparable results from an analysis of lidar metrics from the Geoscience Laser Altimetry System (GLAS) instrument on the Ice, Cloud, and Elevation Satellite (ICESAT). In the Peruvian Amazon Basin, Asner *et al.* (2010) recently used airborne lidar to document variations in the standing stock of carbon in aboveground vegetation airborne and the influence of land-use change at a spatial resolution of 0.1 ha.

In addition to the development of fine resolution data sets, there have been other recent attempts at improving the measurement of error and uncertainty associated with determining carbon and nutrient budgets from field studies (Rastetter *et al.,* 2010; Yanai *et al.,* 2010).

Besides scaling and uncertainty considerations, there are some natural phenomena that influence greenhouse gas emissions that need more attention in land surface models. One such phenomenon is how warming-induced permafrost degradation and associated thermokarst dynamics influence GHG emissions.

To address the need for more observations of the influence of ecosystem dynamics on land GHG emissions (Schimel *et al.,* 2000, 2001), a number of observing networks have recently been initiated including a network of eddy covariance sites (FLUXNET; http://www.fluxnet.ornl.gov), the National Ecological Observatory Network (NEON; Schimel *et al.,* 2007; http://www.neoninc.org) and the Arctic Observatory Network (AON; http://www.aoncadis.org).

5.2 Future Developments

New measurement technologies are beginning to emerge that have the potential to dramatically reduce the uncertainty of GHG emissions estimates. Also, further advances in the knowledge of source and sink processes and oceanic and atmospheric circulations, and the resultant improvements in the accuracy of process models will further lower uncertainties. Finally, the inclusion of reliable economic, production and trade flow data along with the GHG measurement data could also improve emissions estimates. Some examples are briefly outlined below.

5.2.1 High-frequency carbon dioxide, methane and nitrous oxide isotopologue observations

For greenhouse gases that have natural, anthropogenic, industrial and biogenic emissions, such as CO_2, CH_4 and N_2O, measurements of atmospheric abundances alone are often inadequate to differentiate precisely among these different sources. High frequency *in situ* measurements of not just the total mole fractions of these gases, but also their isotopic compositions (^{12}C, ^{13}C, ^{14}C, ^{14}N, ^{15}N, ^{16}O, ^{18}O, H, D) are a new frontier in global monitoring and hold the promise of revolutionizing understanding of the natural cycles of these gases and verifying claims of emission reductions. High-frequency *in situ* isotopic measurements are now becoming feasible using optical (laser) detection. Recent improvements in mid-infrared quantum cascade lasers (QCL) enable continuous wave (CW) operation near room temperature with higher power, narrower line-widths, and higher spectral mode purity than previously possible. For CH_4 and N_2O, automated cryogenic pre-concentration will be necessary to measure their isotopic compositions with the precision necessary to differentiate their various surface fluxes (biogenic, anthropogenic) and photochemical sinks.

While optical instruments to measure the stable isotopic composition of ambient CO_2 currently exist, their sensitivity needs improvement. Current optical CH_4 and N_2O isotopic instruments are capable of analyzing the stable isotopic composition of these gases at the much-elevated concentrations near their sources, but they lack the sensitivity to measure this composition at ambient concentrations. A combination of automated pre-concentration and optical detection could conceivably achieve this sensitivity. In this respect, MIT has recently received a 4-year NSF-MRI grant to develop and deploy two automated high frequency laser-based instruments for analysis of the isotopologues and isotopomers of N_2O. Isotopic ratios will be monitored using tunable infrared laser differential absorption spectroscopy (TILDAS) with CW-QC lasers. This

technology is well suited for long term deployment at remote sites as the instruments are fully automated and can also be accessed and controlled via the Internet. The new instruments will monitor four isotopologues/isotopomers of nitrous oxide ($^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{14}N^{14}N^{18}O$ and $^{14}N^{14}N^{16}O$) with a precision of at least 0.025 per mil (‰) for the ^{15}N isotopomers of N_2O. The projected precision for $^{14}N^{14}N^{18}O$ is about 0.05‰. The development tasks for the nitrous oxide instrument include a detailed optical design, infrared detector optimization, calibration system design, and the design and implementation of the cryogenic pre-concentration system. This pre-concentration will be achieved through development of a new generation high efficiency cryo-focusing trap and a sample transfer module that is also being designed to serve for CH_4 isotopic measurements. The instrument development and deployment will be staged over a four-year period. During the first year, we are focusing on instrument design and development. During the second year we will construct the first prototype instrument capable of quantifying the aforementioned isotopomer/isotopologue abundances that will be deployed during the third year at one of the AGAGE stations. During the third year, we will also design and construct the second isotope monitor using the experience gained with the prototype instrument. This instrument will be based at MIT and be used primarily for measurements at strongly emitting surface sites (*e.g.,* soils) to characterize for the first time their isotopic signatures at high frequency. During the fourth year, we will continue testing and improving the instruments as we perform sample analyses with the MIT instrument and monitor and support the instrument deployed at the AGAGE station. Experience gained from the AGAGE deployment will then be used to finalize the instrument designs. These final designs will form the basis for more extensive N_2O and CH_4 isotope monitor deployments at AGAGE and other global network stations in the future.

5.2.2 Space-Based Differential Absorption Lidar (DIAL)

Current space-based greenhouse gas observations rely on spectral measurements of backscattered or reflected sunlight (particularly in the near-infrared). This limits these observations to the daytime and at low-latitude, and therefore could induce a bias in the derived emissions. Plans are underway for active systems in which space-based instruments detect CO_2 concentrations using lidar. Such potential missions are NASA Ascends (Michalak *et al.,* 2008) and the ESA's A-SCOPE (Kaminski *et al.,* 2010). The use of lidar will allow measurements throughout the day at all latitudes. Further, a measurement of the atmospheric path is obtained, providing information about scattering by aerosols. As summarized in the NRC Report (Pacala *et al.,* 2010), DIAL techniques have significant potential for measuring both vertical profiles and column amounts of important GHGs. Ehret *et al*. (2008) estimated systematic errors in measurements of CO_2, CH_4, and N_2O columns from satellite-borne DIAL instruments and concluded that they were less than 0.4% for CO_2, 0.6% for CH_4, and 0.3% for N_2O. DIAL observations from aircraft are significantly easier than satellite measurements due to much shorter distance to surface and the lack of interference from high- and mid-level clouds. NASA has carried out studies of aircraft-borne DIAL measurements of CO_2 1.57 μm as a step toward satellite measurements (Browell *et al.,* 2008; Abshire *et al.,* 2009). Deploying a second lidar that

simultaneously measures the column amount of oxygen (O_2), that is a very accurate indicator of the total amount of dry air in the column, avoids the problem of having to convert a column measurement to a mole fraction. Instrumentation problems, such as maintaining and monitoring long-term laser stability, are among the main challenges in the development of the needed precise DIAL systems.

5.2.3 Improved and new estimates of air-sea exchange of CO_2

Obtaining global patterns of the air-sea fluxes of greenhouse gases are difficult. As explained in Section 3.1, the most available dataset of the air-sea fluxes of CO_2 are those of Takahashi *et al.* (2009) calculated from direct pCO_2 measurements. However there are significant uncertainties with these estimates (maybe as much as 50%). Inverse estimates using a suite of ocean general circulation model (GCM) have also been undertaken (*e.g.,* Mikaloff Fletcher *et al.,* 2007; Gruber *et al.,* 2009). These additional estimates (and there comparisons to the pCO_2 estimate have provided greater understanding of these fluxes. However additional and separate methods do need to be advanced in this regard. The model framework we suggest in this report would be one way forward. However we suggest that additional observation-only based inversion techniques such as those done for heat by Macdonald *et al.* (2003) may offer a new way forward for calculating air-sea fluxes of carbon dioxide. From an understanding the inventory of carbon from observations, constrained velocity fields and enforcing conservation, this method could provide information of where carbon must enter or leave the ocean.

5.2.4 Profiling Lagrangian Platforms for measuring ocean biogeochemical data

The international Argo float program (described in Section 3.1.3) presents a huge monitoring array of various physical aspects of the ocean. In the near future many of these floats will include chlorophyll and backscattering sensors. Recently new technology has allowed an oxygen sensor to be added to these floats successfully (Johnson *et al.,* 2009). Technology advances (in different degrees) is underway to additional attach nitrate, pCO_2, pH, optical sensors to these profiling floats. Such an array of floats would vastly improve the sampling of the important biogeochemical properties over the global ocean.

5.2.5 Enhanced coupled Forward Models and their Adjoints

In this report we recommend a modeling framework that will:

• Contain a detailed economics model that will provide initial estimates of release rates of anthropogenic greenhouse gases to the atmosphere, and will help attribute emissions to the nations responsible through use of trade-flow information on fuels, agricultural products and energy-intensive goods.

• Simulate atmospheric and oceanic trace gas transport and chemistry using the highest resolution meteorological and oceanic analyses available.

• Simulate terrestrial sources and sinks of CO_2, CH_4 and N_2O using a natural and managed ecosystem model, constrained offline by meteorological data and hydrological measurements.

- Simulate natural oceanic sources and sinks of CO_2, CH_4 and N_2O using a physical-biogeochemical-ecosystem model.

- Be fully coupled between each model component, such that global budgets of all greenhouse gases are fully accounted for at all times and change strictly, in addition to emissions, according to known physical and biogeochemical conservation laws.

- Be fully adjoined in order to quantify the sensitivity of all of the described measurements throughout the model environment, to changes in each uncertain model parameter. This adjoint system will allow the incorporation of the current measurements, and desired future observations, to improve the accuracy of estimates of both emissions and uncertain model parameters. The simultaneous determination of uncertain anthropogenic and natural model parameters is crucial, since this will allow covariance information between various model components and the residual uncertainties to be quantified.

5.2.6 Inclusion of Reliable Economic Data

The accuracy of emission estimates is expected to be significantly improved by inclusion of a reliable data-based economics model that will provide initial estimates of release rates of anthropogenic greenhouse gases to the atmosphere, and will help attribute emissions to the nations responsible through use of trade-flow information on fuels, agricultural products and energy-intensive goods. The most efficient way to incorporate economic data is to develop an accounting framework that in the first step takes advantage of available data (as discussed in Section 3.4). The required model could follow the IPCC three-tier methodology with the tier level being determined based on data availability, the level of detail needed to adequately constrain emissions estimates, and the degrees of freedom in the inverse approach. Within the model, the trade of emission-containing goods between countries will be accounted for using trade data so that measured emissions from *in situ* stations and satellite networks will match the emissions of country consumption, not production. Although the methodology is laid out, additional work will need to be done to construct a system for mapping the economic data to a global grid. The most crucial improvement in economic data is greater spatial detail (ideally gridded at 0.5° latitude x 0.5° longitude, or finer). This would include detail on the location of large point sources of emissions (*e.g.,* power plants, *etc*.). Such data generally exist at some level but need to be assembled into a digitized global database. Similarly data on transport networks are needed.

Glossary

Measurables
CFC = chlorofluorocarbons
Chl = chlorophyll (generally Chl a)
DIC = dissolved inorganic carbon
DIN = dissolved inorganic nitrogen
DOC = dissolved organic carbon
DON = dissolved organic nitrogen
DOP = dissolved organic phosphorus
GHG = greenhouse gas
HCFC = hydrochlorofluorocarbon
HFC = hydrofluorocarbon
HPLC = high-performance liquid chromatography
LLGHG = long-lived greenhouse gas
PAR = photosynthetically available radiation
pCH_4 = partial pressure of methane
pCO_2 = partial pressure of carbon dioxide
PFC = perfluorocarbon (CF_4, C_2F_6, C_3F_8, *etc.*)
PIC = particulate inorganic carbon
pN_2O = partial pressure of nitrous oxide
POC = particulate organic carbon
PON = particulate organic nitrogen
POP = particulate organic phosphorus

Acronyms and terminology
ACTM = Atmospheric chemical transport model
AD = automatic differentiation
AFEAS = Alternative Fluorocarbons Environmental Acceptability Study (http://www.afeas.org/)
AGAGE = Advanced Global Atmospheric Gases Experiment (http://agage.eas.gatech.edu/)
AIRS = NASA Atmospheric Infrared Sounder (http://airs.jpl.nasa.gov/)
AMT = Atlantic Meridional Transect (http://www.amt-uk.org)
AMOC = Atlantic Meridional Overturning Circulation (http://www.atlanticmoc.org/)
AON = Arctic Observatory Network (http://www.aoncadis.org)
ATM = Atmospheric Transport and Chemistry Model
AVHRR = Advanced Very High-Resolution Radiometer
BATS = Bermuda Atlantic Timeseries (http://bats.bios.edu/)
Bio-ECCO = an ocean biogeochemical and ecology model
CarboEurope = Project to assess European carbon balance (http://www.carboeurope.org/)
CARIACO = Carbon Retention in a coloured ocean project (Cariaco basin time series station)

CARIBIC = Civil Aircraft for the Regular Investigation of the Atmosphere Based on an
   Instrument Container (http://www.caribic-atmospheric.com/)

CARINA = Carbon dioxide in the Atlantic Ocean (http://cdiac.ornl.gov/oceans/CARINA/)

CCGG = Carbon Cycle Greenhouse Gases Group (http://www.esrl.noaa.gov/gmd/ccgg/)

CDIAC = Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/)

CIAB = Coal Industry Advisory Board, http://www.iea.org/ciab/

CLIVAR = Climate Variability and Predictability (http://www.clivar.org/)

CLM = Community Land Model; UCAR model of biogeophysics, hydrologic cycle,
   biogeochemistry and dynamic vegetation (http://www.cgd.ucar.edu/tss/clm/)

CMIP = Coupled Model Intercomparison Project (http://www-pcmdi.llnl.gov/projects/cmip/)

CPR = Continuous Plankton Recorder (http://www.sahfos.ac.uk/)

CRF = Common Reporting Format

CTM = chemical transport model

CTV = climate verification treaty

CW = continuous wave

DIAL= differential absorption lidar

DNDC = The DeNitrification-DeComposition model of nitrogen and carbon biogeochemistry

