

Sources and Sinks of Anthropogenic CO₂: Integrated Assessment Using Biogeochemical Modeling and Inversion of Atmospheric Tracer Transport

A crucial issue in predicting and developing appropriate responses to global environmental change is the need for reliable assessment of future atmospheric concentrations of CO₂ and other greenhouse gases. Research to quantify the present, and to predict the future carbon budget, will necessarily involve multiple components of the Earth system, including the atmosphere, the oceans, the terrestrial biosphere, and anthropogenic emissions. A joint research program between the University of California at Santa Barbara (UCSB) and Princeton University will be developed to calculate the sources and sinks of atmospheric CO₂ (including anthropogenic emissions) by inversion of atmospheric observations using atmospheric chemical tracer transport models. Unlike previous studies, this inverse modeling will constrain the CO₂ budget using the isotopic composition of atmospheric CO₂, and will incorporate the seasonal as well as the spatial variability of the natural carbon cycle.

The objective of this study is to provide a quantitative assessment of the current CO₂ budget of the atmosphere. This objective will be accomplished by inversion of atmospheric tracer transport of CO₂ as constrained by simultaneous observations of the seasonal and spatial variability of the atmospheric concentration of CO₂, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$. The inversion calculation will require basis functions for fluxes of each isotopic species of CO₂ at the earth's surface, which will be developed from terrestrial and marine isotope biogeochemistry models developed under this project. The surface flux basis functions will include a temporal component with sufficient resolution in time to include the redistribution of the isotopic tracers by nonlinear covariance between the fluxes and atmospheric transport (rectification). This will involve resolved seasonal cycles for marine basis functions and resolved diurnal cycles for terrestrial basis functions.

Specific tasks that will be undertaken in support of the major objective will include:

1. The development of a next-generation model of terrestrial biogeochemistry to predict the isotopic composition of CO₂ fluxes, including fractionation during photosynthetic carbon assimilation, the isotopic composition of various carbon pools of varying ages at multiple depths in the soil, and the isotopic composition of water in the terrestrial hydrologic cycle. This model will be derived from the Simple Biosphere Model (SiB2) at UCSB.
2. Development of a model of global air-sea exchange of ¹³CO₂ and CO¹⁸O at seasonal as well as annual time scales. This will be done in the context of the Ocean Biogeochemistry Model at Princeton University, by combining remotely sensed seasonal ocean color data with existing physical, chemical, and biological ocean models.
3. Coupling of the above-mentioned terrestrial and marine flux models to three atmospheric circulation and chemical tracer transport models, to investigate the influence of surface isotope exchanges on the spatial and temporal variability of atmospheric CO₂ and its isotopes.
4. Inverse calculation of sources and sinks of atmospheric CO₂ using the results of the three atmospheric models coupled to the terrestrial and marine isotope BGC models, as constrained by atmospheric observations. The results from these inversions will also be used to suggest improvements to the component models.

The proposed research directly addresses both priorities of the MMIA initiative:

- a. The inversion method integrates atmospheric, terrestrial, and marine processes with anthropogenic emissions, providing a direct calculation of the current carbon budget and enhancing our ability to monitor compliance with emissions agreements or international treaties; and
- b. The development and enhancement of the component models of terrestrial and marine biogeochemistry, climate, atmospheric chemical tracer transport, and transport inversion will significantly improve our understanding of the relevant processes that control the rate of increase of atmospheric CO₂. The application of observational constraints through the inversion calculation during the development of the biogeochemical component models will enhance the applicability of these models for integrated assessments.

**This proposal is to be considered as a linked effort with another proposal by
PI/PD Jorge L. Sarmiento and Co-PI Songmiao Fan at Princeton University.**

Sources and Sinks of Anthropogenic CO₂: Integrated Assessment Using Biogeochemical Modeling and Inversion of Atmospheric Tracer Transport

1. Introduction

A crucial issue in predicting and developing appropriate responses to global change is the need for reliable prediction of future concentrations of atmospheric greenhouse gases, notably carbon dioxide (CO₂). Current scenarios using assumed emission projections and transient climate simulations suggest rapid warming and moistening of the atmosphere over the next century, with potentially serious consequences for human society and natural systems (Kattenberg et al., 1996). Such calculations are sensitively dependent on the assumed behavior of the natural carbon cycle as well as future industrial emissions, yet unfortunately, a quantitative description of the natural carbon budget of the atmosphere remains out of reach.

Natural fluxes of labile carbon among the atmospheric, terrestrial, and marine reservoirs are much larger than the anthropogenic contribution, and are characterized by such spatial and temporal variability as to preclude direct measurement in the foreseeable future (Schimel et al, 1996). Uptake of CO₂ by the oceans and terrestrial biosphere currently accounts for about half of the anthropogenic emissions, yet there is still considerable uncertainty about the relative proportions of the terrestrial and marine sinks, the exact mechanisms involved, and the prospect for continued operation of these mechanisms. The feasibility of accurate transient simulations of future climate, and in particular the development of models to project the response of atmospheric composition and climate to policy decisions, will depend on our ability to understand and predict the changing uptake of anthropogenic CO₂ by these large natural reservoirs.

Research to quantify the current carbon budget of the atmosphere, and to allow mechanistic prediction of its response to changes, will necessarily involve multiple components of the Earth system, including the atmosphere, the ocean, the terrestrial biosphere, and anthropogenic emissions. We propose an integrated program to develop methods to assess the current carbon budget, and at the same time to build the tools to allow mechanistic study of the processes involved so that realistic prediction of changes to these processes may become more feasible. The work we propose involves direct calculation of the sources and sinks of atmospheric CO₂ through inversion of observational data using global three-dimensional tracer transport models. Unlike previous studies, we will perform this calculation using CO₂ *and* its stable isotopic composition, including the effects of tight coupling between these fluxes and atmospheric circulation (the rectifier effect). This will be accomplished using state-of-the-art models of the biogeochemical cycling of CO₂ at the surface of both the land and the ocean, providing mechanistic coupling between surface climate, atmospheric circulation, and carbon fluxes at high time resolution.

The proposed research directly addresses both priorities of the Methods and Models for Integrated Assessment initiative:

- (a) The inversion method integrates atmospheric, terrestrial, and marine processes with anthropogenic emissions, providing a direct calculation of the current carbon budget and enhancing our ability to monitor compliance with emissions agreements or international treaties; and
- (b) The development and enhancement of the component models of terrestrial and marine biogeochemistry, climate, atmospheric chemical tracer transport, and transport inversion will significantly improve our understanding of the relevant processes that control the rate of increase of atmospheric CO₂. The application of observational constraints through the inversion calculation during the development of the biogeochemical component models will enhance the applicability of these models for integrated assessment.

NOTE: The research proposed here is a group effort with Investigators Jorge Sarmiento and Song-Miao Fan at Princeton University, who are submitting a linked proposal along with this one. The two proposals are essentially identical.

**This proposal is to be considered as a linked effort with another proposal by
PI/PD Jorge L. Sarmiento and Co-PI Songmiao Fan at Princeton University.**

2. Background

The spatial and temporal distribution of CO₂ concentration in the atmosphere contains information regarding sources and sinks at the surface. Quantitative interpretation of this information requires the use of a chemical tracer transport model (CTM) [Fung et al. 1983; Fung, 1986; Fung et al., 1987; Keeling et al., 1989; Tans et al., 1990; Enting et al., 1995]. The problem of inverting the tracer transport model to obtain emissions from concentration data is complicated by the fact that regional sources and sinks may produce nearly identical concentration patterns in the present observational network, which cannot be distinguished on the basis of CO₂ concentrations alone. A sink resulting from nitrogen fertilization of the Boreal forest, for example, might produce the same depression in observed CO₂ concentration at 50°N latitude as a sink of the same magnitude resulting from uptake by enhanced phytoplankton productivity in the North Atlantic Ocean. The transformation matrix, which must be inverted to estimate these sinks, is nearly singular.

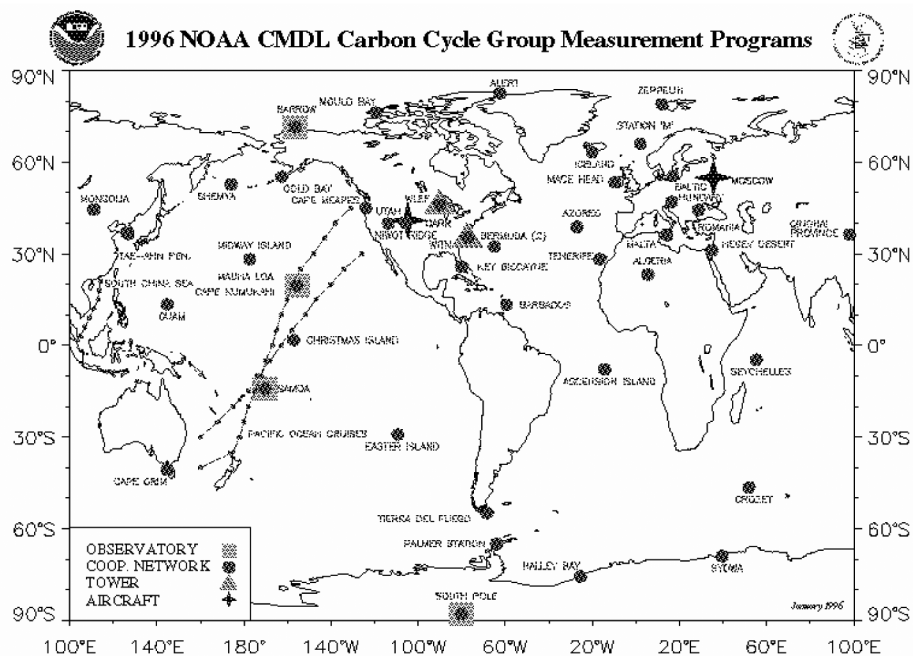


FIGURE 1: Stations in the NOAA flask network, which will be used for the inversion studies proposed here.

Observations of the stable isotopic ratios, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, of atmospheric CO₂ have since provided important additional constraints on the carbon budget inversion problem. Plant discriminates against carbon-13. By contrast, atmospheric $\delta^{13}\text{C}$ is nearly unchanged by the uptake of CO₂ into the surface oceans. The fractionation of carbon isotopes during air-sea exchange is small because the atmosphere is near equilibrium with the surface ocean with regard to the isotopic composition of CO₂. Therefore, we can use the $\delta^{13}\text{C}$ ratio of CO₂ to distinguish terrestrial from marine fluxes [Keeling et al., 1989; Tans et al., 1993; Ciais et al., 1995]. In plant tissues, CO₂ equilibrates with the water in which it is dissolved. Photosynthesis acts on CO₂ dissolved in water, which is enriched in ¹⁸O near evaporation sites in the leaves of terrestrial plants. The $\delta^{18}\text{O}$ of CO₂ can therefore be used to distinguish changes in photosynthesis (with a leaf $\delta^{18}\text{O}$ signature) from changes in respiration (with a soil $\delta^{18}\text{O}$ signature) [Farquhar et al., 1993; Ciais et al., 1997a,b].

Weekly atmospheric samples are collected routinely from about 50 sites in the remote troposphere, with analysis of CO₂, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ by the NOAA/CMDL Carbon Cycle Group Flask Sampling Network

(P. Tans, personal communication, see Fig 1). A carbon budget inversion calculation that used observations of all three atmospheric tracers (CO_2 , $\delta^{13}\text{C}$, and ^{18}O) would be much better constrained than those using only one or two.

In addition to the improvements in the observational system (including better spatial coverage, longer records, and multiple tracers), inversion models themselves have undergone major improvements in the past few years. Early attempts to constrain the carbon budget with observational data and 3-D transport models were essentially iterative series of forward simulations in which the surface forcing data were adjusted to produce a good fit [Fung et al, 1983, 1986, 1987]. Later studies [Keeling et al, 1989; Tans et al, 1990] used the synthesis inversion technique, in which surface fluxes were defined as basis functions and linear combinations were fit to the observational data by least-squares techniques. The synthesis inversion method was improved by Enting et al. [1995] who combined the Bayesian optimization with the singular value decomposition (SVD) method for inverting matrices. Recently, researchers at Princeton University have demonstrated significant progress with a new inversion technique [First Carbon Modeling Consortium (CMC) Meeting Report, 1995; Second Carbon Modeling Consortium (CMC) Meeting Report, 1996, see Fig 2]. The technique and its algorithm have been tested and evaluated using model data generated in a few established 3-D tracer models. Unlike the Bayesian technique of Enting et al [1995], the Princeton inversion approach does not require weighting functions using prior estimates of the regional fluxes.

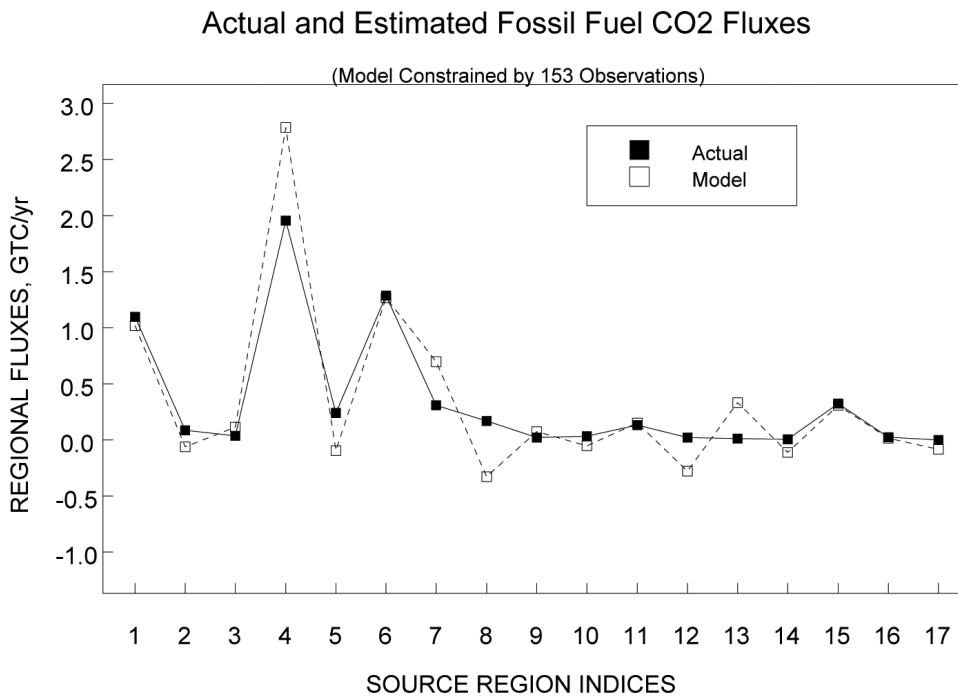


FIGURE 2: Preliminary result using the Princeton inversion technique to recover known (prescribed) emission fields for 17 geographic regions from simulated concentration data. The basis functions used are seventeen uniform source regions. Continental regions are high latitude Eurasia (1) and North America (2), mid latitude Eurasia (4) and North America (6), Africa (8), South America (11), and South Asia plus Australia (15).

Another major area of innovation in carbon cycle inversion modeling is the use of more detailed chemical tracer transport models. Fung et al [1983] first demonstrated the improvements obtained by simulating tracer transport in three dimensions, and this has been continued in many later studies. The GISS CTM used in many of these studies represents horizontal advection using a 4 hour time step, with vertical mixing by cumulus convection specified only in terms of monthly means. This model requires the use of a non-physical tunable diffusion parameter to match observations of anthropogenic tracers such as CFC-11 and Krypton-85. Denning [1994] demonstrated that when the tracer transport calculation is performed on-line in a general circulation model (GCM) with a time step of 0.1 hour, such tuning is

unnecessary. Furthermore, when vertical mixing due to atmospheric turbulence and cumulus convection is represented by the more detailed physical parameterizations in the GCM, nonlinear covariance between vertical motion and surface carbon flux produces first-order spatial structure in the simulated CO₂ distribution [Denning et al, 1995]. This “rectifier effect” will significantly change the carbon budget inferred by inversion of the observational data [Denning et al, 1996b], yet requires a transport model with detailed sub-grid scale physical parameterizations and a short time step to be properly simulated (Fig 3).

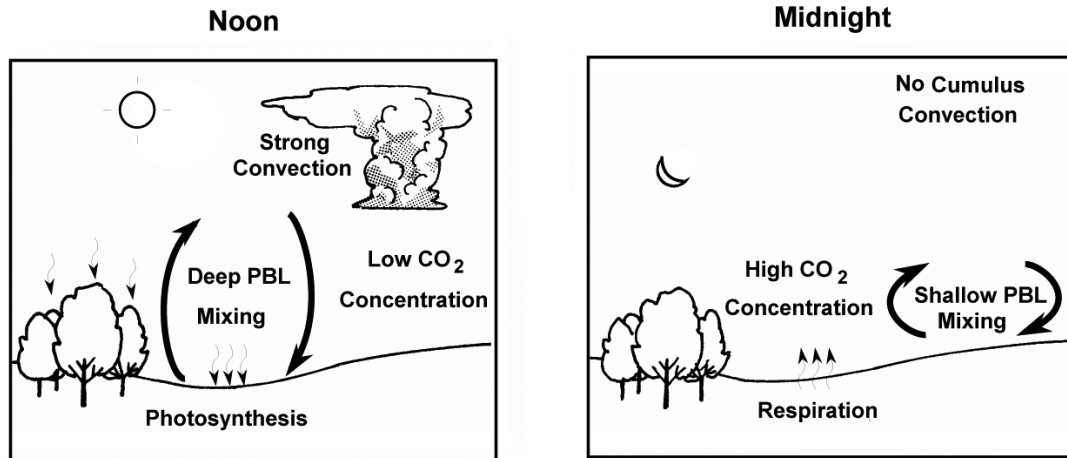


FIGURE 3: The Atmospheric rectifier effect that results from systematic covariance between terrestrial carbon flux, near-surface atmospheric turbulence, and deep cumulus convection [Denning et al, 1996b].