ECCO = Estimating the Circulation and Climate of the Ocean (http://www.ecco-group.org)

ECD = electron capture detector; used to measure trace species such as SF_6

EDGAR = Emissions Database for Global Atmospheric Research

EIA = U.S. Energy Information Administration (http://www.eia.doe.gov/)

ENSO = El Niño/Southern Oscillation

ESIA = European Semiconductor Industry Association (http://www.eeca.eu/)

ESRL = NOAA Earth System Research Laboratory (http://www.esrl.noaa.gov/)

EVI = Enhanced Vegetation Index

FLUXNET = network of CO_2 flux towers (http://www.fluxnet.ornl.gov)

FTIR = Fourier transform infrared spectrometer

GC = gas chromatograph(y)

GEOSECS = Geochemical Ocean Sections Study

GEOTRACES = program investigating marine biogeochemistry (http://www.geotraces.org/)

GLODAP = Global Ocean Data Analysis Project (http://cdiac.ornl.gov/oceans/glodap/)

GMD = NOAA-ESRL Global Monitoring division

GOSAT = Japan Aerospace Exploration Agency Greenhouse Gases Observing SATellite
   (http://www.jaxa.jp/projects/sat/gosat/index_e.html)

GTAP v7 = Global Trade Analysis Project version 7 (http://www.gtap.agecon.purdue.edu/)

GWP = global warming potential

HAIPER = High-Performance Instrumented Airborne Platform for Environmental Research

Hessian = matrix of second partial derivatives of observations to state vector elements

HIPPO = HAIPER Pole-to-Pole Observations

HOTS = Hawaii Ocean Time Series (http://hahana.soest.hawaii.edu/hot/hot_jgofs.html)

IBUKI = GOSAT (http://www.jaxa.jp/projects/sat/gosat/index_e.html)

IBP = International Biological Programme, predates the LTER

IDE = Institute of Developing Economics, (http://www.ide.go.jp/English/)

IEA = International Energy Agency, (http://www.iea.org/)

IFA = International Fertilizer Association, (http://www.fertilizer.org/)

ILTER = International Long Term Ecological Research network, (http://www.ilternet.edu)

IPCC = Intergovernmental Panel on Climate Change

IRRI = International Rice Research Institute, (http://irri.org/)

Jacobian = matrix of first partial derivatives of observations to state vector elements

JGOFS = Joint Global Ocean Flux Study (http://usjgofs.whoi.edu/)

Kerfix = Southern Ocean Time series station – 50S 68E

Lidar = Light detection and ranging

Medusa = GC-MS system with preconcentration used in the AGAGE network for measuring

MITgcm = MIT general circulation model (http://mitgcm.org)

MODIS = Moderate-resolution Imaging Spectroradiometer (http://oceancolor.gsfc.nasa.gov/)

MOMENTO = Marine Methane and Nitrous Oxide

MOZART = Model for Ozone and Related Tracers; chemical transport model developed at
     NCAR

MS = mass spectrometry

NAO = North Atlantic Oscillation

NASA = U.S. National Aeronautics and Space Administration

NCAR = U.S. National Center for Atmospheric Research

NCEP = U.S. National Center for Environmental Prediction

NDACC = Network for the Detection of Atmospheric Composition Change
     (http://www.ndsc.ncep.noaa.gov/)

NDVI = Normalized Difference Vegetation Index; an index used to determine whether a point
     on the surface has live vegetation or not

NEON = National Ecological Observatory Network (http://www.neoninc.org)

NIST = U.S. National Institute for Standards and Technology

NOAA = U.S. National Oceanic and Atmospheric Administration

NOBM = NASA Ocean Biogeochemistry Model

OCO = Orbiting Carbon Observatory (http://oco.jpl.nasa.gov/)

OSSE = Observing System Simulation Experiment

OWS-I = Ocean Weather Station "India"

OWS-M = Ocean Weather Station "Mike"

PAPA = Ocean Weather Station "Papa"

QCL = quantum cascade laser

SCIAMACHY = Scanning Imaging Absorption Spectrometer for Atmospheric Chartography

SeaBASS = SeaWiFS Bio-optical Archive and Storage System
     (http://seabass.gsfc.nasa.gov/seabass/)

SeaWiFS = Sea-viewing Wide Field-of-view Sensor (http://oceancolor.gsfc.nasa.gov/)

SOLAS = Surface Ocean Lower Atmosphere Study (http://www.solas-int.org)

TCCON = Total Carbon Column Observing Network (http://www.tccon.caltech.edu/)

TEM = Terrestrial Ecosystem Model; model of land-based ecosystems developed at the
Marine Biology Laboratory, Woods Hole Oceanographic Institute

TILDAS = tunable infrared laser differential absorption spectroscopy

TRAGNET = Trace Gas Network

TTO = Transient Tracers in the Oceans

UCAR = University Corporation for Atmospheric Research (http://www2.ucar.edu/)

UNFCC = United Nations Framework Convention on Climate Change

UQ = uncertainty quantification

VERTIGO = VERtical Transport In the Global Ocean
(http://cafethorium.whoi.edu/website/projects/vertigo.html)

WIOD = World Input-Output Database (http://www.wiod.org/)

WMO-GAW = World Meteorological Organization's Global Atmosphere Watch program
(http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html)

WOA = World Ocean Atlas (http://www.nodc.noaa.gov/OC5/WOA09/woa09data.html)

WOCE = World Ocean Circulation Experiment

REFERENCES

Abshire, J.B., H. Riris, G.R. Allan, C. Weaver, J. Mao, and W. Hasselbrack, 2009: Airborne lidar measurements of atmospheric CO_2 column absorption and line shapes from 3-11 km altitudes. *Geophysical Research Abstracts*, 11, EGU2009-11507.

AFEAS, 2007. Alternative Fluorocarbons Environmental Acceptability Study [Online] (Updated 30 November 2009) Available at: http://www.afeas.org/ [Accessed 6 October 2010].

AIM, 2008. Asia-Pacific Integrated Model [Online] (Updated 14 February 2008) Available at: http://www-iam.nies.go.jp/aim/index.htm [Accessed 5 October 2010].

Alluvione, F., A.D. Halvorson and S.J. Del Grosso, 2009: Nitrogen, tillage, and crop rotation effects on carbon dioxide and methane fluxes from irrigated cropping systems. *Journal of Environmental Quality,* 38(5), 2023-2033.

Alvain, S., C. Moulin, Y. Dandonneau, and H. Loisel (2008), Seasonal distribution and succession of dominant phytoplankton groups in the global ocean: A satellite view, *Global Biogeochemical Cycles*, 22, GB3001, doi: 10.1029/2007GB003154.

Amthor, J. S., J. M. Chen, J. S. Clein, S. E. Frolking, M. L. Goulden, R. F. Grant, J. S. Kimball, A. W. King, A. D. McGuire, N. T. Nikolov, C. S. Potter, S. Wang and S. C. Wofsy, 2001: Boreal forest exchange and evapotranspiration predicted by nine ecosystem process models: intermodal comparisons and relationships to field measurements. *J. Geophys. Res.* 106(D24), 33,623-33,648.

Andreae, M. O., and P. Merlet, 2001. Emissions and trace gases and aerosols from biomass burning, *Global Biogeochemical Cycles*, 15(4): 955-966.

Asner, G. P., G. N. Powell, J. Mascaro, D. E. Knapp, J. K. Clark, J. Jacobson, T. Kennedy-Bowdoin, A. Balaji, G. Paez-Acosta, E. Victoria, L. Secada, M. Valqui and R. F. Hughes (2010) High-resolution forest carbon stocks and emissions in the Amazon. *Proceedings of the National Academy of Sciences* 107: 16,738-16,742, doi: 10.1073/pnas.1004875107.

Aumont, O., E. Maier-Reimer, S. Blain and P. Monfray, 2003: An ecosystem model of the global ocean including Fe, Si, P colimitations. *Global Biogeochem. Cycles*, 17(2): 1060, doi:10.1029/2001GB001745.

Baccini, A., N. Laporte, S.J. Goetz, M. Sun, and H. Dong. 2008: A first map of tropical Africa's above-ground biomass derived from satellite imagery. *Environmental Research Letters,* 3: 045011, doi: 10.1088/1748-9326/3/4/045011.

Baker-Blocker, A., T. M. Donaje and K. H. Mancy, 1977: Methane flux from wetland areas. *Tellus* 29, 245-250, doi: 10.1111/j.2153-3490.1977.tb00731.x.

Balch, W. M., D. T. Drapeau, T. L. Cucci, R. D. Vaillancourt, K. A. Kilpatrick, and J. J. Fritz, 1999: Optical backscattering by calcifying algae: Separating the contribution of particulate inorganic and organic carbon fractions. *J. Geophys. Res.*, 104(C1), 1541–1558, doi:10.1029/1998JC900035.

Balshi, M. S., A. D. McGuire, P. Duffy, M. Flannigan, D. W. Kicklighter and J. Melillo, 2009: Vulnerability of carbon storage in North American boreal forests to wildfires during the 21st century. *Global Change Biology*, 15, 1491-1510, doi: 10.1111/j.1365-2486.2009.01877.x.

Balshi, M.S., A.D. McGuire, Q. Zhuang, J. Melillo, D.W. Kicklighter, E. Kasischke, C. Wirth, M. Flannigan, J. Harden, J. S. Clein, T.J. Burnside, J. McAllister, W.A. Kurz, M. Apps and A. Shvidenko, 2007: The role of historical fire disturbance in the carbon dynamics of the pan-boreal region: a process-based analysis. *J. Geophys. Research,* 112, G02029, doi: 10.1029/2006JG000380.

Bange, H.W., *et al.*, 2009: MEMENTO: a proposal to develop a database of marine nitrous oxide and methane measurements. *Environ Chem.,* 6: 195-197, doi:10.1071/EN09033.

Bange, H.W., U.H. Bartell, S. Rapsomanikis, M.O, Andreae, 1994. Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochem. Cycles*, 8(4): 465-480.

Bartlett, K.B., P.M. Crill, J.A. Bonassi, J.E. Richey and R. C. Harriss, 1990: Methane flux from the Amazon River floodplain: emissions during rising water. *J. Geophys. Res.* 95(D10), 16,773-16,788.

Bates, N.R., 2007: Interannual variability of the oceanic CO_2 sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades. *J. Geophys. Res*., 112, C09013, doi:10.1029/2006JC003759.

Beer, C., W. Lucht, D. Gerten, K. Thonicke, and C. Schmullius, 2007: Effects of soil freezing and thawing on vegetation carbon density in Siberia: A modeling analysis with the Lund-Potsdam-Jena Dynamic Global Vegetation Model (LPJ-DGVM). *Global Biogeochemical Cycles*, 21, GB1012, doi:10.1029/2006GB002760.

Bennington,V., G. A. McKinley, S. Dutkiewicz, and D. Ullman, 2009: What does chlorophyll variability tell us about export and air-sea CO_2 flux variability in the North Atlantic? *Global Biogeochemical Cycles*, 23, GB3002, doi:10.1029/2008GB003241.

Bergamaschi, P., *et al*., 2009: Inverse modeling of global and regional CH_4 emissions using SCIAMACHY satellite retrievals. *Journal of Geophysical Research*, 114, D22301 (http://www.agu.org/pubs/crossref/2009/2009JD012287.shtml).

Bey, I., *et al*., 2001: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *J. of Geophysical Research*, 106(D19), 23073-23095 (http://www.agu.org/pubs/crossref/2001/2001JD000807.shtml).

Bishop, A., P. Messina, *et al.*, 2009: *Scientific Grand Challenges in National Security: The Role of Computing at the Extreme Scale*, Report from the U.S. Department of Energy (DOE) Workshop, October 6-8, 2009, Washington DC, [online] http://science.energy.gov/~/media/ascr/pdf/program-documents/docs/Nnsa_grand_challenges_report.pdf [Accessed 20 June 2011]

Bohn, T.J., D.P. Lettenmaier, K. Sathulur, L. C. Bowling, E. Podest, K. C. McDonald, and T. Friborg, 2007: Methane emissions from western Siberian wetlands: heterogeneity and sensitivity to climate change. *Environmental Research Letters* 2, 045015, doi: 10.1088/1748-9326/2/4/045015.

Bonan, G.B., 2008: Carbon cycle: fertilizing change. *Nature Geoscience,* 1: 645-646.

Bonan, G.B., and S. Levis, 2010: Quantifying carbon-nitrogen feedbacks in the Community Land Model (CLM4). *Geophysical Research Letters*, 37: L07401, doi: 10.1029/2010GL042430.

Bond, W. J., F. I. Woodward and G. F. Midgley, 2005: The global distribution of ecosystems in a world without fire. *New Phytologist*, 165(2), 525-538, doi: 10.1111/j.1469-8137.2004.01252.x.

Bondeau, A., P. C. Smith, S. Zaehle, S. Schaphoff, W. Lucht, W. Cramer, D. Gerten, H. Lotze-Campen, C. Müller, M. Reichstein and B. Smith, 2007: Modeling the role of agriculture for the 20th century global terrestrial carbon balance. *Global Change Biology* 13: 679-706, doi: 10.1111/j.1365-2486.2006.01305.x.

Bouwman, A. F., *et al*., 2002: Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biochemical Cycles*, 16(4): 6-1 to 6-13.

Bracher, A., M. Vountas, T. Dinter, J.P. Burrows, R. Röttgers, and I. Peeken (2009), Quantitative observation of cyanobacteria and diatoms from space using PhytoDOAS on SCIAMACHY data, *Biogeosciences*, 6: 751-764.

Brenninkmeijer, C.A., *et al*., 2007. Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system. *Atmospheric Chemistry & Physics*, 4953-4976.