The convergence of improved observational systems, inversion techniques, and transport models described above provides an opportunity for much more reliable carbon cycle calculations as part of the integrated assessment process. Future carbon budget inversions using multiple independent tracers and sophisticated transport models can provide estimates of regional emissions as well as global sink terms. More importantly, they will leverage the observational data, allowing evaluation of mechanistic process models operating on regional scales, which will be crucial for predicting the response of the natural carbon cycle to global change. Finally, inversion models provide a framework for determination of optimal placement of new observational sites, so that the most information can be obtained from new stations at minimal cost.

What is needed before such an inversion calculation can be performed?

1. Regional descriptions of the spatial and temporal distributions of surface fluxes of CO₂, ¹³CO₂, CO¹⁸O, and O₂ over both land and ocean, to be used to develop realistic basis functions for the SVD process. Key features of these basis functions are spatial patterns, seasonal cycles, and (for terrestrial fluxes) diurnal cycles. This will require significant maturation of terrestrial and marine isotope biogeochemistry (BGC) models at the global scale.
2. An atmospheric transport model which is coupled to the relevant terrestrial physiology in such a way as to correctly represent the covariance between photosynthesis and latent heat flux, so that the atmospheric rectifier effect is properly simulated for all four tracers. This will require simulation of the *linkages* between terrestrial isotope BGC, physiology, biophysics, hydrology, boundary-layer turbulence, and large-scale atmospheric circulation, in a self-consistent model framework.

These are ambitious goals, but much of the preliminary work has already been done at Princeton University and Colorado State University (by Scott Denning who is now at the University of California, Santa Barbara). The collection of tools and expertise at the two institutions is precisely what is needed to develop the capabilities described above. In the next section, we describe the current state of the carbon model components at the two institutions, and outline our specific proposal to achieve the objective of performing integrated multitracer inversion calculations.

3. Proposed Research

3.1 Constrained Inversion

Atmospheric transport is a linear operator on the tracer concentration variables, such that we can divide the total concentration $C(x,t)$ at a given location x and time t into a sum of source specific components transported separately [Keeling et al., 1989; Tans et al., 1990; Enting et al., 1995]. For instance, we may decompose atmospheric CO₂ budget into contributions by fossil fuel emissions (ϕ_{FF}), land use change emissions (ϕ_{LU}), atmosphere-ocean exchange (ϕ_{AO}), annually balanced atmosphere-biosphere exchange (ϕ_{AB}), and a residual source component (ϕ_{RE}). The first four source components, including their spatial and temporal patterns, can be estimated based on national statistics of fossil fuel combustion, deforestation and other land use changes, ocean biogeochemistry models, and terrestrial ecosystem models, respectively. Sources and sinks that are not accounted for by the statistics or by the models are lumped into the residual flux. In a global tracer model, CO₂ from these sources can be transported separately, and sum up to the observed CO₂ (minus an offset due to historical emissions), given that the model transport is realistic. That is,

$$C_{\text{obs}}(x,t) = C_{\text{mod}}(x,t) = C_{\text{FF}}(x,t) + C_{\text{LU}}(x,t) + C_{\text{AO}}(x,t) + C_{\text{AB}}(x,t) + C_{\text{RE}}(x,t) \quad (1)$$

where the subscripts, from left to right, indicate observation, model prediction, and model prediction for respective source components.

The global integral of ϕ_{RE} can be obtained by mass balance, ie, from the difference between the observed trend of atmospheric CO₂ and the sum of ϕ_{FF} , ϕ_{LU} , ϕ_{AO} , and ϕ_{AB} . However, we do not know the nature nor the spatial and temporal variability of the residual source. Our strategy is to estimate ϕ_{RE} by combining observations with the best biogeochemical models for predicting ϕ_{AO} and ϕ_{AB} .

In principle, the residual source may be divided into source regions as small as the size of a horizontal grid cell. A global tracer model can be used to calculate $a_j(x,t)$, the distribution of CO₂ resulting from a unit flux of, say, 1 Pmol of C per year, through source region j . We can write the residual CO₂ as a linear combination of contributions by the source regions,

$$C_{RE}(x,t) = \sum_j a_j(x,t) \phi_j \quad (2)$$

where the coefficient ϕ_j is a multiplier of 1 PmolC/yr indicating the magnitude of flux through source region j . Combine Eqs. (1) and (2), and use the vector and matrix notations, we can write

$$C_{\text{obs}} = C_{\text{FF}} + C_{\text{LU}} + C_{\text{AO}} + C_{\text{AB}} + \mathbf{A}\Phi \quad (3)$$

where the length of the concentration vectors and the number of rows in matrix \mathbf{A} are determined by the number of measurement stations times the number of monthly mean observations at each station, the length of Φ equals the number of source regions. The magnitudes of flux through each source region can be calculated from

$$\Phi = \mathbf{A}^{-1} (C_{\text{obs}} - C_{\text{FF}} - C_{\text{LU}} - C_{\text{AO}} - C_{\text{AB}}) \quad (4)$$

This is in fact a least-squares fit that gives the optimal combination of sources. In practice, the number of source regions must be equal or smaller than the number of independent measurement stations that are sufficiently separated in space. The globe is necessarily divided into a small number of large geographical regions. The spatial and temporal patterns within each source region must be assumed or prescribed in the tracer model simulations, which consist a set of ‘‘basis functions’’. The simulated concentration field is allowed to come to equilibrium with the surface fluxes. The basis functions to be used is described in section 3.5

The use of the isotopic composition of atmospheric CO₂ allows a much tighter constraint on the inversion problem. The challenge in developing an integrated multitracer inversion model is to provide appropriate basis functions which capture the variations of the surface fluxes of CO₂, ¹³CO₂, and CO¹⁸O in an internally consistent manner. Even the annually balanced fluxes interact strongly with seasonal (and diurnal) variations in atmospheric transport to produce first-order spatial structure in the annual mean, so it is crucial to realistically simulate the variations of these fluxes at time scales comparable to those of changes in the relevant transport (seasonal for ocean fluxes, diurnal for terrestrial fluxes).

Following Tans et al [1993], the instantaneous effects of surface carbon fluxes on the isotopic composition of CO₂ are given by

$$C_a \frac{\partial \delta_a}{\partial t} + T(C_a \delta_a) = F_{FF}(\delta_{FF} - \delta_a) + F_{BB}(\delta_{BB} - \delta_a) + F_{OA}(\delta_o - \delta_a + \epsilon_{OA}) + \Delta_{pho} F_{pho} + F_{resp}(\delta_{resp} - \delta_a + \epsilon_{resp}) \quad (5)$$

Here F_{FF} , F_{BB} , F_{OA} , F_{pho} , and F_{resp} are the instantaneous fluxes of CO₂ to the atmosphere due to fossil fuel combustion, biomass burning, ocean-atmosphere transfer, terrestrial photosynthesis, and terrestrial respiration, respectively. C_a is the atmospheric concentration of CO₂, and δ is the isotopic ratio associated with the atmosphere and with each carbon flux, defined in the usual way. T is the transport operator. ϵ_{OA} is the kinetic fractionation factor associated with transfer across the air-sea interface and ϵ_{resp} represents isotopic fractionation associated with respiration, if any. Δ_{pho} is the isotopic discrimination associated with terrestrial photosynthesis.

Specification of basis functions for the multitracer inversion involves spatial and temporal maps of CO₂ flux as in previous studies, and also specification of each term in the above equation.

In the following subsections, the parameterization of the various terms in Eq (5) is described. The transport term is calculated by three atmospheric tracer transport models, described in section 3.2. The first two terms on the right-hand-side of Eq (5) relate to the isotopic fluxes associated with fossil fuel combustion and biomass burning. The isotopic composition of both the fossil fuel reservoir and the biomass is assumed to be constant; thus these terms are simple multiples of the fluxes from each of these activities. The third term on the rhs represents the isotopic fluxes associated with air-sea carbon flux. It is calculated using a new version of the Princeton Ocean Biogeochemistry Model (OBM), as described in section 3.3. The last two terms in Eq (5) are calculated using a land-surface biogeochemistry model (based on SiB2), as described in section 3.4. A set of basis functions to be used is then described in section 3.5.