Brovkin, V., M. Claussen, E. Driesschaert, T. Fichefet, D. Kicklighter, M. F. Loutre, H. D. Matthews, N. Ramankutty, M. Schaeffer and A. Sokolov (2006) Biogeophysical effects of historical land cover changes simulated by six earth system models of intermediate complexity. *Climate Dynamics,* 26(6), 587-600, doi: 10.1007/s00382-005-0092-6.

Browell, E.V., M.F. Dobbs, J. Dobler, S. Kooi, Y. Choi, F.W. Harrison, B. Moore III, and T.S. Zaccheo, 2008: Airborne demonstration of 1.57-micron laser absorption spectrometer for atmospheric CO_2 measurements, in: *Proceedings of the 24th International Laser Radar Conference*, Boulder, Colo., January 12-15, pp. 697.

Buchwitz, M., *et al*., 2005: Atmospheric methane and carbon dioxide from SCIAMACHY satellite data: initial comparison with chemistry and transport models. *Atmospheric Chemistry & Physics*, 5, 941-962 (http://www.atmos-chem-phys.net/5/941/2005/).

Buesseler, K.O., *et al*., 2007: Revisiting Carbon Flux Through the Ocean's Twilight Zone. *Science,* 316(5824): 567-570, doi: 10.1126/science.1137959.

Buesseler, K.O., M.P. Bacon, J.K. Cochran, H.D. Livingston, 1992: Carbon and nitrogen export during the JGOFS North Atlantic bloom experiment estimated from ^{234}Th:^{238}U disequilibria. *Deep-Sea Research*, 39(7/8): 1115-1137.

Burrows, J., *et al*., 1995. SCIAMACHY - scanning imaging absorption spectrometer for atmospheric chartography. *Acta Astronautica*, 35(7), 445-451, doi:10.1016/0094-5765(94)00278-T.

Butterbach-Bahl, K., M. Kock, G. Willibald, B. Hewett, S. Buhagiar, H. Paper and R. Kiese, 2004: Temporal variations of fluxes of NO, NO_2, N_2O, CO_2, and CH_4 in a tropical rain forest ecosystem. *Global Biogeochemical Cycles* 18, GB3012, doi: 10.1029/2004GB002243.

Carr, M.-E., *et al*., 2006: A comparison of global estimates of marine primary production from ocean color. *Deep-Sea Research II,* 53, 741-770, doi:10.1016/j.dsr2.2006.01.028.

CDIAC, 2010. *Carbon Dioxide Information Analysis Center: Fossil Fuel CO₂ Emissions* [Online] Available at: http://cdiac.ornl.gov/trends/emis/meth_reg.html [Accessed 6 October 2010].

Chahine, M.T., *et al*., 2008. Satellite remote sounding of mid-tropospheric CO_2. *Geophysical Research Letters*, 35, L17807 (http://www.agu.org/pubs/crossref/2008/2008GL035022.shtml).

Chambers, J.Q., J.I. Fisher, H. Zeng, E.L. Chapman, D.B. Baker and G.C. Hurtt, 2007: Hurricane Katrina's carbon footprint on U. S. Gulf Coast forests. *Science* 318, 1107, doi: 10.1126/science.1148913.

Chemical Week, 1999: Product focus: adipic/adiponitrile, *Chemical Week*, 10 March 1999, pp. 31.

Chevallier, F., *et al*., 2009: On the accuracy of the CO_2 surface fluxes to be estimated from the GOSAT observations. *Geophys. Res. Lett.*, 36, L19807, doi:10.1029/2009GL040108.

Chevallier, F., F. Bréon, and P.J. Rayner, 2007: Contribution of the Orbiting Carbon Observatory to the estimation of CO_2 sources and sinks: Theoretical study in a variational data assimilation framework. *J. Geophys. Res.*, 112, D09307 (http://www.agu.org/pubs/crossref/2007/2006JD007375.shtml).

Chipperfield, M.P., 2006: New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer experiments. *Quarterly Journal of the Royal Meteorological Society*, 132(617), 1179-1203 (http://doi.wiley.com/10.1256/qj.05.51).

CIAB, 1994: *Global Methane and the Coal Industry* [Online] Available at: http://www.iea.org/publications/free_new_Desc.asp?PUBS_ID=1398 [Accessed 6 October 2010].

Ciotti, A., and A. Bricaud, 2006: Retrievals of a size parameter for phytoplankton and spectral light absorption by colored detrital matter from water-leaving radiances at SeaWiFS channels in a continental sheld region off Brazil, *Limnol. Oceangr. Methods*, 4, 237-253.

Clein, J.S., B.L. Kwiatkowski, A.D. McGuire, J.E. Hobbie, E.B. Rastetter, J.M. Melillo, D.W. Kicklighter, 2000: Modeling carbon responses of moist tundra ecosystems to historical and projected climate: A comparison of fine- and coarse-scale ecosystem models for identification of process-based uncertainties. *Global Change Biology,* 6 (Suppl. 1), 127-140.

Connor, B.J., *et al*., 2008: Orbiting Carbon Observatory: Inverse method and prospective error analysis. *J. Geophys. Research*, 113, D05305. (http://www.agu.org/pubs/crossref/2008/2006JD008336.shtml).

Conway, T. J., P. P. Tans, L. S. Watermann, K. W. Thoning, D. R. Kitzis, K. A. Masarie, and N. Zhang, 1994: Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network. *J. Geophys. Re*s., 99: 22,831–22,855, doi:10.1029/94JD01951.

Corbiere, A., N. Metzl, G. Reverdin, C. Brunet and T. Takahashi, 2007: Interannual and decadal variability of the oceanic carbon sink in the North Atlantic subpolar gyre, *Tellus B*, 59: 158-178.

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

Cramer, W., A. Bondeau, F.I. Woodward, I.C. Prentice, R. Betts, V. Brovkin, P. Cox, V. Fisher, J. Foley, A.D. Friend, C. Kucharik, M.R. Lomas, N. Ramankutty, S. Sitch, B. Smith, A. White and C. Young Molling, 2001: Global response of terrestrial ecosystems structure and function to CO_2 and climate change: results from six dynamic global vegetation models. *Global Change Biology,* 7, 357-374.

Crevoisier, C., *et al*., 2009: Tropospheric methane in the tropics – first year from IASI hyperspectral infrared observations. *Atmospheric Chemistry and Physics*, 9(17), 6337-6350.

Crisp, D., *et al*., 2004: The Orbiting Carbon Observatory (OCO) mission. Advances in Space Research, 34: 700-709 (http://linkinghub.elsevier.com/retrieve/pii/S0273117704003539).

Curtin, D., H. Wang, F. Selles, B.G. McConkey, C.A. Campbell, 2000: Tillage effects on carbon fluxes in continuous wheat and fallow-wheat rotations. *Soil Science Society of America Journal,* 64: 2080-2087.

Dargaville, R.J., M. Heimann, A.D. McGuire, I.C. Prentice, D.W. Kicklighter, F. Joos, J. Clein, G. Esser, J. Foley, J. Kaplan, R. Meier, J.M. Melillo, B. Moore III, N. Ramankutty, T. Reichenau, A. Schloss, S. Sitch, H. Tian, L. Williams and U. Wittenberg, 2002: Evaluation of terrestrial carbon cycle models with atmospheric CO_2 measurements: Results from transient simulations considering increasing CO_2, climate and land-use effects. *Global Biogeochem. Cycles*. 16(4), 1092, doi:10.1029/2001GB001426.

Davidson, E.A., F.Y. Ishida and D.C. Nepstad, 2004: Effects of an experimental drought on soil emissions of carbon dioxide, methane, nitrous oxide and nitric oxide in a moist tropical forest. *Global Change Biology*, 10: 718-730.

Davidson, E. A., F. Y. Ishida and D. C. Nepstad, 2008: Effects of an experimental drought and recovery on soil emissions of carbon dioxide, methane, nitrous oxide and nitric oxide in a moist tropical forest. *Global Change Biology,* 14: 2582-2590.

Davidson, E. A., and I. A. Janssens. 2006: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature,* 440: 165-173, doi: 10.1038/nature04514.

Dlugokencky, E.J., *et al*., 1994: The growth rate and distribution of atmospheric methane. *J. Geophysical Research*, 99(D8): 17021-17043 (http://www.agu.org/pubs/crossref/1994/94JD01245.shtml).

Doney, S., K. Lindsay, K. Caldeira, J.-M. Campin, H. Drange, J.-C. Dutay, M. Follows, Y. Gao, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, G. Madec, E. Maier-Reimer, J. Marshall, R. Matear, P. Monfray, A. Mouchet, R. Najjar, J. Orr, G.-K. Plattner, J. Sarmiento, R. Schlitzer, R. Slater, I. Totterdell, M.-F. Weirig, Y. Yamanaka, A. Yool, 2004: Evaluating global ocean carbon models: the importance of realistic physics, *Global Biogeochem. Cycles*, 18, GB3017, doi:10.1029/2003GB002150.

Doorn, M. O., *et al*., 1997: *Estimates of Global Greenhouse Gas Emissions from Industrial and Domestic Wastewater Treatment* (EPA-600/R-99-089) [Online] http://nepis.epa.gov/ [Accessed 6 Oct. 2010].

Doorn, M. R. J. and D. S. Liles, 1999: *Quantification of Methane Emissions and Discussion of Nitrous Oxide, and Ammonia Emissions from Septic Tanks, Latrines, and Stagnant Open Sewers in the World* (EPA-600/R-97-091) [Online] Available at: http://nepis.epa.gov/ [Accessed 6 October 2010].

Dunne, J.P., J.L. Sarmiento and A. Gnanadesikan, 2007: A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor. *Global Biogeochem. Cycles,* 20, doi:10.1029/2006GB002907.

Dunne, J.P., R. Armstrong, A. Gnanadesikan, J. Sarmiento and R. Slater, 2005: Empirical and mechanistic models for particle export ratio. *Global Biogeochem. Cycles*, 18, doi:10.1029/2004GB002390.

Dutkiewicz, S., M. J. Follows, and J. G. Bragg, 2009: Modeling the coupling of ocean ecology and biogeochemistry. *Global Biogeochem. Cycles*, 23, GB4017, doi:10.1029/2008GB003405.

Dutkiewicz, S., M. Follows, P. Heimbach, and J. Marshall, 2006: Controls on ocean productivity and air-sea carbon flux: an adjoint model sensitivity study. *Geophysical Research Letters*, 33, L02603, doi:10.1029/2005GL024987

Dutkiewicz. S., A. Sokolov, J. Scott and P. Stone, 2005: *A Three-Dimensional Ocean-Seaice-Carbon Cycle Model and its Coupling to a Two-Dimensional Atmospheric Model: Uses in Climate Change Studies*. Report 122, MIT Joint Program of the Science and Policy of Global Change, May, 47 p. [Online] (http://globalchange.mit.edu/files/document/MITJPSPGC_Rpt122.pdf).

Ehret, G., C. Kiemle, M. Wirth, A. Amediek, A. Fix, and S. Houweling, 2008: Space-borne remote sensing of CO_2, CH_4, and N_2O by integrated path differential absorption lidar: A sensitivity analysis, *Applied Physics B*, 90: 593-608.

EIA, 2010: *International Energy Outlook 2010* [Online] (Updated 27 July 2010). U.S. Energy Information Administration Report, available at: http://www.eia.doe.gov/oiaf/ieo/index.html [Accessed 6 Oct. 2010].

Emmons, L.K., *et al*., 2010: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4). *Geoscientific Model Development*, 3: 43-67 (http://www.geosci-model-dev.net/3/43/2010/).

EPA, 2006: *Global Anthropogenic non-CO_2 Greenhouse Gas Emissions: 1990-2020* (Updated 25 February 2010), U.S. Environmental Protection Agency Report 430-R-06-003 [Online] Available at: http://www.epa.gov/climatechange/economics/downloads/GlobalAnthroEmissionsReport.pdf [Accessed 6 October 2010].

EPA, 2010: *Methane and Nitrous Oxide Emissions From Natural Sources* (April 2010)*, U.S. Environmental Protection Agency, Report EPA 430-R-10-001 [Online] Available at: http://www.epa.gov/nitrousoxide/pdfs/Methane-and-Nitrous-Oxide-Emissions-From-Natural-Sources.pdf [Accessed 20 June 2011].

ESIA, 2010: *European Semiconductor Industry Association: Market Statistics* [Online] Available at: http://www.eeca.eu/index.php/market_stats/en/ [Accessed 6 October 2010].

EURACOAL, 2008. *European Association for Coal and Lignite - Statistics* [Online] Available at: http://www.euracoal.be/pages/medien.php?idpage=261 [Accessed 6 October 2010].

Euskirchen, E. S., A. D. McGuire, F. S. Chapin III, S. Yi and C. C. Thompson, 2009: Changes in vegetation in northern Alaska under scenarios of climate change, 2003-2100: implications for climate feedbacks. *Ecological Applications,* 19(4): 1022-1043.

Euskirchen, E.S., A.D. McGuire, D.W. Kicklighter, Q. Zhuang, J.S. Clein, R.J. Dargaville, D.G. Dye, J. S. Kimball, K.C. McDonald, J.M. Melillo, V.E. Romanovsky and N.V. Smith, 2006: Importance of recent shifts in soil thermal dynamics on growing season length, productivity and carbon sequestration in terrestrial high-latitude ecosystems. *Global Change Biology*, 12(4): 731-750, doi: 10.1111/j.1365-2486.2006.01113.x.

EXIOPOL, 2010: *A New Environmental Accounting Framework using Externality Data and Input-output Tools for Policy Analysis* [Online] at: http://www.feem-project.net/exiopol/ [Accessed 6 Oct. 2010].

FAO, 2010: *Food and Agriculture Organization of the United Nations - Statistics* [Online] Available at: http://www.fao.org/corp/statistics/en/ [Accessed 6 October 2010].

Farr, T.G., P.A. Rosen, E. Caro, R. Crippen, R. Duren, S. Hensley, M. Kobrick, M. Paller, E. Rodriguez, L. Roth, D. Seal, S. Shaffer, J. Shimada, J. Umland, M. Werner, M. Oskin, D. Burbank and D. Alsdorf, 2007: The shuttle radar topography mission. *Reviews of Geophysics,* 45, RG2004, 33pp., doi: 10.1029/2005RG000183.