3.2 Atmospheric models

Three atmospheric chemical tracer transport models are in use at the two institutions: the GCTM (at Princeton) is a fast, computationally efficient code for rapid evaluation and prototyping of transport problems; the SKYHI model (also at Princeton) is a high-resolution code for on-line tracer transport; and the CSU GCM (at UCSB) is a moderate resolution GCM with detailed sub-grid scale physics and links to terrestrial physiology and biophysics.

The GFDL SKYHI model has a spatial resolution of 3° x 3.6° latitude by longitude in the horizontal, and 40 layers in the vertical from the surface to 80 km altitude, with up to 16 layers in the tropical troposphere) [Fels et al., 1980; Mahlman et al., 1994]. GCTM uses equal area grids and offline winds generated by an early atmospheric GCM developed at GFDL [Mahlman and Moxim, 1978; Levy et al., 1982]. Evaluation of SKYHI model transport was conducted using ²²²Rn, ⁸⁵Kr, CFC-11, fossil fuel CO₂, and the Fung model of biospheric CO₂. The GCTM model transport was evaluated using ²²²Rn, ⁸⁵Kr, SF₆, fossil fuel CO₂, and the Carnegie-Ames-Stanford approach (CASA) model of biospheric CO₂ [Potter et al., 1993]. Model simulated tracer profiles were compared with observations. Both tracer models demonstrate good agreements with observations, indicating good simulations of the large-scale transport (Fig. 1).

The Colorado State University (CSU) General Circulation Model (GCM) was derived from the UCLA GCM by D. Randall and colleagues. The model includes state-of-the-art parameterizations of the effects of moist cumulus convection [Randall and Pan, 1993] and cloud microphysics [Fowler et al, 1996]. A key feature of the model is its formulation in a modified sigma coordinate which is defined such that the top of the planetary boundary layer (PBL) is a coordinate surface [Suarez et al, 1983]. The depth of the turbulent PBL is determined as a prognostic variable in the model using a second-order bulk method based on the turbulence kinetic energy equation [Randall et al, 1992]. Surface fluxes of momentum, energy, water, and carbon at land grid points are calculated on-line using the Simple Biosphere Model (SiB2, see section 3.4 below) [Sellers et al, 1996a,b; Randall et al, 1996]. The model is typically integrated on a $4^\circ \times 5^\circ$ grid with 17 levels, at a time step of 0.1 hr.

Tracer transport was added to the CSU GCM by Denning [1994], including large-scale advection and sub-grid scale vertical transport by penetrative cumulus convection, dry convective mixing, and boundary-layer turbulence and entrainment. The effects of downdrafts in cumulus clouds are also included. Tracer experiments using ^{85}Kr , ^{222}Rn , and SF_6 agree quite well with observational data without the need for tuning with non-physical diffusion. When the terrestrial carbon flux calculated by SiB2 was coupled to the tracer transport code, the resulting spatial and temporal distributions of CO_2 at the land surface compared very favorably with both the NOAA flask data and the limited data from continental experiments [Denning et al, 1996a,b].

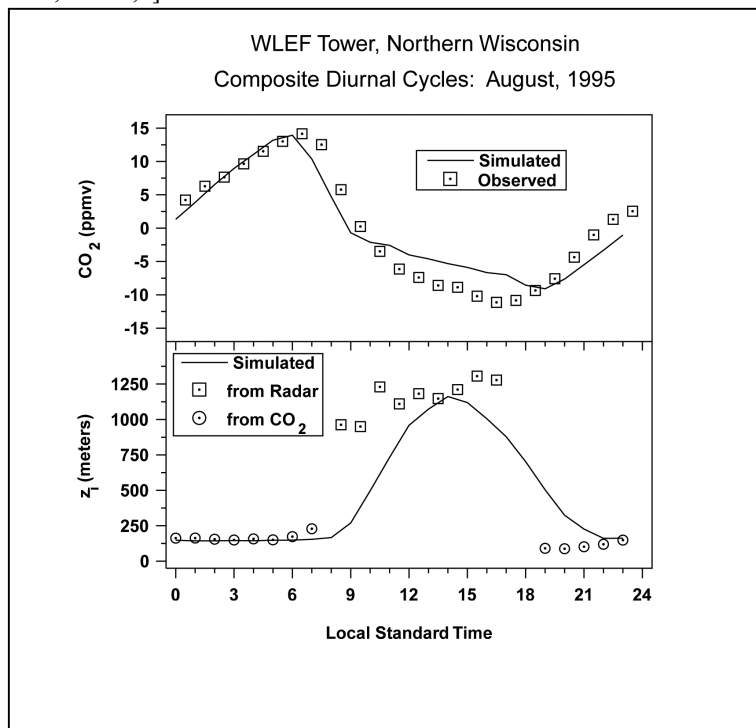


FIGURE 3: Simulation and observation of the atmospheric rectifier effect at a 496 m tall TV transmitter tower in Northern Wisconsin. Model results from SiB2 in the CSU GCM are taken from a global simulation without site-specific calibration. CO_2 observations were made in August of 1995 at 76 m above the ground. PBL depth was estimated using radar reflectivity during the day, and by locating the level of the nocturnal inversion from the CO_2 gradient at night.

The sub-grid scale vertical transport in the atmosphere and the assimilation of CO_2 by terrestrial photosynthesis are both largely driven by solar radiation, and so are highly correlated (turbulence and convection tend to covary with photosynthesis). This leads to a systematic ventilation of low- CO_2 air that has been influenced by photosynthesis and an accumulation of respiration dominated air that tends to be trapped near the surface by low level nocturnal (or seasonal) inversions [Denning et al, 1995, 1996b]. The realism of this phenomenon can only be tested by long-term measurements of both CO_2 flux and atmospheric structure. Preliminary analysis of data collected at a 496 m tall tower in northern Wisconsin suggests that the GCM captures the relevant physics of this atmospheric rectifier effect by correctly simulating the coupled diurnal evolution of CO_2 concentration and PBL turbulence at the site [Fig 3, Denning et al, 1996c].

3.3 Ocean biogeochemistry model

Seasonal air-sea fluxes of O₂, CO₂ and the isotopes of CO₂ will be produced by a new version of the ocean biogeochemistry model (OBM) under development at Princeton. The current OBM is embedded in a 4° annual mean version of the GFDL MOM code. We first discuss some of the features of the current OBM before describing the changes that are being implemented by others in our group to produce a seasonal OBM.

We use an annual mean 4° version of the GFDL primitive equation MOM code [*Pacanowski et al.*, 1993]. The original circulation model, its ability to reproduce the observed uptake of ¹⁴C, small modifications to the model, and the impact of these changes on tracer transport, are described elsewhere [*Toggweiler et al.*, 1989, *Toggweiler and Samuels*, 1993a, *Toggweiler and Samuels*, 1993b]. The total model depth of 5000 m is represented by twelve levels of increasing thickness. The thickness of the top, second, and bottom levels is 50.9 m, 68.4 m, and 869 m, respectively.

The connection between atmospheric CO₂ and oceanic carbon is established via gas exchange. Gas exchange is driven by a difference between the partial pressure of CO₂ in the ocean and atmosphere. We model this in the usual way as the product of a gas transfer velocity k_w times the atmosphere-ocean difference in CO₂ concentration:

$$f = k_w(1-\gamma_{ice})[\alpha(pCO_2)_{atm} - (CO_2)_{oc}] \quad (6)$$

The first term in parentheses on the right hand side is a correction for the fraction of ice cover. Inside the brackets are α , the solubility of CO₂; $(pCO_2)_{atm}$, the atmospheric partial pressure corrected to 100% humidity at the temperature of surface water (see [*Sarmiento et al.*, 1992]) and $(CO_2)_{oc}$, which is the surface ocean concentration of CO₂ found mostly in the hydrolyzed form H₂CO₃.

The set of chemical reactions that play a role in determining the concentration of $(CO_2)_{oc}$ are solved using a procedure analogous to one given in Peng et al. [*Peng et al.*, 1987] with equilibrium constants as summarized in Table 1. We use model values of DIC, TA, temperature, and salinity to solve the carbon system equations.

The gas transfer velocity, k_w , is a function of wind speed, U , and Schmidt number, Sc , following the bomb radiocarbon calibrated relationship of Wanninkhof [1992]:

$$k_w = 0.39U^2 \left(\frac{Sc}{660}\right)^{-0.5} \quad (7)$$

The observational analysis of Esbensen and Kushnir [1981] provides the wind speed, U . The Schmidt number, Sc , is a function of temperature [*Jahne et al.*, 1987]. Temperature is obtained from the ocean circulation model. The fraction of sea ice cover γ_{ice} is specified using the observational analysis of Alexander and Mobley [1976]. CO₂ solubility, α , is taken from Weiss [1974]. The magnitude of $(pCO_2)_{atm}$ is specified. The pre-industrial $(pCO_2)_{atm}$ we use is 278.2 ppmv (dry atmosphere value).