Felzer, B. S., T. W. Cronin, J. M. Melillo, D. W. Kicklighter and C. A. Schlosser, 2009: Importance of carbon-nitrogen interactions and ozone on ecosystem hydrology during the 21[st]century. *Journal of Geophysical Research,* 114, G01020, doi: 10.1029/2008JG000826.

Felzer, B., J. Reilly, J. Melillo, D. Kicklighter, M. Sarofim, C. Wang, R. Prinn, Q. Zhuang, 2005: Future effects of ozone on carbon sequestration and climate change policy using a global biogeochemical model. *Climatic Change* 73, 345-373, doi: 10.1007/s10584-005-6776-4.

Felzer, B., D. Kicklighter, J. Melillo, C. Wang, Q. Zhuang and R. Prinn, 2004: Effects of ozone on net primary production and carbon sequestration in the conterminous United States using a biogeochemistry model. *Tellus B*, 56: 230-248.

Follows, M.J., S. Dutkiewicz, S. Grant, and S.W. Chisholm, 2007: Emergent biogeography of microbial communities in a model ocean. *Science*, 315: 1843-1846, doi:10.1126/science.1138544.

Fondazione Eni Enrico Mattei, 2010: *World Induced Technical Change Hybrid Model* [Online] Available at: http://www.witchmodel.org/index.html [Accessed 5 October 2010].

Frankenberg, C., *et al.*, 2005: Assessing methane emissions from global space-borne observations. *Science*, 308: 1010-1014.

Frankenberg, C., *et al.*, 2008: Tropical methane emissions: A revised view from SCIAMACHY onboard ENVISAT. *Geophysical Research Letters*, 35, L15811.

Frey, K. E., J. W. McClelland, R. M. Holmes and L. C. Smith, 2007: Impacts of climate warming and permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea. *Journal of Geophysical Research*, 112: G04S58, doi: 10.1029/2006JG000369.

Friedlingstein, P., J.-L. Dufresne, P. M. Cox and P. Rayner, 2003: How positive is the feedback between climate change and the carbon cycle? *Tellus B*, 55: 692-700.

Friedlingstein, P., I. Fung, E. Holland, J. John, G. Brasseur, D. Erickson and D. Schimel, 1995: On the contribution of CO_2 fertilization to the missing biospheric sink. *Global Biogeochem. Cycles* 9, 541-556.

Friedrichs, M.A.M., *et al.*, 2009: Assessing the uncertainties of model estimates of primary productivity in the tropical Pacific Ocean. *J. Marine Systems*, 76(1-2):113-133 doi: 10.1016/j.jmarsys.2008.05.010

Friedrichs, M.A.M., J. Dusenberry, L.A. Anderson, R. Armstrong, F. Chai, J.R. Christian, S.C. Doney, J. Dunne, M. Fujii, R. Hood, D. McGillicuddy, J.K. Moore, M. Schartau, Y.H. Spitz, and J.D. Wiggert, 2007: Assessment of skill and portability in regional marine biogeochemical models: the role of multiple planktonic groups, *J. Geophys. Res. Oceans*, 112, C08001, doi:10.1029/2006JC003852.

Frolking, S., *et al.*, 1996: Modeling temporal variability in the carbon balance of a spruce/moss boreal forest. Global Change Biology2: 343-366.

Galbraith, E.D., A. Gnanadesikan, J.P. Dunne, and M.R. Hiscock, 2010: Regional impacts of iron-light colimitation in a global biogeochemical model. *Biogeosciences*, 7, 1043-1064.

Galford, G., J. Melillo, D. Kicklighter, J. F. Mustard, T. W. Cronin, C. E. P. Cerri and C. C. Cerri, 2011: Historical carbon emissions and uptake from the agricultural frontier of the Brazilian Amazon. *Ecological Applications*, 21: 750-763, doi: 10.1890/09-1957.1.

Galford, G. L., J. M. Melillo, D. W. Kicklighter, T. W. Cronin, C. E. P. Cerri, J. F. Mustard and C. C. Cerri, 2010: Greenhouse gas emissions from alternative futures of deforestation and agricultural management in the southern Amazon. *Proceedings of the National Academy of Sciences,* 107, 19,649-19.654, doi: 10.1073/pnas.1000780107.

Garcia, H. E., R. A. Locarnini, T. P. Boyer, and J. I. Antonov, 2010a: *World Ocean Atlas 2009, Volume 3: Dissolved Oxygen, Apparent Oxygen Utilization, and Oxygen Saturation*. S. Levitus (editor), NOAA Atlas NESDIS 70, U.S. Government Printing Office, Washington, D.C., 344 pp.

Garcia, H. E., R. A. Locarnini, T. P. Boyer, and J. I. Antonov, 2010b: *World Ocean Atlas 2009, Volume 4: Nutrients (phosphate, nitrate, silicate)*. S. Levitus (ed.), NOAA Atlas NESDIS 71, U.S. Government Printing Office, Washington, D.C., 398 pp.

Gent, P., and J. McWilliams, 1990: Isopycnal mixing in ocean circulation models. *Journal of Physical Oceanography*, 20, 150-155.

GFED, 2007: *Global Fire Emissions Database, Version 2.1* [Online] (Updated 22 June 2010), at: http://daac.ornl.gov/VEGETATION/guides/global_fire_emissions_v2.1.html [Accessed 6 Oct. 2010].

Giering, R., and T. Kaminski, 1998: Recipes for adjoint code construction. *ACM Transactions on Mathematical Software*, 24, 437-474.

Gregg, W.W., P. Ginoux, P.S. Schopf, N.W. Casey, 2003: Phytoplankton and iron: validation of a global three-dimensional ocean biogeochemical model. *Deep-Sea Res. II,* 50: 3143-3169.

Griewank, A., and A. Walther, 2008: Evaluating Derivatives. In: *Principles and Techniques of Algorithmic Differentiation*. Frontiers in Applied Mathematics, Vol. 19, SIAM, Philadelphia.

Gritti, E. S., B. Smith and M. T. Sykes, 2006: Vulnerability of Mediterranean Basin ecosystems to climate change and invasion by exotic plant species. *Journal of Biogeography* 33: 145-157.

Gruber, N., M. Gloor, S.E. Mikaloff-Fletcher, S.C. Doney, S. Dutkiewicz, M. Follows, M. Gerber, A.R. Jacobson, F. Joos, K. Lindsay, D. Menemenlis, A. Moucheta S.A. Muller, J. L. Sarmiento, and T. Takahashi, 2009: Oceanic sources, sinks and transport of atmospheric CO_2. *Global Biogeochemical Cycles*, 23, GB1005, doi:10.1029/2008GB003349.

Hack, J.J., 1994: Parameterization of moist convection in the National Center for Atmospheric Research community climate model (CCM2). *Journal of Geophysical Research*, 99(D3), 5551-5568.

Hall, B.D., G. Dutton and J. Elkins, 2007: The NOAA nitrous oxide standard scale for atmospheric observations. *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954.

Hall, S.J., and P.A. Matson, 1999: Nitrogen oxide emissions after nitrogen additions in tropical forests. *Nature,* 400: 152-155,

Hansell, D.A., N.R. Bates and K. Gunderson, 1995: Mineralization of dissolved organic carbon in the Sargasso Sea. *Marine Chemistry*, 51: 201-212.

Hasselmann, K., 1997: Climate-change research after Kyoto. *Nature*, 390: 225-226.

Hasselmann, K., S. Hasselmann, R. Giering, V. Ocaña, and H. v. Storch, 1997: Sensitivity study of optimal CO_2 emission paths using a simplified Structural Integrated Assessment Model (SIAM). *Climatic Change*, 37: 345 – 386.

Hayes, D.J., A.D. McGuire, D.W. Kicklighter, K.R. Gurney, T.J. Burnside, and J.M. Melillo, 2011: Is the northern high latitude land-based CO_2 sink weakening? Submitted to *Global Biogeochemical Cycles.*

Heimann, M., 2010: Foreword to the Special Issue on the 8th International Carbon Dioxide Conference, ICDC8, in Jena, Germany, September 2009. *Tellus B*, 62(5): 315.

Heimann, M., G. Esser, A. Haxeltine, J. Kaduk, D.W. Kicklighter, W. Knorr, G.H. Kohlmaier, A.D. McGuire, J. Melillo, B. Moore, R. D. Otto, I. C. Prentice, W. Sauf, A. Schloss, S. Sitch, U. Wittenberg and G. Würth, 1998: Evaluation of terrestrial carbon cycle models through simulations of the seasonal cycle of atmospheric CO_2: First results of a model intercomparison study. *Global Biogeochemical Cycles,* 12, 1-24.

Heimbach, P., C. Hill and R. Giering, 2005: An efficient exact adjoint of the parallel MIT general circulation model, generated via automatic differentiation. *Future Generation Computer Systems*, 21(8), 1356-1371.

Heimbach, P., 2008: The MITgcm/ECCO adjoint modelling infrastructure. *CLIVAR Exchange*, 44, 13-17.

Helfter, C., *et al*., 2010. Controls of carbon dioxide concentrations and fluxes above central London. *Atmospheric Chemistry and Physics Discussions*, 10: 23739-23780.

Hickman, A.E., S. Dutkiewicz, R.G. Williams, and M.J. Follows, 2010: Modeling the effects of chromatic adaptation on phytoplankton comunity structure in the oligotrophic ocean. *Marine Ecology Progress Series*, 406: 1-17, doi:10.3354/meps08588.

Hirata, T., J. Aiken, N. Hardman-Mountford, T.J. Smyth, and R.G. Barlow, 2008: An absorption model to determine phytoplankton size classes from satellite ocean colour. *Remote Sensing of Environ*., 112: 3153-3159.

Hirsch, A.I., *et al*., 2006. Inverse modeling estimates of the global nitrous oxide surface flux from 1998-2001. *Global Biogeochemical Cycles*, 20, GB1008, doi:10.1029/2004GB002443.

Holtslag, A.A., and B.A. Boville, 1993: Local Versus Nonlocal Boundary-Layer Diffusion in a Global Climate Model. *Journal of Climate*, 6, 1825-1842.

Hood, R.R., E.A. Laws, R.A. Armstrong, N.R Bates, C.W. Brown, C.A. Carlson, F. Chai, S.C. Doney, P.G. Falkowski, R.A. Feely, M.A.M Friedrichs, M.R. Landry, J.K. Moore, D.M. Nelson, T.L. Richardson, B. Salihoglu, M. Schartau, D.A. Toole, J.D. Wiggert, 2006: Pelagic functional group modeling: Progress, challenges and prospects. *Deep-Sea Res. Part II*, 53(5-7): 459-512.

Huang, J., *et al*., 2008. Estimation of regional emissions of nitrous oxide from 1997 to 2005 using multinetwork measurements, a chemical transport model, and an inverse method. *J. Geophysical Research*, 113, D17313 (http://www.agu.org/pubs/crossref/2008/2007JD009381.shtml).

Hungate, B. A., J. S. Dukes, M. R. Shaw, Y. Luo and C. B. Field, 2003: Nitrogen and climate change. *Science*, 302: 1512-1513.

Ichihara, S. M., *et al*., 2009: Combining Geoprocessing and Interregional Input-Output Systems: An Application to the State of São Paulo in Brazil, 56th Annual North American Meetings of the Regional Science Association International, November 18-21, 2009, San Francisco, USA.

IDE, 2010: *Institute of Developing Economics-Japan External Trade Organization: Data and Resources* [Online] Available at: http://www.ide.go.jp/English/Data/index.html [Accessed 6 October 2010].

IEA, 2010: *International Energy Agency Statistics and Balances* [Online] Available at: http://www.iea.org/stats/index.asp [Accessed 6 October 2010].

IFA, 2010: *International Fertilizer Industry Association: IFADATA [*Online] Available at: http://www.fertilizer.org/ifa/ifadata/search [Accessed 6 October 2010].

IIASA, 1995: *Model for Energy Supply Strategy Alternatives and their General Environmental Impact* [Online] (Updated 14 March 2006) Available at: http://www.iiasa.ac.at/Research/ECS/docs/models.html#MESSAGE [Accessed 5 October 2010].

IPCC, 2007: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. In: S. Solomon *et al*. (editors), *Climate Change 2007: The Physical Science Basis*. Cambridge University Press, Cambridge, UK and New York, USA.

IPCC, 2006: *2006 IPCC Guidelines for National Greenhouse Gas Inventories* [Online] Available at: http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html [Accessed 6 October 2010].

IRRI, 2010: *International Rice Research Institute: World Rice Statistics* [Online] Available at: http://irri.org/our-science/social-science-economics/world-rice-statistics [Accessed 6 October 2010].

Jabro, J. D., U. Sainju, W. B. Stevens and R. G. Evans, 2008: Carbon dioxide flux as affected by tillage and irrigation in soil converted from perennial forages to annual crops. *Journal of Environmental Management,* 88: 1478-1484, doi: 10.1016/jenvman.2007.07.012.

Jenkins, J. C., R. A Birdsey and Y. Pan, 2001: Biomass and NPP estimation for the mid-Atlantic region (USA) using plot-level forest inventory data. *Ecological Applications*, 11(4): 1174-1193.

Jin, X., and Gruber, N., 2003: Offsetting the radiative benefit of ocean iron fertilization by enhancing N_2O emission. *Geophys. Res. Lett*. 30(24), 2249, doi:10.1029/2003GL018458.

Johnson, K.S., *et al.,* 2009: Observing biogeochemical cycles at global scales with profiling floats and gliders. *Oceanography*, 22(3): 216-225.

Joint Global Change Research Institute, 2006. *GCAM* [Online] Available at: http://www.globalchange.umd.edu/models/gcam/ [Accessed 5 October 2010].

Kalnay, E., *et al.,* 1996: The NCEP/NCAR 40-Year Reanalysis Project. *Bulletin of the American Meteorological Society*, 77(3), 437-471.

Kaminski, T., and M. Heimann, 2001: Inverse modeling of atmospheric carbon dioxide fluxes. *Science*, 294(5541), 259.

Kaminski, T., *et al*, 2010: Quantifying the benefit of A-SCOPE data for reducing uncertainties in terrestrial carbon fluxes in CCDAS. *Tellus B*, 62(5), 784-796, doi:10.1111/j.1600-0889.2010.00483.x.

Kaminski, T., W. Knorr, P. J. Rayner and M. Heimann, 2002: Assimilating atmospheric data into a terrestrial biosphere model: a case study of the seasonal cycle. *Global Biogeochemical Cycles* **16**(4), 1066, doi: 10.1029/2001GB001463.

Kaminski, T., M. Heimann, R. Giering, 1999: A coarse grid three-dimensional global inverse model of the atmospheric transport 1. Adjoint model and Jacobian matrix. *Journal of Geophysical Research*, 104(D15), 18535-18553.

Kawa, S.R., *et al.,* 2004: Global CO_2 transport simulations using meteorological data from the NASA data assimilation system. *J. Geophysical Research*, 109, D18312 (http://www.agu.org/pubs/crossref/2004/2004JD004554.shtml).

Kettle, H., 2009: Using satellite-derived backscattering coefficients in addition to chlorophyll data to constrain a simple marine biogeochemical model. *Biogeosci.*, 6: 4201-4231, doi:10.5194/bgd-6-4201.

Key, R.M., A. Kozyr, C.L. Sabine, K. Lee, R. Wanninkhof, J. Bullister, R.A. Feely, F.J. Millero, C. Mordy, T.-H. Peng, 2004: A global ocean carbon climatology: Results from GLODAP. *Global Biogeochemical Cycles*, 18, GB4031, doi:10.1029/2004GB002247.

Khatiwala S., F. Primeau, and T. Hall 2009: Reconstruction of the history of anthropogenic CO_2 concentrations in the ocean. *Nature*, 462: 346-349, doi:10.1038/nature08526.

Kicklighter, D. W., M. Bruno, S. Dönges, G. Esser, M. Heimann, J. Helfrich, F. Ift, F. Joos, J. Kaduk, G.H. Kohlmaier, A. D. McGuire, J. M. Melillo, R. Meyer, B. Moore III, A. Nadler, I. C. Prentice, W. Sauf, A. L. Schloss, S. Sitch, U. Wittenberg and G. Würth, 1999: A first-order analysis of the potential role of CO_2 fertilization to affect the global carbon budget: A comparison study of four terrestrial biosphere models. *Tellus B,* 51: 343-366.

Kicklighter, D.W., J.M. Melillo, W.T. Peterjohn, E.B. Rastetter, A.D. McGuire and P.A. Steudler, 1994: Aspects of spatial and temporal aggregation in estimating regional carbon dioxide fluxes from temperate forest soils. *Journal of Geophysical Research,* 99: 1303-1315.

Kiese, R., and K. Butterbach-Bahl, 2002: N_2O and CO_2 emissions from three different tropical forest sites in the wet tropics of Queensland, Australia. *Soil Biology and Biochemistry,* 34, 975-987.

Kiese, R., B. Hewett, A. Graham and K. Butterbach-Bahl, 2003: Seasonal variability of N_2O emissions and CH_4 uptake by tropical rainforest soils of Queensland, Australia. *Global Biogeochemical Cycles*, 17, 1043-1055.

Kimball, J. S., M. Zhao, A. D. McGuire, F. A. Heinsch, J. Clein, M. Calef, W. M. Jolly, S. Kang, S. E. Euskirchen, K. C. McDonald and S. W. Running, 2007: Recent climate-driven increases in vegetation productivity for the Western Arctic: evidence of an acceleration of the northern terrestrial carbon cycle. *Earth Interactions,* 11(4), 30pp.

Kirchgessner, D. A., *et al.,* 1993: Estimation of methane emissions from a surface coal mine using open-path FTIR spectroscopy and modeling techniques, *Chemosphere,* 26: 23-44.

Kishi, M.J., Motono, H., Kashiwai, M., Tsuda, A., 2001: An ecological–physical coupled model with ontogenetic vertical migration of zooplankton in the northwestern Pacific. *J. Oceanogr.*, 57: 499-507.

Kleypas, J.A., and S.C. Doney, 2001: Nutrients, Chlorophyll, Primary Production and Related Biogeochemical Properties in the Ocean Mixed Layer – A Compilation of Data Collected at Nine JGOFS Sites. *NCAR Technical Note NCAR/TN-447+STR*, 55 pp. http://dss.ucar.edu/datasets/ds259.0/

Knorr, W., T. Kaminski, M. Scholze, N. Gobron, B. Pinty, R. Giering and P.-P. Mathieu, 2010: Carbon cycle data assimilation with a generic phenology model. *J. Geophys. Res.*, 115, G04017.

Kopacz, M., *et al.,* 2010: Global estimates of CO sources with high resolution by adjoint inversion of multiple satellite datasets (MOPITT, AIRS, SCIAMACHY, TES). *Atmospheric Chemistry and Physics*, 10(3), 855-876 (http://www.atmos-chem-phys.net/10/855/2010/).

Kostadinov, T.S., D.A. Siegel, S. Maritorena, 2009: Retrieval of the particle size distribution from satellite ocean color observations, *J. Geophys. Res.,* 114, C09015, doi: 1029/2009JC005303.

Krinner, G., N. Viovy, N. de Noblet-Ducoudré, J. Ogée, J. Polcher, P. Friedlingstein, P. Ciais, S. Sitch, I.C. Prentice, 2005: A dynamic global vegetation model for studies of the coupled atmosphere-biosphere system. *Global Biogeochemical Cycles,* 19, GB1015, doi: 10.1029/2003GB002199.

Krol, M., *et al.,* 2005: The two-way nested global chemistry-transport zoom model TM5: algorithm and applications. *Atmosph. Chem. & Physics*, 5: 417-432. (http://www.atmos-chem-phys.net/5/417/2005/).

Kuroda, H., M.J. Kishi, 2004: A data assimilation technique applied to estimate parameters for the NEMURO marine ecosystem model. *Ecological Modelling,* 172: 69–85.

Kurz, W.A., and M. J. Apps, 1999: A 70-year retrospective analysis of carbon fluxes in the Canadian forest sector. *Ecological Applications*, 9(2): 526-547.

Kurz, W. A., C. C. Dymond, G. Stinson, G. J. Rampley, E. T. Neilson, A. L. Carroll, T. Ebata and L. Safranyik, 2008: Mountain pine beetle and forest carbon feedback to climate change. *Nature* 452, 987-990, doi: 10.1038/nature06777.

Kwon, E.Y., and F. Primeau 2008: Optimization and sensitivity of a global biogeochemistry ocean model using combined in-situ DIC, alkalinity and phosphate data *J. Geophys. Res.*,113,C08011, doi10.1029/2007JC004520.

Lamarque, J., *et al.,* 2005: Response of a coupled chemistry-climate model to changes in aerosol emissions: Global impact on the hydrological cycle and the tropospheric burdens of OH, ozone, and NOx. *Geophys. Res. Lett.*, 32, L16809 (http://www.agu.org/pubs/crossref/2005/2005GL023419.shtml).

Large, W. G., J. C. McWilliams, and S. C. Doney 1994: Oceanic vertical mixing: a review and a model with nonlocal boundary layer parameterization. *Rev. Geophys.*, 32: 363-403.

Le Quéré, C., M.R. Raupach, J.G. Canadell, G. Marland, *et al.*, 2009: Trends in the sources and sinks of carbon dioxide. *Nature Geosciences*, 2: 831-836, doi:10.1038/ngeo689.

Le Quéré, C., S.P. Harrison, I.C. Prentice, *et al.*, 2005: Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models. *Global Change Biol.*, 11: 2016-2040.

Lee, T., and 26 others, 2009: *Ocean State Estimation for Climate Research*. Community White Paper, OceanObs'09, Venice; [online] available at http://www.oceanobs09.net/blog/ [Accessed June 2011].

Leuven, K.U., 2008: *The GEM-E3 Model* [Online] (Updated 22 May 2008) Available at: http://www.gem-e3.net/ [Accessed 5 October 2010].

Levis, S., P. E. Thornton, G. B. Bonan and C. J. Kucharik, 2009: Modeling land use and land management with the Community Land Model. *iLEAPS Newsletter No. 7,* June 2009, pp. 10-12.

Li, C., S. Frolking and T.A. Frolking, 1992: A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *J. Geophysical Research,* 97(D9): 9759-9776.

Lin, S., and R.B. Rood, 1997: An explicit flux-form semi-Lagrangian shallow-water model on the sphere. *Quarterly Journal of the Royal Meteorological Society*, 123(544), 2477-2498 (http://doi.wiley.com/10.1002/qj.49712354416).

Liss, P.S., L. Merlivat, 1986: Air-sea gas exchange rates: introduction and synthesis. In: *The Role of Air-Sea Exchange in Geochemical Cycling,* P. Buat-Menard (editor). D. Reidel Publishing Co., Holland, pp. 113–127.

Liu, Z., and M. Alexander, 2007: Atmospheric bridge, oceanic tunnel, and global climatic teleconnections. *Rev. Geophys.*, 45, RG2005.

Macdonald, A.M., S. Mecking, J.M Toole, P.E. Robbins, G.C. Johnson. S.E. Wiffels, L.D. Talley, and M. Cook, 2009: The WOCE-era 3-D Pacific Ocean circulation and heat budget. *Prog. Oceanogr*, 82, 281-315.

Manizza, M., M. J. Follows, S. Dutkiewicz, J. W. McClelland, D. Menemenlis, C.N. Hill, A. Townsend-Small, and B. J. Peterson, 2009: Modeling transport and fate of riverine dissolved organic carbon in the Arctic Ocean, *Global Biogeochemical Cycles*, 23, GB4006, doi:10.1029/2008GB003396.

Mariko, S., T. Urano and J. Asanuma, 2007: Effects of irrigation on CO_2 and CH_4 fluxes from Mongolian steppe soil. *Journal of Hydrology,* 333(1), 118-123, doi: 10.1016/jhydrol.2006.07.027.

Marotzke, J., R. Giering, K.Q. Zhang, D. Stammer, C. Hill, and T. Lee, 1999: Construction of the adjoint MIT ocean general circulation model and application to Atlantic heat transport variability. *J. Geophys. Res.*, 104(C12): 29,529-29,547.

Marshall, J.C., C. Hill, L. Perelman and A. Adcroft 1997a: Hydrostatic, quasi-hydrostatic and non-hydrostatic ocean modeling. *Journal of Geophysical Research*, 102, 5,733-5,752.

Marshall, J.C., A. Adcroft, C. Hill, L. Perelman, and C. Heisey, 1997b: A finite-volume, incompressible Navier-Stokes model for the studies of the ocean on parallel computers. *J. Geophys. Res.*, 102: 5,753-5,766.

Matson, P. A., C. Volkmann, K. Coppinger and W. A. Reiners, 1991: Annual nitrous oxide flux and soil nitrogen characteristics in sagebrush steppe ecosystems. *Biogeochemistry,* 14, 1-12.

Matsumoto, K., J. L. Sarmiento, R. M. Key, O. Aumont, J. L. Bullister, K. Caldeira, J.-M. Campin, S. C. Doney, H. Drange, J.-C. Dutay, M. Follows, Y. Gao, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, K. Lindsay, E. Maier-Reimer, J. C. Marshall, R. J. Matear, P. Monfray, A. Mouchet, R. Najjar, G.-K. Plattner, R. Schlitzer, R. Slater, P. S. Swathi, I. J. Totterdell, M.-F. Weirig, Y. Yamanaka, A. Yool, and J. C. Orr, 2004: Evaluation of ocean carbon cycle models with data-based metrics, *Geophys. Res. Lett.*, 31, L07303, doi:10.1029/2003GL018970.

McClelland, J. W., R. M. Holmes, B. J. Peterson and M. Stieglitz, 2004: Increasing river discharge in the Eurasian Arctic: consideration of dams, permafrost thaw and fires as potential agents of change. *Journal of Geophysical Research,* 109, D18102, doi: 10.1029/2004JD004583.

McCulloch, A., *et al.,* 2003. Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere. *Atmospheric Environment,* 37(7): 889-902.

McGuire, A. D., D. J. Hayes, D. W. Kicklighter, M. Manizza, Q. Zhuang, M. Chen, M. J. Follows, K. R. Gurney, J. W. McClelland, J. M. Melillo, B. J. Peterson and R. G. Prinn, 2010: An analysis of the carbon balance of the Arctic Basin from 1997 to 2006. *Tellus B,* 62: 455-474, doi: 10.1111/j.1600-0889.2010.00497.x.

McGuire, A. D., S. Sitch, J. S. Clein, R. Dargaville, G. Esser, J. Foley, M. Heimann, F. Joos, J. Kaplan, D. W. Kicklighter, R. A. Meier, J. M. Melillo, B. Moore III, I. C. Prentice, N. Ramankutty, T. Reichenau, A. Schloss, H. Tian, L. J. Williams and U. Wittenberg, 2001: Carbon balance of the terrestrial biosphere in the twentieth century: analyses of CO_2, climate and land-use effects with four process-based ecosystem models. *Global Biogeochemical Cycles,* 15(1): 183-206.

McGuire, A. D., J. M. Melillo, D. W. Kicklighter, Y. Pan, X. Xiao, J. Helfrich, B. Moore III, C. J. Vorosmarty and A. L. Schloss, 1997: Equilibrium responses of global net primary production and carbon storage to doubled atmospheric carbon dioxide: Sensitivity to changes in vegetation nitrogen concentration. *Global Biogeochemical Cycles,* 11: 173-189.

McGuire, A. D., J. M. Melillo, D. W. Kicklighter and L. A. Joyce, 1995: Equilibrium responses of soil carbon to climate change: Empirical and process-based estimates. *J. Biogeography,* 22: 785-796.