The gas transfer velocity for ¹³CO₂ is corrected for kinetic fractionation effects (Table 1) and a -0.2‰ OH⁻ correction such that

$$\frac{{}^{13}k_w}{k_w} = 0.9993 \quad (8)$$

The preindustrial atmospheric $\delta^{13}C$ of CO₂ = -6.52 ‰ and equilibrium fractionation factors (Table 1) for carbon isotopes in the different DIC species were used to calculate $({}^{13}CO_2)_{oc}$ and $({}^{13}CO_2)_{atm}$, where $(CO_2)_{atm} = \alpha(pCO_2)$. The fractional ice coverage remains unchanged.

Tracers in the OBM which affect $(CO_2)_{oc}$ and $({}^{13}CO_2)_{oc}$ are phosphate, dissolved inorganic carbon (DIC) and $DI^{13}C$, total alkalinity (TA), and labile dissolved organic carbon (LDOC) and $LDO^{13}C$.

Formulation of biology, strengths and weaknesses of the OBM are described in detail in a linked proposal submitted to the MMIA program by Princeton group.

A seasonal ocean ecosystem model is currently being implemented in the OBM to calculate the biological processes using SeaWiFS Coastal Zone Color Scanner (CZCS) data and TOPEX/Poseidon wind measurements. The carbon-nitrogen ecosystem model is derived from the nitrogen based ecosystem model of Fasham et al. [1993]. The addition of carbon to the model is based on work by T. Anderson. Phytoplankton, zooplankton, and bacteria each have a unique stoichiometric C:N ratio. We altered the carbonate:organic carbon ratio from the values set by T. Anderson so that the export of carbonate and surface ocean alkalinities are in better agreement with observations. We plan to incorporate the cycling of carbon isotopes in a manner analogous to that used in the OBM: carbon fractionation during photosynthesis, but none during remineralization or grazing.

Surface ocean $pCO^{18}O$ will be diagnosed from surface ocean salinity and model pCO_2 . This is possible because of the short time required for isotopic equilibration of the oxygen isotopes in CO_2 via hydrolysis reactions. The net air-sea flux of $CO^{18}O$ will then be given by:

$$^{18}f = k_{wo^{18}}(1-\gamma_{ice})[\alpha_{18}(pCO^{18}O)_{atm} - (CO^{18}O)_{oc}] \quad (9)$$

where $k_{wo^{18}}$ is the piston velocity for $CO^{18}O$, $(CO^{18}O)_{oc}$ is the dissolved concentration of $CO^{18}O$ in the surface layer, and $\alpha_{18}(pCO^{18}O)_{atm}$ is the concentration of $CO^{18}O$ in the surface layer in equilibrium with the atmosphere. The $^{18}O/^{16}O$ ratio of CO_2 is related to that of seawater by a temperature dependent coefficient [Ciais et al., 1997]. The $^{18}O/^{16}O$ ratio of seawater was found to be a linear function of salinity, S (in unit g/Kg) [Craig and Gordon, 1965; Farquhar et al., 1993]:

$$\delta^{18}O_{sw} = a_1 + a_2 S \quad (10)$$

where $a_1 = -16.75$ permil and $a_2 = 0.5$ permil $g^{-1} Kg$ are empirical coefficients.

Table 1. Equilibrium constants and concentrations used for carbon chemistry calculations

Equilibrium constant or fractionation factor	Reference
Carbon K_1, K_2	[Goyet and Poisson, 1989]
Borate K	[Dickson, 1990]
Silicate K	[Sjoberg et al., 1981]
Phosphoric Acid K_1, K_2, K_3	[Dickson and Riley, 1979b]
Water K	[Dickson and Riley, 1979a]
Carbon kinetic gas fractionation	(Siegenthaler and Münnich, 1981)
Carbon $\alpha_{g:a}, \alpha_{a:b}, \alpha_{a:c}$	(Mook, 1986)
Term	Source
Carbon $\alpha_{CaCO_3:b}$	(Rubinson and Clayton, 1969)
Carbon $\alpha_{C_{org}:a}$	(Freeman and Hayes, 1992)
Total Borate ¹	$S_{\text{‰}} \cdot 11.88 \mu\text{mol kg}^{-1} \text{‰}^{-1}$
Total Phosphate	$2.15 \mu\text{mol/kg}$
Total Silica ²	$S_{\text{‰}} \cdot 3.143 \mu\text{mol kg}^{-1} \text{‰}^{-1}$
Total Sulfate ²	$S_{\text{‰}} \cdot 0.8067 \text{mmol kg}^{-1} \text{‰}^{-1}$
Total Fluorine ²	$S_{\text{‰}} \cdot 1.981 \mu\text{mol kg}^{-1} \text{‰}^{-1}$
β_{SO_4}	[Khoo et al., 1977]

β_{HF}

[Dickson and Riley, 1979b]

Ionic strength/salinity relation for seawater

50.3781 = 1.00311S

3.4 The Simple Biosphere Model and Terrestrial BGC Studies at UCSB

The Simple Biosphere Model [Sellers, 1986] has recently undergone major revision and is now referred to as SiB2 [Sellers et al, 1996a,b,c,d; Randall et al, 1996; Denning et al, 1996a,b]. Key changes are

1. A simpler canopy structure with fewer biome-dependent parameters;
2. The use of satellite vegetation data to constrain parameter values;
3. Coupling of the hydrologic and carbon cycling at the land surface through a physiologically realistic parameterization of stomatal conductance in terms of photosynthetic carbon; and
4. Inclusion of a rudimentary model of annually balanced soil carbon to allow seasonal and diurnal carbon fluxes to be coupled to the atmospheric tracer calculation.

The use of remotely sensed vegetation data forces the model to produce reasonably realistic seasonal and interannual variability in physiological behavior, and constrains the spatial distribution of the fluxes as well. Specifically, parameters such as albedo, leaf area index, surface roughness, and canopy greenness are prescribed according to time-varying imagery rather than from maps of biome distributions. The equations for leaf-level photosynthesis and stomatal conductance are scaled to the canopy level using an assumed optimal relationship between leaf nitrogen (and photosynthetic capacity) and light attenuation in the canopy, which is again determined using remotely sensed data rather than prescribed a priori.

SiB2 is ideally suited for the terrestrial portion of the carbon cycle inversion problem, because the surface energy budget and carbon assimilation rate are related by the ball-Berry-Collatz stomatal model [Ball, 1988; Collatz et al, 1991, 1992] and an enzyme kinetic model of photosynthesis [Farquhar et al, 1980]. This structure allows representation of the interactions between surface CO₂ flux and atmospheric transport with respect to their influence on ventilation of photosynthesis-influenced air [the atmospheric rectifier; Denning et al, 1996a,b,c] and the fractionation of stable carbon and oxygen isotopes during assimilation [Ciais et al, 1995, 1997a,b; Fung et al, submitted to GBC].

Isotopic variations due to terrestrial carbon fluxes are represented according to Fung et al [submitted to GBC] for $\delta^{13}\text{C}$, and according to Ciais et al [1997a] for $\delta^{18}\text{O}$.

Isotopic fractionation of carbon due to photosynthesis involves four steps: diffusion through the laminar leaf boundary layer and stomatal opening, dissolution in interstitial water, diffusion through the mesophyll tissue, and carboxylation reaction. Each step enriches the air in ¹³C as the plant gets depleted. For C3 plants, the overall relation is

$$\Delta = a + (b - a) \frac{C_i}{C_a} \quad (11)$$

where C_a and C_i are the partial pressure of CO₂ in the atmosphere and the intercellular leaf water, respectively (calculated every 6 minutes by SiB2), and a and b are empirical coefficients ($a = 4.4$, $b = 27.5$) [Berry, 1989]. For C4 plants, C_i is concentrated by a biochemical mechanism so that the discrimination is determined by diffusion alone, with $\Delta = 4.4$ permil.

Changes in isotopic composition of carbon due to respiration are due to the disequilibrium in $\delta^{13}\text{C}$ that results from the time lag between photosynthetic uptake and respiratory release of carbon, and the steady decline in the $\delta^{13}\text{C}$ ratio of atmospheric CO₂ due to the accumulation of fossil carbon. We assume that there is no isotopic fractionation associated with the $\delta^{13}\text{C}$ of respiration, so

$$C_a \left(\frac{\partial \delta^{13}_a}{\partial t} \right)_{resp} = F_{resp} (\delta^{13}_{resp} - \delta^{13}_a) \quad (12)$$

This term is represented by simulating the ecosystem respiration flux F_{resp} and the $\delta^{13}\text{C}$ of respired carbon as the flux-weighted mean isotopic composition of the photosynthate derived from atmospheric carbon at the time corresponding to the age of the respired carbon. To calculate this quantity, we apply the photosynthetic discrimination factor to atmospheric $\delta^{13}\text{C}$ of ages corresponding to the age of the various carbon pools defined in the model. Initially, we will use the published estimates of Fung et al [submitted] derived using the CASA soil carbon model to specify these ages.

A new soil model will be built as part of this integrated research program which will incorporate carbon pools of various ages into SiB, so that the transfers among pools and the ages of the pools can be determined consistently with photosynthesis, land-surface hydrology, and atmospheric climate as simulated by the model. The new integrated photosynthesis/respiration/climate model (SiB3) will include a layered structure with carbon and nitrogen pools of various ages at physically referenced layer depths. Preliminary work has already begun on the development and testing of such a structure in the CSU GCM. Transformations of C and N among these pools will be determined using local temperature and moisture determined in a physically consistent framework. Preliminary work has already begun on this model, with 6 to 10 layers, a root profile with decreasing organic content with depth, and an organic litter layer. Preliminary results [Denning et al, 1996d] suggest that the new model fits the atmospheric seasonal cycle of CO_2 better than the earlier two-layer soil thermodynamic model [Denning et al, 1996a].

The isotopic composition of oxygen in atmospheric CO_2 is determined by that of the last water in which the CO_2 was dissolved, as modified by fractionation during both photosynthetic assimilation and diffusion out of soils [Ciais et al, 1997a]:

$$C_a \frac{\partial \delta_a^{18}}{\partial t} = \Delta_{pho} F_{pho} + F_{resp} (\delta_{resp}^{18} - \delta_a^{18} + \epsilon_{resp}) \quad (13)$$

Photosynthetic discrimination is given by

$$\Delta_{pho} = -\epsilon_d + \frac{C_i}{C_a - C_i} \cdot (\delta_L^{18} - \delta_a^{18}) \quad (14)$$

where ϵ_d represents kinetic fractionation during diffusion, and δ_L is the isotopic composition of the leaf intercellular water.

The isotopic composition of CO_2 fluxes evolved from respiration in soils (both autotrophic and heterotrophic) is assumed to be equal to that of water in the surface of the soil. This reflects the long time scale for upward diffusion of CO_2 relative to that of isotopic equilibration between CO_2 and water. In early experiments, we will represent the fluxes according to the method of Denning et al [1996a] and the isotopic composition of the various water pools according to Ciais et al [1997a].

We will also develop the capability to predict the isotopic composition of water in the full hydrologic cycle of the CSU GCM, following methods originally detailed by Jouzel [1988] for the GISS GCM. The CSU GCM incorporates a cloud microphysics scheme [Fowler et al, 1996], so this will be more detailed than was possible in previous studies. This capability will allow new observational constraints to be applied to the simulated atmospheric hydrologic cycle. More importantly, when coupled to the multilayer soil hydrology and canopy model (SiB3), this new parameterization will allow prediction of $\delta^{18}\text{O}$ of CO_2 in a closed, self-consistent system without the need to use "off the shelf" isotopic estimates from the literature.

3.5 Construction of Basis Functions

The basis functions contain the spatial and temporal patterns of various sources and sinks. The basis functions for "known" sources/sinks are constructed from maps of tracer sources and sinks at yearly, monthly, or hourly time resolutions. Annual fossil fuel emissions of CO_2 from 1950-1990 are compiled by Andres et al. [1996] for 1 degree grid cells. Deforestation sources estimated by Houghton et al. are available from the CDIAC, Oak Ridge National Laboratory. Monthly air-sea exchanges of CO_2 , $^{13}\text{CO}_2$, and CO^{18}O will be modeled in the Princeton OBM. Hourly fluxes between the atmosphere and the terrestrial biosphere will be modeled in the SiB3 model for the tracers of interest.

Two sets of basis functions will be constructed for the "unknown" sources/sinks because we are uncertain about the nature and spatial distribution of the missing flux components. The first set is composed of uniform fluxes through the land and oceanic regions; the second set is composed of unit fluxes through latitudinal bands with sub-regional spatial patterns as predicted due to regrowth of deforested land [Houghton et al., 1996], CO₂ fertilization, N fertilization, or a combination of CO₂ and N fertilization [Friedlingstein et al. [1995].

4. **Research Plan**

4.1 First Year: Further development of the component models:

Development of the seasonal OBM at Princeton is supported by NOAA grant to the NOAA/Princeton Carbon Modeling Consortium (CMC). Preliminary OBM results for the air-sea exchange of CO₂ are compared with data-based estimates of Taro Takahashi. There are many similarities in both the spatial pattern and seasonal trends of air-sea CO₂ fluxes. As a part of the proposed study, we will implement the biogeochemistry of ¹³CO₂ and CO¹⁸O in the seasonal OBM as outlined above, and carry out model simulations to calculate air-sea fluxes of ¹³CO₂ and CO¹⁸O in addition to CO₂.

At UCSB, the first year of the integrated project will be spent implementing the isotopic calculations on-line in SiB2 and the CSU GCM, using the previously published methods outlined in Section 3.4 above. This will entail on-line fractionation of both ¹³C and ¹⁸O in CO₂ at the model time step of 6 minutes, as well as routine prediction of the isotopic composition of CO₂ in the atmospheric tracer code. Preliminary experiments will be performed to evaluate the effects of the atmospheric rectification of the isotope fluxes in the model, and the results of these experiments will be submitted for publication. In addition, work will begin on implementing the new soil submodel (SiB3) with multilayer carbon pools coupled to improved soil hydrology and thermodynamics. Finally, work will begin on designing the isotopic fractionation in the atmospheric hydrologic cycle (direct prediction of the $\delta^{18}\text{O}$ of water, for later use in the CO₂ inversions).

4.2 Second Year: Synthesis modeling of atmospheric CO₂, ¹³CO₂, and CO¹⁸O

We will simulate atmospheric CO₂, ¹³CO₂, and CO¹⁸O for anthropogenic emissions and the modeled air-sea and the atmosphere-biosphere exchange fluxes. Two GFDL atmospheric tracer models, GCTM and SKYHI, and the CSU GCM will be used in this study. Atmospheric responses to the sum of all sources will be compared to the observed temporal and spatial patterns for each tracer. We analyze the consistency among the multi-tracer distributions, a lack of which would likely indicate inaccurate modeling of the equilibrium and/or the disequilibrium surface fluxes of isotopes. The intercomparison involving multiple tracers is also expected to elucidate strengths and weaknesses of the land and ocean biogeochemistry models used for surface flux calculations. Observational data will be extracted from published literature and will be provided to us by courtesy of Pieter Tans, Tom Conway, Peter Bakwin, and their colleagues at the CMDL. The most critical area for collecting data of carbon and oxygen isotopes in CO₂ is the midlatitude Northern Hemisphere, where a large uptake of fossil fuel CO₂ has previously been suggested [Keeling et al., 1989; Tans et al., 1990].

At UCSB, work will continue on the development of the new soil carbon model under the constraints of the new isotopic predictions. This work will be presented at the Fall meeting of the AGU, and submitted for publication. Implementation of the isotopic composition of atmospheric and soil water will also be performed in year 2, and will be presented at a scientific conference.

4.3 Third Year: Inverse modeling of atmospheric CO₂, ¹³CO₂, and CO¹⁸O

Our long-term goal of inverse modeling is to develop a modeling capability for monitoring global carbon cycle, including compliance with an international carbon emission treaty under negotiation. A study of optimal sampling of the atmosphere will expose weaknesses in the present monitoring network, and suggest observations we will need to constrain the spatial distribution of CO₂ sources. The feasibility

of long-term monitoring is best evaluated by carrying out an inverse modeling of atmospheric CO₂, ¹³CO₂, and CO¹⁸O observed in the present global network. This intermediate goal is thus one of the major objectives of the present proposal.

As a first step, we will follow the inverse modeling method outlined above for the estimation of annual mean fluxes. The length of vectors for atmospheric observations and atmospheric responses to various sources/sinks will be extended to include ¹³CO₂ and CO¹⁸O data. The flux-to-concentration transformation matrix is to be modified accordingly. The inversion results will give an integrated assessment of the CO₂ sources and sinks simultaneously satisfying all tracer constraints, and will estimate the longitudinal as well as the latitudinal distributions of the uptake of fossil fuel CO₂.

An error analysis is essential to establishing the credibility of the inverse modeling results. We will attempt to quantify errors associated with various causes: measurement noises due to natural variability as well as to instrumental noises, discretization of source regions, imperfect model transport, and non-optimal distribution of observation stations in the existing network. Given the range of uncertainties, the inverse modeling estimated source/sink strengths from the source regions may be compared to direct estimates based on field data of air-sea pCO₂ gradient or ocean models, and to the potential terrestrial uptake due to forest regrowth and deforestation [Houghton et al., 1996], and due to CO₂ and N fertilization [Friedlingstein et al., 1995].