McGuire, A. D., L. A. Joyce, D. W. Kicklighter, J. M. Melillo, G. Esser and C. J. Vorosmarty, 1993: Productivity response of climax temperate forests to elevated temperature and carbon dioxide: a North American comparison between two global models. *Climatic Change,* 24: 287-310.

McGuire, A. D., J. M. Melillo, L. A. Joyce, D. W. Kicklighter, A. L. Grace, B. Moore III and C. J. Vorosmarty, 1992: Interactions between carbon and nitrogen dynamics in estimating net primary productivity for potential vegetation in North America. *Global Biogeochemical Cycles,* 6: 101-124.

McKinley, G. A., M. J. Follows, and J. Marshall, 2004: Mechanisms of air-sea CO_2 flux variability in the equatorial Pacific and the North Atlantic. *Global Biogeochem. Cycles*, 18, GB2011, doi:10.1029/2003GB002179.

Meirink, J.F., H.J. Eskes, A.P. Goede, 2006: Sensitivity analysis of methane emissions derived from SCIAMACHY observations through inverse modeling. *Atmospheric Chemistry and Physics Discussions*, 6, 9405-9445. (http://www.atmos-chem-phys-discuss.net/5/9405/2005/).

Melillo, J. M., J. M. Reilly, D. W. Kicklighter, A. C. Gurgel, T. W. Cronin, S. Paltsev, B. S. Felzer, X. Wang, A. P. Sokolov and C. A. Schlosser, 2009: Indirect emissions from biofuels: how important? *Science* **326**, 1397-1399, doi: 10.1126/science.1180251.

Melillo, J.M., C.B. Field, and B. Moldan, 2003: Element interactions and the cycles of life: an overview. In: *Interactions of the Major Biogeochemical Cycles,* J.M. Melillo *et al.* (editors), Island Press, Washington, D.C., pp. 1-12.

Melillo, J.M., A.D. McGuire, D.W. Kicklighter, B. Moore III, C.J. Vorosmarty and A.L. Schloss, 1993: Global climate change and terrestrial net primary production. *Nature,* 363: 234-240.

Melillo, J.M., P.A. Steudler, J.D. Aber and R. D. Bowden, 1989: Atmospheric deposition and nutrient cycling, in: *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, M.O. Andreae and D. S. Schimel (eds.), John Wiley & Sons Ltd., pp. 263-280.

Melillo, J. M., J. Fruci, R.A. Houghton, B. Moore III and D.L. Skole, 1988: Land-use change in the Soviet Union between 1850 and 1980: Causes of a net release of CO_2 to the atmosphere. *Tellus B*, 40: 116-128.

Melillo, J. M., and J. R. Gosz, 1983: Interactions of biogeochemical cycles in forest ecosystems, in: *The Major Biogeochemical Cycles and Their Interactions*, B. Bolin and R. B. Cook (eds.), John Wiley and Sons, New York, pp. 177-222.

MERGE, 2004. *A Model for Evaluating the Regional and Global Effects of GHG Reduction Policies* [Online] Available at: http://www.stanford.edu/group/MERGE/ [Accessed 5 October 2010].

Michalak, A., *et al.*, 2008: ASCENDS—active Sensing of CO_2 Emissions over Nights, Days, and Seasons Mission, Technical report, University of Michigan in Ann Arbor, Michigan.

Mikaloff Fletcher, S.E., N.P. Gruber, A.R. Jacobson, M. Gloor, S.C. Doney, S. Dutkiewicz, M. Gerber, M. Follows, K. Lindsay, D. Menemenlis, A. Mouchet, S.A. Muller, and J. Sarmiento, 2007: Inverse estimates of the oceanic sources and sinks of natural CO_2 in and their implied oceanic transport. *Global Biogeochemical Cycles*, 21, GB1010, doi:10.1029/2006GB002751.

Miller, B.R., *et al.,* 2008. Medusa: A sample preconcentration and GC/MS detector system for *in situ* measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds. *Analytical Chemistry*, 80(5): 1536-1545.

Monteiro, F., M. J. Follows and S. Dutkiewicz, 2010: Distribution of diverse nitrogen fixers in the global ocean. *Global Biogeochemical Cycles*, 24, GB3017, doi:10.1029/2009GB00

Montzka, S., *et al.,* 1993: Global tropospheric distribution and calibration scale of HCFC-22. *Geophysical Research Letters*, 20(8), 703-706.

Montzka, S., *et al.,* 1994: Early trends in the global tropospheric abundance of hydrochlorofluorocarbon-141b and 142b. *Geophysical Research Letters*, 21(23), 2483-2486.

Moore, J.K., O. Braucher, 2008: Sedimentary and Mineral Dust Sources of Dissolved Iron to the World Ocean. *Biogeosciences*, 5, 631-656.

Moore, J.K., S.C. Doney and K. Lindsay, 2004: Upper ocean ecosystem dynamics and iron cycling in a global 3D model. *Global Biogeochem. Cycles,* 18: GB4028, doi:10.1029/2004GB002220.

Mouw, C.B., and J.A. Yoder, 2010: Optical determination of phytoplankton size distribution from global SeaWiFS imagery. *J. Geophys. Res.,* 115, C12018, doi:10.1029/2010JC006337.

Mueller, J.L., G.S. Fargion and C.R. McClain, 2003: *Ocean Optics Protocols For Satellite Ocean Color Sensor Validation, Revision 5, Volume V: Biogeochemical and Bio-Optical Measurements and Data Analysis Protocols*, NASA GODDARD report NASA/TM-2003 [online] [Accessed 20 June 2011] ftp://ftp.nist.gov/pub/physics/lunarproject/References/SIMBIOS/SimbiosTMSeries/SIMBIOS_Protoc olsVol5.pdf.

Mühle, J., *et al.,* 2010: Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane. *Atmospheric Chemistry & Physics*, 10(11): 5145-5164 (http://www.atmos-chem-phys.net/10/5145/2010/).

NASA, 2010: *NASA Carbon Monitoring System Scoping Study Workshop Report*, 13-14 July 2010, Boulder, CO, [online] Available at: http://cce.nasa.gov/cce/cms/about [Accessed 20 June 2011] (http://cce.nasa.gov/cce/cms/2010%20CMS_Scoping%20Study%20Workshop%20Report.pdf).

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

O'Neill, K. P., E. S. Kasischke and D. D. Richter, 2003: Seasonal and decadal patterns of soil carbon uptake and emission along an age sequence of burned black spruce stands in interior Alaska. *Journal of Geophysical Research*, 108(D1), 8155, doi: 10.1029/2001JD000443.

Oden, T. R. Moser and O. Ghattas, 2010a: Computer Predictions with Quantified Uncertainties. Part I. *SIAM News*, 43(9).

Oden, T. R. Moser and O. Ghattas, 2010b: Computer Predictions with Quantified Uncertainties. Part II. *SIAM News*, 43(10).

OECD, 2005: *Organization for Economic Co-operation and Development: Input Output Tables* [Online] Available at: http://www.oecd.org/sti/inputoutput [Accessed 6 October 2010].

Oren, R., D.S. Ellsworth, K.H. Johnson, *et al.*, 2001: Soil fertility limits carbon sequestration by forest ecosystems in a CO_2-enriched atmosphere. *Nature*, 411: 469-472.

Orr, J. C., E. Maier-Reimer, U. Mikolajewicz, P. Monfray, J. L. Sarmiento, J.R. Toggweiler, N.K. Taylor, J. Palmer, N. Gruber, C. L. Sabine, C. Le Quéré, R. M. Key, and J. Boutin, 2001: Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models, *Global Biogeochem. Cycles,* 15(1): 43-60.

Pacala, S., *et al.,* 2010: *Verifying Greenhouse Gas Emissions: Methods to Support International Climate Agreements* [Online], Report of the Committee on Methods for Estimating Greenhouse Gas Emissions, National Research Council, U.S. National Academies Press: Washington D.C., Available at: http://www.nap.edu/catalog.php?record_id=12883 [Accessed 20 June 2011]

Paltsev, S., J.M. Reilly, H.D. Jacoby, R.S. Eckaus, J. McFarland, M. Sarofim, M. Asadoorian and M. Babiker*,* 2005: *The MIT Emissions Prediction and Policy Analysis (EPPA) Model: Version 4.* Report 125, MIT Joint Program on the Science and Policy of Global Change, August, 72 p. [Online] (http://globalchange.mit.edu/files/document/MITJPSPGC_Rpt125.pdf).

Pan, Y., A. D. McGuire, J. M. Melillo, D. W. Kicklighter, S. Sitch and I. C. Prentice, 2002: A biogeochemistry-based dynamic vegetation model and its application along a moisture gradient in the continental United States. *Journal of Vegetation Science,* 13: 369-382.

Partensky, F., W.R. Hess and D. Vaulot, 1999: Prochlorococcus, a marine photosynthesic prokaryote of global significance. *Microbiol. Mol. Biol. Rev.*, 63: 106-127.

PBL Netherlands Environmental Assessment Agency, 2010: *Integrated Model to Assess the Global Environment* [Online] Available at: http://www.pbl.nl/en/themasites/image/index.html [Accessed 5 October 2010].

Peylin, P., P. Bousquet, C. Le Quere, S. Sitch, P. Friedlingstein, G. McKinley, N. Gruber, P. Rayner, and P. Ciais, 2005: Multiple constraints on regional CO_2 flux variations over land and oceans, *Global Biogeochem. Cycles*, 19 GB1011, doi:10.1029/2003GB002214.

Pfister, G.G., *et al.,* 2008: Impact of the summer 2004 Alaska fires on top of the atmosphere clear-sky radiation fluxes. *Journal of Geophysical Research*, 113, D02204. Available at: http://www.agu.org/pubs/crossref/2008/2007JD008797.shtml.

Plattner, G.-K., R. Knutti, F. Joos, T. F. Stocker, W. von Bloh, V. Brovkin, D. Cameron, E. Driesschaert, S. Dutkiewicz, M. Eby, N. R. Edwards, T. Fichefet, J. C. Hargreaves, C. D. Jones, M. F. Loutre, H. D. Matthews, A. Mouchet, S. A. Müller, S. Nawrath, A. Price, A. Sokolov, K. M. Strassmann, and A. J. Weaver, 2008: Long-term climate commitments projected with climate-carbon cycle models. *Journal of Climate,* 21: 2721-2751, doi: 10.1175/2007JCLI1905.1.

Post, W. M., A. W. King and S. D. Wullschleger, 1997: Historical variations in terrestrial biospheric carbon storage. *Global Biogeochemical Cycles,* 11: 99-109.

Potsdam Institute for Climate Impact Research, 2008. *ReMIND Code* [Online] (Updated 4 June 2008) Available at: http://www.pik-potsdam.de/research/research-domains/sustainable-solutions/models/remind/remind-code [Accessed 20 June 2011].

Prinn, R.G., *et al.,* 2001: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades. *Science*, 292: 1882-1888.

Prinn, R.G., *et al.,* 2000. A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *Journal of Geophysical Research*, 105(D14), 17751-17792, doi:10.1029/2000JD900141 (http://www.agu.org/pubs/crossref/2000/2000JD900141.shtml).

Prinn, R.G., H.D. Jacoby, A.P. Sokolov, C. Wang, X. Xiao, Z.L. Yang, R.S. Eckaus, P.H. Stone, A.D. Ellerman, J.M. Melillo, J. Fitzmaurice, D.W. Kicklighter, G.L. Holian, and Y. Liu, 1999: Integrated Global System Model for climate policy assessment: Feedbacks and sensitivity studies. *Climatic Change*, 41(3): 469-546, doi: 10.1023/A:1005326126726 (http://globalchange.mit.edu/files/document/MITJPSPGC_Reprint99-4.pdf).

Raich, J. W., E. B. Rastetter, J. M. Melillo, D. W. Kicklighter, P. A. Steudler, B. J. Peterson, A. L. Grace, B. Moore III and C. J. Vorosmarty, 1991: Potential net primary productivity in South America: application of a global model. *Ecological Applications,* 1: 399-429.

Raitsos, D., S. Lavender, C. Maravelias, J. Haralabous, A. Richardson, and P. Reid, 2008: Indentifying four phytoplankton functional types from space: An ecological approach. *Limnol. Oceangr.,* 53(2): 605-613.

Randerson, J. T., C. J. Still, J. J. Ballé, I. Y. Fung, S. C. Doney, P. P. Tans, T. J. Conway, J. W. C. White, B. Vaughn, N. Suits and A. S. Denning, 2002: Carbon isotope discrimination of arctic and boreal biomes inferred from remote atmospheric measurements and a biosphere-atmosphere model. *Global Biogeochemical Cycles,* 16(3): 1028, doi: 10.1029/2001GB001435.

Rastetter, E.B., 1996: Validating models of ecosystem response to global change. *BioScience,* 46(3): 190-198.

Rastetter, E.B., A.W. King, B.J. Cosby, G. M. Hornberger, R. V. O'Neill and J. E. Hobbie, 1992: Aggregating fine-scale ecological knowledge to model coarser-scale attributes of ecosystems. *Ecological Applications,* 2: 55-70.

Rastetter, E.B. M. Williams, K.L. Griffin, B.L. Kwiatkowski, G. Tomasky, M.J. Potosnak, P.C. Stoy, G.R. Shaver, M. Stieglitz, G.W. Kling, and J.E. Hobbie, 2010: Application of the Ensemble Kalman Filter to Assimilate Eddy Covariance Flux data into a Model of Arctic Carbon Exchange. *Ecological Applications,* 20: 1285-1301.

Rastetter, E. B., J. D. Aber, D. P. C. Peters, D. S. Ojima, and I. Burke, 2003: Using Mechanistic Models to Scale Ecological Processes Across Space and Time. *BioScience,* 53: 68-76.

Rayner, P. J., M. Scholze, W. Knorr, T. Kaminski, R. Giering and H. Widmann, 2005: Two decades of terrestrial carbon fluxes from a carbon cycle data assimilation system (CCDAS). *Global Biogeochemical Cycles,* 19, GB2026, doi: 10.1029/2004GB002254.