5. Management Plan:

Personnel:

The PI/PDs at Princeton and UCSB have ample expertise in developing and implementing the model calculations proposed here. Denning has been involved for more than 5 years in building land-surface biogeochemistry into the CSU GCM, and using the atmospheric model to understand the carbon budget. He implemented the calculation of the concentration and transport of atmospheric CO₂ in the GCM, and has performed many experiments with the model (Denning, 1994; Denning et al., 1995; Denning et al, 1996a,b,c,d; Zhang et al, 1996). He coordinates a major international effort (TransCom) to compare the transport properties of more than a dozen tracer transport codes. He has already begun testing new formulations for a multilayer soil carbon and thermodynamics submodel to replace the current soil module in SiB2 (Denning et al, 1996d). Sarmiento has been a recognized leader in unraveling the global carbon cycle for more than 15 years. He has pioneered the coupling of ocean biogeochemistry, ecology, and physical oceanography in the Princeton Ocean Model, and leads a large group of other researchers investigating the carbon budget of the atmosphere and oceans. Fan has experience both in conducting field measurement campaigns (Fan et al, 1990), and in global modeling. He has already built much of the preliminary structure of the inversion calculations proposed here.

Denning has requested funds to support a M. S. Research Associate for 6 months per year in support of this project. The search for this person has already begun under other funding, and several very high quality applicants have been found. The Research Associate will be trained in the use of SiB and the CSU GCM by the time this project is funded. In addition, Denning is requesting funding for a Ph.D. student to work on this project.

Computing:

The CSU GCM requires about 96 hours of CPU time on a Cray J-90 computer to run one year of the tracer transport simulation on a 4x5 grid with 17 levels at a 6 minute time step. With 60 tracers representing regional basis functions of emissions of atmospheric CO₂, ¹³CO₂, and CO¹⁸O, the model requires about 30 megawords (240 MB) of memory. Supercomputer time will be requested at the Scientific Computing Division of the National Center for Atmospheric Research to support this research. Each inversion experiment will be run for 4 simulated years. We will request 1200 General Accounting Units (GAU) per year to perform these simulations in parallel (6 processors) on the Cray J-90 machines (paiute and ouray) at NCAR/SCD. This will allow up to three full inversion runs to be performed per year.

The PI/PD is a new investigator in his initial tenure-track faculty appointment. If NSF prefers to allocate funds for the purchase of local computing equipment in support of this and future research projects, then NSF-funded supercomputer time would not be needed. An 8-processor Silicon Graphics Power Challenge with 1 GB of RAM would cost about \$100,000, but would eliminate the need for about 3600 NCAR GAUs for this project alone, and would be used by other federally sponsored research projects in the future. This would be extremely cost effective for the government, as the replacement value of the computing resources required would be only \$27 per GAU. The purchase would be justified on a cost basis for this project alone; future use of the machine for federally sponsored research would result in even greater savings.

Collaboration:

In addition to collaboration between UCSB and Princeton, this project requires the use of data provided by NOAA/CMDL Carbon Cycle group (Pieter Tans, PI), and the CSU GCM (David Randall, PI). Please see the attached letters of permission (*Special Information and Supplementary Documentation -- Proposal Section I*) regarding the use of these external resources.

6. References Cited

- Alexander, R. C., and R. L. Mobley, Monthly average sea surface temperatures and ice pack limits on a 1° global grid, *Mon. Weather Rev.*, *104*, 143-148, 1976.
- Andres, R.J., G. Marland, I. Fung, and E. Matthews, A 1° x 1° distribution of carbon dioxide emissions from fossil fuel consumption and cement manufacture, 1950-1990, *Global Biogeochem. Cycles*, **10**, 419-429, 1996.
- Ball, J. T., 1988: An analysis of stomatal conductance. Ph.D. Thesis, Stanford University, Stanford, Calif., 89 pp.
- Berry, J. A., 1989. Studies of mechanisms affecting the fractionation of carbon isotopes in photosynthesis. In: P. W. Rundel, J. R. Ehleringer, and K. A. Nagy (Eds.), *Stable Isotopes in Ecological Research*, Springer-Verlag, 82-94.

- Ciais, P., P.P. Tans, J.W. White, M. Trolier, R. Francey, J.A. Berry, D. Randall, P.J. Sellers, J.G. Collatz, and D.S. Schimel, Partitioning of ocean and land uptake of CO₂ as inferred by $\delta^{13}\text{C}$ measurements from the NOAA Climate Monitoring and Diagnostic Laboratory global air sampling network, *Journal of Geophysical Research*, **100**, 5051-5070, 1995.
- Ciais, P., P.P. Tans, M. Trolier, J.W.C. White, and R.J. Francey, A large northern hemisphere terrestrial sink induced by the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO₂, *Science*, **269**, 1098-1102, 1995.
- Ciais, P., A. S. Denning, P. P. Tans, J. A. Berry, D. A. Randall, G. J. Collatz, P. J. Sellers, J. W. C. White, M. Trolier, H. J. Meijer, R. J. Francey, P. Monfray, and M. Heimann: A three-dimensional synthesis study of $\delta^{18}\text{O}$ in atmospheric CO₂. Part 1: Surface fluxes. *Journal of Geophysical Research*, in press.
- Ciais, P., P. P. Tans, A. S. Denning, R. J. Francey, M. Trolier, H. J. Meijer, J. W. C. White, J. A. Berry, D. A. Randall, G. J. Collatz, P. J. Sellers, P. Monfray, and M. Heimann: A three-dimensional synthesis study of $\delta^{18}\text{O}$ in atmospheric CO₂. Part 2: Simulations with the TM2 transport model. *Journal of Geophysical Research*, in press.
- Collatz, G. J., J. T. Ball, C. Grivet, and J. A. Berry, Physiological and environmental regulation of stomatal conductance, photosynthesis, and transpiration: a model that includes a laminar boundary layer, *Agric. and Forest Meteorol.*, **54**, 107-136, 1991.
- Collatz, G. J., M. Ribas-Carbo, and J. A. Berry, Coupled photosynthesis-stomatal conductance model for leaves of C4 plants, *Aust. J. Plant Physiol.*, **19**, 519-538, 1992.
- Denning, A. S., Investigations of the transport, sources, and sinks of atmospheric CO₂ using a general circulation model. Atmospheric Science Paper No. **564**, Colorado State University, 1994.
- Denning, A. S., I. Y. Fung, and D. A. Randall, 1995: Latitudinal gradient of atmospheric CO₂ due to seasonal exchange with land biota. *Nature*, **376**, 240-243.
- Denning, A. S., J. G. Collatz, C. Zhang, D. A. Randall, J. A. Berry, P. J. Sellers, G. D. Colello, and D. A. Dazlich, 1996. Simulations of terrestrial carbon metabolism and atmospheric CO₂ in a general circulation model. Part 1: Surface carbon fluxes. *Tellus*, **48B**, 521-542.
- Denning, A. S., D. A. Randall, G. J. Collatz, and P. J. Sellers, 1996. Simulations of terrestrial carbon metabolism and atmospheric CO₂ in a general circulation model. Part 2: Spatial and temporal variations of atmospheric CO₂. *Tellus*, **48B**, 543-567.
- Denning, A. S., P. S. Bakwin, K. J. Davis, W. M. Angevine and D. A. Randall, 1996. Simulations and observations of terrestrial carbon flux and atmospheric turbulence: Implications for the "missing carbon" problem. Presented at the Second International Scientific Conference on the Global Energy and Water Cycle, Washington, DC, June 17-21, 1996.
- Denning, A. S., D. A. Dazlich, and D. A. Randall, 1996. Simulations of soil temperature, snowpack, and carbon fluxes with an atmospheric general circulation model. Presented at 1996 Fall Meeting of the American Geophysical Union A32D-2.
- Enting, I.G., C.M. Trudinger, and R.J. Francey, A synthesis inversion of the concentration and $\delta^{13}\text{C}$ of atmospheric CO₂, *Tellus*, **47B**, 35-52, 1995.
- Esbensen, S. K., and Y. Kushnir, The heat budget of the global ocean: An atlas based on estimates from surface marine observations, *Climate Research Institute Report*, **29**, Oregon State University, 1981.
- Farquhar, G. D., S. von Caemmerer and J. A. Berry, A biochemical model of photosynthetic CO₂

- assimilation in C3 plants, *Planta*, 149, 78-90, 1980.
- Farquhar, G.D., J. Lloyd, J.A. Taylor, L.B. Flanagan, J.P. Syvertsen, K.T. Hubick, S.C. Wong, and R. Ehleringer, Vegetation effects on the isotope composition of oxygen in atmospheric CO₂, *Nature*, 363, 439-443, 1993.
- Fasham, M. J. R., J. L. Sarmiento, R. D. Slater, H. W. Ducklow, and R. Williams, A seasonal three-dimensional ecosystem model of nitrogen cycling in the North Atlantic euphotic zone: A comparison of the model results with observation from Bermuda Station "S" and OWS "India", *Global Biogeochem. Cycles*, 7, 379-415, 1993.
- Fowler, L. A., Randall, D. A. and Rutledge, S. A., 1996. Liquid and ice cloud microphysics in the CSU General Circulation Model. Part I: Model description and simulated microphysical processes. *J. Clim.*, 9, 489-529.
- Fung, I., K. Prentice, E. Matthews, J. Lerner and G. Russell, 1983: Three-dimensional tracer model study of atmospheric CO₂ Response to seasonal exchanges with the terrestrial biosphere. *Jour. Geophys. Res.*, **88**, 1281-1294.
- Fung, I. Y., 1986: Analysis of seasonal and geographic patterns of atmospheric CO₂ distributions with a three-dimensional tracer model. In: J. R. Trabalka and D. E. Reichle (Eds.), *The Changing Carbon Cycle: A Global Analysis*, Springer-Verlag, New York, 459-473.
- Fung, I. Y., C. J. Tucker and K. C. Prentice, 1987: Application of very high resolution radiometer vegetation index to study atmosphere-biosphere exchange of CO₂. *Jour. Geophys. Res.* **92**, 2999-3015.
- Fung, I., C. B. Field, J. A. Berry, M. V. Thompson, J. T. Randerson, C. M. Malmstrom, P. M. Vitousek, G. J. Collatz, P. J. Sellers, D. A. Randall, A. S. Denning, F. Badeck, and J. John: Carbon-13 exchanges between the atmosphere and biosphere. Submitted to *Global Biogeochemical Cycles*.
- Houghton, R.A., R.D. Boone, J.R. Fruci, J.E. Hobbie, J.M. Mellilo, C.A. Palm, B.J. Peterson, G.R. Shaver, G.M. Woodwell, B. Moore, D.L. Skole, and N. Myers, The flux of carbon from terrestrial ecosystems to the atmosphere in 1980 due to changes in land use : geographic distribution of the global flux, *Tellus*, 39B, 122-139, 1987.
- Jahne, B., G. Heinz, and W. Dietrich, Measurements of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.*, 92, 10,767-10,776, 1987.
- Jouzel, J., G.L. Russell, R.J. Suozzo, R.D. Koster, J.W.C. White, and W.S. Broecker, Simulations of the HDO and H₂¹⁸O atmospheric cycles using the NASA/GISS general circulation model : The seasonal cycle for present-day conditions, *Journal of Geophysical Research*, 92, 14739-14760, 1987.
- Kattenberg, A., F. Giorgi, H. Grassl, G. A. Meehl, J. F. B. Mitchell, R. J. Stouffer, T. Tokioka, A. J. Weaver, T. M. L. Wigley, 1996. Climate models – Projections of future climate. In: J. T. Houghton, L. G. Meira-Filho, B. A. Callander, N. Harris, A. Kattenberg, and H. Maskell (Eds.), *Climate Change 1995: The Science of climate Change*. IPCC, University Press, Cambridge, 285-357.
- Keeling, C.D., S.C. Piper, and M. Heimann, A three-dimensional model of atmospheric CO₂ transport based on observed winds: 4 Mean annual gradients and interannual variations, in *Aspects of Climate Variability in the Pacific and the Western Americas* AGU monograph **55**, edited by D.H. Peterson, 305-363, AGU, Washington D.C., 1989.
- Pacanowski, R., K. Dixon, and A. Rosati, The G.F.D.L. Modular Ocean Model Users Guide, *GFDL Ocean*

- Group Technical Report #2*, Geophysical Fluid Dynamics Laboratory, 1991, 1993.
- Peng, T. H., T. Takahashi, and W. S. Broecker, Seasonal variability of carbon dioxide, nutrients and oxygen in the northern Atlantic surface water: observations and a model, *Tellus*, 39B, 439-458, 1987.
- Randall, D. A., Q. Shao and C.-H. Moeng, 1992: A second-order bulk boundary-layer model. *Jour. Atmos. Sci.*, **49**, 1903-1923.
- Randall, D. A. and Pan, D.-M., 1993. Implementation of the Arakawa-Schubert parameterization with a prognostic closure. In: *The Representation of Cumulus Convection in Numerical Models* (eds. K. Emanuel and D. Raymond) American Meteorological Society, Boston, 137-144.
- Randall, D. R., P. J. Sellers, J. A. Berry, D. A. Dazlich, C. Zhang, J. A. Collatz, A. S. Denning, S. O. Los, C. B. Field, I. Fung, C. O. Justice, and C. J. Tucker, 1996: A revised land-surface parameterization (SiB2) for GCMs. Part 3: The greening of the Colorado State University General Circulation Model. *Journal of Climate*, **9**, 738-763.
- Sarmiento, J. L., J. C. Orr, and U. Sighenthaler, A Perturbation Simulation of CO₂ Uptake in an Ocean General Circulation Model, *J. Geophys. Res.*, **97**, 3621-3646, 1992.
- Sarmiento, J. L., R. D. Slater, M. J. R. Fasham, H. W. Ducklow, J. R. Toggweiler, and G. T. Evans, A seasonal three-dimensional ecosystem model of nitrogen cycling in the North Atlantic euphotic zone., *Global Biogeochem. Cycles*, **7**, 417-450, 1993.
- Schimel, D., D. Alves, I. Enting, M. Heimann, F. Joos, D. raynaud, T. Wigley, M. Prather, R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, X. Zhou, P. Jonas, R. Charlson, H. Rodhe, S. Sadasivan, K. P. Shine, Y. Fouquart, V. Ramaswamy, S. Solomon, J. Srinivasan, D. Albritton, I. Isaksen, M. Lal, and D. Wuebbles, 1996. *Radiative forcing of climate change*. In: J. T. Houghton, L. G. Meira-Filho, B. A. Callander, N. Harris, A. Kattenberg, and H. Maskell (Eds.), *Climate Change 1995: The Science of climate Change*. IPCC, University Press, Cambridge, 65-132.
- Sellers, P. J., Y. Mintz, Y. C. Sud, and A. Dalcher, A simple biosphere model (SiB) for use within general circulation models, *J. Atmos. Sci.*, **43**, 505-531, 1986.
- Sellers, P. J., J. A. Berry, G. J. Collatz, C. B. Field, and F. G. Hall, Canopy reflectance, photosynthesis, and transpiration. III. A reanalysis using enzyme kinetics - electron transfer models of leaf physiology. *Remote Sens. Environ.*, **42**, 1-20, 1992.
- Sellers, P.J., D.A. Randall, G.J. Collatz, J.A. Berry, C.B. Field, D.A. Dazlich, C. Zhang, G.D. Collelo and L. Bounoua, 1996, A Revised land surface parameterization (SiB2) for atmospheric GCMs. Part I: Model formulation. *Journal of Climate*, **9**, 676-705.
- Sellers, P.J., S.O. Los, C.J. Tucker, C.O. Justice, D.A. Dazlich, G.J. Collatz and D.A. Randall, 1996, A Revised land surface parameterization (SiB2) for atmospheric GCMs. Part II: The generation of global fields of terrestrialbiophysical parameters from satellite data. *Journal of Climate*, **9**, 706-737.
- Sellers, P.J., L. Bounoua, G.J. Collatz, D.A. Randall, D.A. Dazlich, S.O. Los, J.A. Berry, I. Fung, C.J. Tucker, C.B. Field and T.G. Jensen, 1996, Comparison of radiative and physiological effects of doubled atmospheric CO₂ on climate. *Science*, **271**, 1402-1406.
- Suarez, M. J., Arakawa, A., and Randall, D. A., 1983. Parameterization of the planetary boundary layer in the UCLA general circulation model: Formulation and results. *Mon Wea. Rev.*, **111**, 2224-2243.
- Tans, P.P., I.Y. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO₂ budget.

Science, **247**, 1431-1438, 1990.

Tans, P., J.A. Berry, and R.F. Keeling, Oceanic ¹³C data: a New Window on CO₂ Uptake by the Oceans, *Global Biogeochemical Cycles*, **7**, 353-368, 1993.

Toggweiler, J. R., K. Dixon, and K. Bryan, Simulation of radiocarbon in a coarse-resolution world ocean model. 1. Steady state prebomb distributions, *J. Geophys. Res.*, **94**, 8217-8242, 1989.

Toggweiler, J. R., and B. Samuels, Is the magnitude of the deep outflow from the Atlantic Ocean actually governed by southern hemisphere winds?, in *The Global Carbon Cycle*, edited by M. Heimann, pp.303-331, Springer-Verlag, 1993a.

Toggweiler, J. R., and B. Samuels, New radiocarbon constraints on the upwelling abyssal water to the ocean's surface, in *The Global Carbon Cycle*, edited by M. Heimann, pp.333-366, Springer-Verlag, 1993b.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, **97**, 7373-7383, 1992.

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