Rees, R. M., M. Wuta, P. A. Furley and C. Li, 2006: Nitrous oxide fluxes from savanna (miombo) woodlands in Zimbabwe. *Journal of Biogeography,* 33(3): 424-437.

Richardson, A.J., A.W. Walne, A.W.G John, T.D. Jonas, J.A. Lindley, D.W. Sims, D. Stevens, M. Witt, 2006: Using continuous plankton recorder data. *Progress in Oceanography*, 68 (1): 27-74.

Rigby, M., *et al.,* 2010: History of atmospheric SF_6 from 1973 to 2008. *Atmospheric Chemistry & Physics*, 10(21): 10305-10320, doi:10.5194/acp-10-10305-2010 (www.atmos-chem-phys.net/10/10305/2010/).

Rigby, M., *et al.,* 2008: Renewed growth of atmospheric methane. *Geophys. Res. Letters*, 35(22), L22805, doi:10.1029/2008GL036037 (http://www.agu.org/pubs/crossref/2008/2008GL036037.shtml).

Roemmich, D., and W.B. Owens, 2000: The Argo Project: global ocean observations for understanding and prediction of climate variability. *Oceanography*, 13(2): 45-50.

Rose, S. K., *et al.,* 2010. *Development of the Preliminary Version 7 Non-CO$_2$ GHG Emissions Dataset* [Online] (Updated 1 October 2010) Available at: https://www.gtap.agecon.purdue.edu/resources/res_display.asp?RecordID=3191.

Rotman, D.A., *et al.,* 2004: IMPACT, the LLNL 3-D global atmospheric chemical transport model for the combined troposphere and stratosphere: Model description and analysis of ozone and other trace gases. *J. Geophys. Res.*, 109, D04303 (http://www.agu.org/pubs/crossref/2004/2002JD003155.shtml).

Roulet, N., T. Moore, J. Bubier and P. Lafleur, 1992: Northern fens: methane flux and climatic change. *Tellus B,* 44: 100-105.

Saba, V.S., *et al.,* 2010: The challenges of modeling depth-integrated marine primary productivity over multiple decades: A case study at BATS and HOT. *Global Biogeochemical Cycles*, 24, GB3020, doi:10.1029/2009GB003655.

Sanchez, P.A., S. Ahamed, F. Carré, A.E. Hartemink, J. Hempel, J. Huising, P. Lagacherie, A.B. McBratney, N.J. McKenzie, M. de Loudres Mendonça-Santos, B. Minasny, L. Montanarella, P. Okoth, C.A. Palm, J.D. Sachs, K.D. Shepherd, T.-G. Vågen, B. Vanlauwe, M.G. Walsh, L.A. Winowiecki, G.-L. Zhang, 2009: Digital soil map of the world. *Science,* 325: 680-681, doi: 10.1126/science.1175084).

Schimel, D.S., J.I. House, K. A. Hibbard, P. Bousquet, P. Ciais, P. Peylin, B.H. Braswell, M.J. Apps, D. Baker, A. Bondeau, J. Canadell, G. Churkina, W. Cramer, A.S. Denning, C.B. Field, P. Friedlingstein, C. Goodale, M. Heimann, R. A. Houghton, J. M. Melillo, B. Moore, D. Murdiyarso, I. Noble, S. W. Pacala, I.C. Prentice, M.R. Raupach, P.J. Rayner, R. J. Scholes, W. L. Steffen, and C. Wirth, 2001: Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. *Nature,* 414: 169‑172.

Schimel, D., W. Hargrove, F. Hoffman, and J. MacMahon, 2007: NEON: a hierarchically designed national ecological network. *Frontiers in Ecology and the Environment,* 5(2): 59‑59.

Schimel, D., J. Melillo, H. Tian, A. D. McGuire, D. Kicklighter, T. Kittel, N. Rosenbloom, S. Running, P. Thornton, D. Ojima, W. Parton, R. Kelly, M. Sykes, R. Neilson and B. Rizzo, 2000: Contribution of increasing CO$_2$ and climate to carbon storage by ecosystems in the United States. *Science,* 287: 2004-2006.

Schmittner, A., A. Oschlies, H.D., Matthews E.D. Galbraith, 2008: Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO$_2$ emission scenario until year 4000 AD. *Global Biogeochem. Cycles,* 22, GB1013, doi:10.1029/2007GB002953.

Scholze, M., T. Kaminski, P. Rayner, W. Knorr and R. Giering, 2007: Propagating uncertainty through prognostic carbon cycle data assimilation system simulations. *Journal of Geophysical Research,* 112, D17305, doi: 10.1029/2007JD008642.

Segers, R., 1998: Methane production and methane consumption: a review of processes underlying wetland methane fluxes. *Biogeochemistry,* 41: 23-51.

Shalapyonok, A., R.J. Olson, and L.S. Shalapyonok, 1998: Ultradian growth in Prochlorococcus spp. *Appl. Environ Microbiol*., 64, 1066-1069.

Sitch, S., C. Huntingford, N. Gedney, P. E. Levy, M. Lomass, S. L. Piao, R. Betts, P. Ciais, P. Cox, P. Friedlingstein, C. D. Jones, I. C. Prentice and F. I. Woodward, 2008: Evaluation of the terrestrial carbon cycle, Future plant geography and climate-carbon cycle feedbacks using five Dynamic Global Vegetation Models (DGVMs). *Global Change Biology* 14, 2015-2039, doi: 10.1111/j.1365-2486.2008.01626.x.

Sitch, S., P. M. Cox, W. J. Collins, and C. Huntingford, 2007: Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature,* 448: 791-793, doi: 10.1038/nature06059.

Sitch, S., B. Smith, I. C. Prentice, A. Arneth, A. Bondeau, W. Cramer, J. O. Kaplan, S. Levis, W. Lucht, M. T. Sykes, K. Thonicke and S. Venevsky, 2003: Evaluation of ecosystem dynamics, plant geography and terrestrial carbon cycling in the LPJ dynamic vegetation model. *Global Change Biology,* 9: 161-185.

Smith, K. A., I. P. McTaggard and H. Tsuruta, 1997: Emissions of N_2O and NO associated with nitrogen fertilization in intensive agriculture, and the potential for mitigation. *Soil Use and Management,* 13: 296-304.

Sokolov, A.P., P.H. Stone, C.E. Forest, R. Prinn, M.C. Sarofim, M. Webster, S. Paltsev, C.A. Schlosser, D. Kicklighter, S. Dutkiewicz, J. Reilly, C. Wang, B. Felzer, J.M. Melillo and H.D. Jacoby, 2009: Probabilistic forecast for twenty-first-century climate based on uncertainties in emissions (without policy) and climate parameters. *J. Climate,* 22: 5175-5204, doi: 10.1175/2009JCLI2863.1.

Sokolov, A.P., D.W. Kicklighter, J.M. Melillo, B.S. Felzer, C.A. Schlosser and T.W. Cronin, 2008: Consequences of considering carbon-nitrogen interactions on the feedbacks between climate and the terrestrial carbon cycle. *Journal of Climate,* 21: 3776-3796, doi: 10.1175/2008JCLI2038.1.

Sokolov, A.P., C.A. Schlosser, S. Dutkiewicz, S. Paltsev, D.W. Kicklighter, H.D. Jacoby, R.G. Prinn, C.E. Forest, J. Reilly, C. Wang, B. Felzer, M.C. Sarofim, J. Scott, P.H. Stone, J.M. Melillo and J. Cohen, 2005: *The MIT Integrated Global System Model (IGSM) Version 2: Model Description and Baseline Evaluation*. Report 124, MIT Joint Program on the Science and Policy of Global Change, July, 40 p. (http://globalchange.mit.edu/files/document/MITJPSPGC_Rpt124.pdf).

Stammer, D., C. Wunsch, R. Giering, C. Eckert, P. Heimbach, J. Marotzke, A. Adcroft, C.N. Hill, and J. Marshall, 2002: The global ocean circulation and transports during 1992-1997, estimated from ocean observations and a general circulation model. *J. Geophys. Res*., 107(C9): 3118.

Stanley, R.H.R., W.J. Jenkins, D. E. Lott, and S.C. Doney, 2010: Noble gas constraints on air-sea gas exchange and bubble fluxes. *J. Geophys. Res.*: *Oceans*, submitted.

Stohl, A., *et al.,* 2009: An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons. *Atmospheric Chemistry and Physics*, 9(5), 1597-1620 (http://www.atmos-chem-phys.net/9/1597/2009/).

Stramski, D., Reynolds, R. A., Kahru, M., and Mitchell, B. G.,1999: Estimation of particulate organic carbon in the ocean from satellite remote sensing. *Science*, 285, 239–242.

Strassmann, K. M., F. Joos and G. Fischer, 2008: Simulating effects of land use changes on carbon fluxes: past contributions to atmospheric CO_2 increases and future commitments due to losses of terrestrial sink capacity. *Tellus B,* 60(4), 583-603, doi: 10.1111/j.1600-0889.2008.00340.x.

Sweeney, C., Gloor, E., Jacobson, A.R., Key, R.M., McKinley,G., Sarmiento, J.L., Wanninkhof, R., 2007: Constraining global air–sea gas exchange for CO_2 with recent bomb ^{14}C measurements. *Glob. Biogeochem. Cycles*, 21, GB2015.

Suntharalingam, P., and Sarmiento, J.L., 2000: Factors governing the oceanic nitrous oxide distribution: Simulations with an ocean general circulation model. *Global Biogeochem. Cycles,* 14(1): 429-454.

Suntharalingam, P., Sarmiento, J. L., and Toggweiler, J. R., 2000: Global significance of nitrous oxide production and transport from oceanic low-oxygen zones: A modeling study. *Global Biogeochem. Cycles,* 14(4): 1353-1370, doi: 10.1029/1999GB900100.

Takahashi, T., S.C. Sutherland and A. Kozyr, 2010: *Global Ocean Surface Water Partial Pressure of CO_2 Database: Measurements Performed During 1957–2009* (Version 2009). ORNL/CDIAC-152, NDP-088(V2009). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/otg.ndp088(V2009).

Takahashi, T., S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, C. Sabine, J. Olafsson, Th. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, Richard Bellerby, A. Körtzinger, T. Steinhoff, M. Hoppema, H. J. W. de Baar, C. S. Wong, Bruno Delille and N. R. Bates, 2009: Climatological mean and decadal changes in surface ocean pCO_2, and net sea-air CO_2 flux over the global oceans. *Deep-Sea Res. II*, 56: 554-577

Tang, E.P.Y., 1995: The allometry of algal growth rates. *J. Plankton Res*., 17: 1325-1235.

Tang, J., and Q. Zhuang, 2009: A global sensitivity analysis and Bayesian inference framework for improving the parameter estimation and prediction of a process-based Terrestrial Ecosystem Model. *Journal of Geophysical Research,* 114, D15303, doi: 10.1029/2009JD011724.

Tanhua, T., van Heuven, S., Key, R. M., Velo, A., Olsen, A., and Schirnick, C., 2010: Quality control procedures and methods of the CARINA database, *Earth Syst. Sci. Data*, 2: 35-49 (http://www.earth-syst-sci-data.net/2/35/2010/).

Tarantola, A., 1987: *Inverse Problem Theory: Methods for data fitting and model parameter estimation*. Elsevier, Amsterdam, 629 pp.

Thonicke, K., S. Venevsky, S. Sitch and W. Cramer, 2001: The role of fire disturbance for global vegetation dynamics: coupling fire into a Dynamic Global Vegetation Model. *Global Ecology and Biogeography,* 10(6): 661-677, doi: 10.1046/j.1466-822X.2001.00175.x.

Thornton, P. E., J.-F. Lamarque, N. A. Rosenbloom and N. M. Mahowald, 2007: Influence of carbon-nitrogen cycle coupling on land model response to CO_2 fertilization and climate variability. *Global Biogeochemical Cycles,* 21, GB4018, doi: 10.1029/2006GB002868.

Tian, H., J. M. Melillo, C. Lu, D. W. Kicklighter, M. Liu, W. Ren, X. Xu, G. Chen, C. Zhang, S. Pan, J. Liu and S. Running, 2011: China's terrestrial carbon balance: contributions from multiple global change factors. *Global Biogeochemical Cycles*, 25, GB1007, doi: 10.1029/2010GB003838.

Tian, H., J. M. Melillo, D. W. Kicklighter, S. Pan, J. Liu, A. D. McGuire, B. Moore III, 2003: Regional carbon dynamics in monsoon Asia and its implications for the global carbon cycle. *Global and Planetary Change,* 37: 201-217, doi:10.1016/S0921-8181(02)00205-9.

Tian, H., J. M. Melillo, D. W. Kicklighter, A. D. McGuire and J. Helfrich, 1999: The sensitivity of terrestrial carbon storage to historical climate variability and atmospheric CO_2 in the United States. *Tellus B,* 51: 414-452.

Tian, H., J. M. Melillo, D. W. Kicklighter, A. D. McGuire, J. V. K. Helfrich III, B. Moore III and C. J. Vörösmarty, 1998: Effect of interannual climate variability on carbon storage in Amazonian ecosystems. *Nature,* 396: 664-667.

Tjiputra, J. F., Polzin, D., and Winguth, A. M. E., 2007: Assimilation of seasonal chlorophyll and nutrient data into an adjoint three-dimensional ocean carbon cycle model: Sensitivity analysis and ecosystem parameter optimization. *Global Biogeochem. Cycles*, 21, GB1001, doi:10.1029/2006GB002745.

Trolier, M., *et al.,* 1996: Monitoring the isotopic composition of atmospheric CO_2: Measurements from the NOAA Global Air Sampling Network. *Journal of Geophysical Research*, 101(D20), 25897-25916 (http://www.agu.org/pubs/crossref/1996/96JD02363.shtml).

Uitz, J., H. Claustre, B. Gentili, and D. Stramski, 2010: Phytoplankton class-specific primary production in the world's oceans: Seasonal and interannual varaibility from satellite observations. *Global Biogeochem. Cycles*, 24, GB3016, doi:10.1029/2009GB003680.

Ullman, D. J., G. A. McKinley, V. Bennington, and S. Dutkiewicz, 2009: Trends in the North Atlantic carbon sink: 1992-2006. *Global Biogeochem. Cycles*, 23, GB4011, doi:10.1029/2008GB003383.

UN, 2006. *United Nations Statistics Division: Industry Statistics* [Online] Available at: http://unstats.un.org/unsd/industry/default.asp [Accessed 6 October 2010].

UNFCCC, 2010. *U.N. Framework Convention on Climate Change: National Inventory Submissions 2010,* http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/5270.php [Accessed 6 October 2010].

Uppala, S.M., *et al.,* 2005: The ERA-40 re-analysis. *Quarterly Journal of the Royal Meteorological Society*, 131(612), 2961-3012 (http://doi.wiley.com/10.1256/qj.04.176).

Upstill-Goddard, R.C., Barnes, J., Frost, T., Punshon, S. and Owens, N.J.P., 2000: Methane in the southern North Sea: Low-salinity inputs, estuarine removal, and atmospheric flux. *Global Biogeochemical Cycles*, 14(4): 1205-1217.

USGS, 2010. *United States Geological Survey: Minerals Information* [Online] (Updated 28 June 2010) Available at: http://minerals.usgs.gov/minerals/ [Accessed 6 October 2010].

Ussiri, D. A. N., and R. Lal, 2009: Long-term tillage effects on soil carbon storage and carbon dioxide emissions in continuous corn cropping system from an alfisol in Ohio. *Soil and Tillage Research,* 104(1), 39-47, doi: 10.1016/j.still.2008.11.008.

Utke, J., U. Naumann, M. Fagan, N. Thallent, M. Strout, P. Heimbach, C. Hill and C. Wunsch, 2008: OpenAD/F: A modular, open-source tool for automatic differentiation of Fortran codes. *ACM Transactions on Mathematical Software* (TOMS), 34(4), doi:10.1145/1377596.1377598.

Van Aardeene, J., *et al.,* 2010: *Emissions Database for Global Atmospheric Research* [Online] (Updated 10 June 2010) Available at: http://edgar.jrc.ec.europa.eu/index.php [Accessed 6 October 2010].

Van Cleve, K. L., C. T. Dyrness, L. A. Viereck, J. Fox, F. S. Chapin III and W. Oechel, 1983: Taiga ecosystems in interior Alaska. *BioScience,* 33: 39-44.

Van Drecht, G., *et al.,* 2003: Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Global Biogeochemical Cycles*, 17, pp. 26-1 to 26-20.

Van Ham, J., (Editor), 2000: *Non-CO_2 Greenhouse Gases: Scientific Understanding, Control and Implementation*, Dordrecht: Kluwer.

Verdy, A., S. Dutkiewicz, M.J. Follows, J. Marshall and A. Czaja, 2007: Carbon Dioxide and oxygen fluxes in the Southern Ocean: mechanisms for interannual variability. *Global Biogeochemical Cycles,* 21, doi:10.1029/2006GB002916.

Vitousek, P., P. Matson, C. Volkmann, J. M. Maass and G. Garcia, 1987: Nitrous oxide flux from dry tropical forests. *Global Biogeochemical Cycles,* 3(4): 375-382, doi: 10.1029/GB003i004p00375.

Wagner-Riddle, C., and G.W. Thurtell, 1998: Nitrous oxide emissions from agricultural fields during winter and spring thaw as affected by management practices. *Nutrient Cycling in Agroecosystems,* 52, 151-163.

Wang X.J., J. R. Christian, R. Murtugudde, A. J. Busalacchi, 2005: Ecosystem dynamics and export production in the central and eastern equatorial Pacific: a modeling study of impact of ENSO. *Geophysical Research Letters*, 32, doi:10.1029/2004GL021538.

Wang, Y.-P., D. Baldocchi, R. Leuning, E. Falge and T. Vesala, 2007: Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, 13, 652-670, doi: 10.1111/j.1365-2486.2006.01225.x.

Wang, Y.-P., R. Leuning, H. A. Cleugh and P. A. Coppin, 2001: Parameter estimation in surface exchange models using nonlinear inversion: how many parameters can we estimate and which measurements are most useful? *Global Change Biology,* 7: 495-510.

Wanninkhof, R., 1992: Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res*., 97: 7373-7382.

Wanninkhof, R.H., Sullivan, K.F., Top, Z., 2004: Air–sea gas transfer in the Southern Ocean. *J. Geophys. Res.* 109(C8): C08S19.

Wanninkhof, R.H., McGillis, W.M., 1999: A cubic relationship between gas transfer and wind speed. *Geophys. Res. Lett*., 26, 1889–1892.

Ward, B.A., M. Friedrichs, T. Anderson and A. Oschlies, 2010: Parameter optimisation techniques and the problem of underdetermination in marine biogeochemical models. *Journal of Marine Systems*, 81(1-2): 34-43, doi:10.1016/j.jmarsys.2009.12.005.

Warneke, T., *et al.,* 2006: Seasonal and latitudinal variation of atmospheric methane: A ground-based and ship-borne solar IR spectroscopic study. *Geophysical Research Letters*, 33, L14812 (http://www.agu.org/pubs/crossref/2006/2006GL025874.shtml).

Weber, M. G., and K. Van Cleve, 1984: Nitrogen transformation in feather moss and forest floor layers of interior Alaska black spruce ecosystems. *Canadian Journal of Forest Research,* 14: 278-290.

Werdell, P.J. and Bailey, S.W., 2005: An improved in situ bio-optical data set for ocean color algorithm development and satellite data product validation. *Remote Sensing of Environment*, 98(1): 122-140.

Werner, C., R. Kiese and K. Butterbach-Bahl, 2007: Soil-atmosphere of N_2O, CH_4 and CO_2 and controlling environmental factors for tropical rain forest sites in western Kenya. *Journal of Geophysical Research,* 112, D03308, doi: 10.1029/2006JD007388.

Wickland, K. P., R. G. Striegl, J. C. Neff and T. Sachs, 2006: Effects of permafrost melting on CO_2 and CH_4 exchange of a poorly drained black spruce lowland. *J. Geophys. Res.,* 111, G02011, doi: 10.1029/2005JG000099.

Wickland, K. P., R. G. Striegl, S. K. Schmidt, M. A. Mast, 1999: Methane flux in subalpine wetland and unsaturated soils in the southern Rocky Mountains. *Global Biogeochemical Cycles,* 13: 101-113, doi: 10.1029/1998GB9000003.

Williams, M., Y. Shimabokuro, D.A. Herbert, S. Pardi-Lacruz, C. Renno, E.B.Rastetter, 2002: Heterogeneity of soils and vegetation in eastern Amazonian rain forest: implications for scaling up biomass and production. *Ecosystems,* 5, 692-704.

WIOD, 2010. *World Input-Output Database* [Online] (Updated 6 July 2010) Available at: http://www.wiod.org/ [Accessed 6 October 2010]

Wunch, D., *et al.,* 2010: Calibration of the total carbon column observing network using aircraft profile data. *Atmospheric Measurement Techniques*, 3, 1351-1362, doi:10.5194/amt-3-1351-2010.

Wunsch, C., 2006: *Discrete Inverse and State Estimation Problems: With Geophysical Fluid Applications*. Cambridge University Press, 400 pp.

Wunsch, C., and P. Heimbach, 2007: Practical global oceanic state estimation. *Physica D*, 230(1-2), 197-208, doi:10.1016/j.physd.2006.09.040.

Wunsch, C., and P. Heimbach, 2006: Estimated decadal changes in the North Atlantic meridional overturning and heat flux 1993-2004. *J. Phys. Oceanogr.*, 36(11): 2012-2024, doi:10.1175/JPO2957.1.

Wunsch, C., P. Heimbach, R. Ponte, I. Fukumori and the ECCO-GODAE Consortium members, 2008: The global general circulation of the ocean estimated by the ECCO Consortium. *Oceanography*, 22(2), 88-103.

Xiao, X., J. M. Melillo, D. W. Kicklighter, A. D. McGuire, R. G. Prinn, C. Wang, P. H. Stone, A. Sokolov, 1998: Transient climate change and net ecosystem production of the terrestrial biosphere. *Global Biogeochemical Cycles* 12, 345-360.

Xiong, X., *et al.,* 2009: Methane plume over south Asia during the monsoon season: satellite observation and model simulation. *Atmospheric Chemistry and Physics*, 9, 783-794 (http://www.atmos-chem-phys.net/9/783/2009/).

Xiong, X., *et al.,* 2008: Characterization and validation of methane products from the Atmospheric Infrared Sounder (AIRS). *Journal of Geophysical Research*, 113, G00A01 (http://www.agu.org/pubs/crossref/2008/2007JG000500.shtml).

Xu-Ri, and I.C. Prentice, 2008: Terrestrial nitrogen cycle simulation with a dynamic global vegetation model. *Global Change Biology,* 14: 1745-1764, doi: 10.1111/j.1365-2486.2008.01625.x.

Yanai, R.D., J. J. Battles, A. D. Richardson, C. A. Blodgett, D. M. Wood, and E. B. Rastetter, 2010: Estimating uncertainty in ecosystem budget calculations. *Ecosystems,* 11: 239-248.

Yakushev, E. V., Pollehne, F., Jost, G., Kuznetso, I., Schneider, B., and Urnlauf, L., 2007: Analysis of the water column oxic/anoxic interface in the Black and Baltic seas with a numerical model. *Marine Chemistry*, 107(3): 388-410, doi:10.1016/j.marchem.2007.06.003.

Yi, S., A. D. McGuire, J. Harden, E. Kasischke, K. Manies, L. Hinzman, A. Liljedahl, J. Randerson, H. Liu, V. Romanovsky, S. Marchenko and Y. Kim, 2009: Interactions between soil thermal and hydrological dynamics in the response of Alaska ecosystems to fire disturbance. *Journal of Geophysical Research***114**, G02015, doi: 10.1029/2008JG000841.

Yokota, T. *et al.,* 2009: Global Concentrations of CO_2 and CH_4 Retrieved from GOSAT : First Preliminary Results. *Scientific Online Letters on the Atmosphere*, 5: 160-163.

Zaehle, S., and A. D. Friend, 2010: Carbon and nitrogen cycle dynamics in the O-CN land surface model: 1. Model description, site-scale evaluation, and sensitivity to parameter estimates. *Global Biogeochemical Cycles* 24, GB1005, doi: 10.1029/2009GB003521.

Zaehle, S., P. Friedlingstein and A.D. Friend, 2010a: Terrestrial nitrogen feedbacks may accelerate future climate change. *Geophysical Research Letters,* 37, L01401, doi: 10.1029/2009GL041345.

Zaehle, S., A. D. Friend, P. Friedlingstein, F. Dentener, P. Peylin and M. Schulz, 2010b: Carbon and nitrogen cycle dynamics in the O-CN land surface model: 2. Role of the nitrogen cycle in the historical terrestrial carbon balance. *Global Biogeochemical Cycles* 24, GB1006, doi: 10.1029/2009GB003522.

Zeng, H., J. Q. Chambers, R. I. Negrón-Juárez, G. C. Hurtt, D. B. Baker and M. D. Powell, 2009: Impacts of tropical cyclones on U.S. forest tree mortality and carbon flux from 1851 to 2000. *Proceedings of the National Academy of Sciences of the United States of America,* 106(19): 7888-7892, doi: 10.1073/pnas.0808914106.

Zhang, G.J., and N.A. Mcfarlane, 1995: Sensitivity of Climate Simulations to the Parameterization of Cumulus Convection in the Canadian Climate Centre General Circulation Model. *Atmosphere-Ocean*, 33(3): 407-446.

Zhang, L., D.J. Jacob, M. Kopacz, D.K. Henze, K. Singh, and D.A. Jaffe, 2009: Intercontinental source attribution of ozone pollution at western U.S. sites using an adjoint method. *Geophys. Res. Lett.*, 36, L11810.

Zhao, C., *et al.,* 2009: Atmospheric inverse estimates of methane emissions from Central California. *J. of Geophysical Research*, 114, D16302 (http://www.agu.org/pubs/crossref/2009/2008JD011671.shtml).

Zhuang, Q., J. M. Melillo, M. C. Sarofim, D. W. Kicklighter, A. D. McGuire, B. S. Felzer, A. Sokolov, R. G. Prinn, P. A. Steudler and S. Hu, 2006: CO_2 and CH_4 exchanges between land ecosystems and the atmosphere in northern high latitudes over the 21st century. *Geophysical Research Letters,* 33, L17403, doi: 10.1029/2006GL026972.

Zhuang, Q., J. M. Melillo, D. W. Kicklighter, R. G. Prinn, A. D. McGuire, P. A. Steudler, B. S. Felzer and S. Hu, 2004: Methane fluxes between terrestrial ecosystems and the atmosphere at northern high latitudes during the past century: a retrospective analysis with a process-based biogeochemistry model. *Global Biogeochemical Cycles,* 18, GB3010, doi:10.1029/2004GB002239.

Zhuang, Q., A. D. McGuire, J. M. Melillo, J. S. Clein, R. J. Dargaville, D. W. Kicklighter, R. B. Myneni, J. Dong, V. E. Romanovsky, J. Harden and J. E. Hobbie, 2003: Carbon cycling in extratropical terrestrial ecosystems of the Northern Hemisphere during the 20th Century: A modeling analysis of the influences of soil thermal dynamics, *Tellus B,* 55: 751-776.

Zhuang, Q., V. E. Romanovsky and A. D. McGuire, 2001: Incorporation of a permafrost model into a large-scale ecosystem model: Evaluation of temporal and spatial scaling issues in simulating soil thermal dynamics. *Journal of Geophysical Research* 106(D24): 33,648-33,670.

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