A. Project Summary

We propose a three-year research program to study the exchanges of CO_2 and $^{13}CO_2$ between the atmosphere, ocean, and terrestrial biosphere, and the processes that govern them. Spatial and temporal variations of these two tracers in the atmosphere contain information about the sources and sinks of CO_2. The stable isotope ratio $\delta^{13}C$ can be used to partition a total flux into terrestrial and marine components, reducing uncertainties in regional monthly fluxes calculated by inversion of tracer transport models. The ratio of ^{12}C to ^{13}C fluxes on land depends on physiological stress (which controls isotopic discrimination via stomatal conductance and C_i/C_a ratios) and the pathways and turnover times of photosynthate in ecosystems (which impacts isotopic disequilibrium). We have developed logic describing these processes on land in the Simple Biosphere model (SiB2), which has been successful at predicting variations in CO_2 and $\delta^{13}C$ on local, regional, and global scales when coupled to an atmospheric model.

The stable isotope code we have already developed and tested will be ported into the Community Climate System Model (CCSM), which is maintained at the National Center for Atmospheric Research (NCAR). The advantages of doing this are: (1) the Community Land Model (CLM) in the CCSM already calculates photosynthesis and respiration using logic very similar to that in SiB2; (2) new functionality is being developed in CLM/CCSM that includes dynamic vegetation (ecosystem succession and disturbance) and biogeochemical cycling of carbon and nitrogen through ecosystem pools, which is important for the calculation of isotopic disequilibrium; (3) a parameterization of the carbon cycle and $\delta^{13}C$ in the ocean has already been developed in the NCAR CCSM Ocean Model (NCOM), allowing prediction of spatial, seasonal, and interannual variations in fractionation and disequilibrium at the air-sea interface; (4) the fully coupled model of the carbon cycle and $\delta^{13}C$ that will be completed when we have ported our code into this model is an ideal testbed for evaluation of the component models against atmospheric and ecosystem data; and (5) the global self-consistent process-based model we build will allow us to develop synthetic atmospheric data sets for testing new approaches to CO_2 inversion using multiple tracers and to recommend future observing priorities.

Inversion of observed patterns in atmospheric CO_2 concentrations to estimate surface fluxes is ill-conditioned because response patterns in the current network are not unique, especially with respect to terrestrial fluxes estimated from stations in the marine boundary layer. We propose to develop new inversion methods that make better use of the $\delta^{13}C$ constraints, including variations in both discrimination and isotopic disequilibrium between the atmosphere and terrestrial ecosystems. These variations can be modeled in the coupled process-based model described above, and their uncertainty estimated to help constrain flux inversions. In addition, we will attempt to use these variations to extract information from the observations about the effects of environmental forcing on physiological stress and pathways and turnover of organic matter. These new inversion methods will be developed and tested using synthetic data produced by the CCSM, and the sensitivity to transport will be investigated using a suite of transport model response functions produced in a model intercomparison study (TransCom). Finally, we will perform an inversion of the past 20 years of atmospheric CO_2 and $\delta^{13}C$ data to estimate regional monthly fluxes, isotopic exchanges, and the processes that control them

B. Table of Contents

C. Project Description

C.1 Results from Previous NSF Support

NSF ATM-9896261: Sources and Sinks of Anthropogenic CO_2: Integrated Assessment Using Biogeochemical Modeling and Inversion of Atmospheric Tracer Transport (Joint with J. Sarmiento, Princeton University) $244,000, 07/01/1998 – 09/30/2000

We investigated the coupled stable isotope biogeochemistry of CO_2 in the atmosphere and the terrestrial biosphere, using numerical models and atmospheric measurements. We developed a parameterization for fractionation and changes in reservoirs of ^{13}C and ^{18}O in CO_2 in the Simple Biosphere Model (SiB2), including mixing and recycling of tracers in a finite-mass canopy air space, and used the model to predict atmospheric CO_2 and isotope ratios that compared favorably to observations. The model has been evaluated both locally (in a Wisconsin forest, an Oklahoma grassland, and a tropical rainforest) and globally (against flask samples of air). Results indicate that variations in $\delta^{13}C$ of atmospheric CO_2 tend to enrich carbon isotopic ratios of living plant carbon over large areas of western continental Eurasia, while depleting them in the southern United States and northern Africa. Results further indicate that recycling of respired CO_2 in the canopy depletes carbon isotope ratios of plant carbon by a few tenths of a per mil (‰). The biogeochemical model was also used to constrain synthesis inversion calculations of regional CO_2 flux.

Suits, N.S., A.S. Denning, J.A. Berry, C.J. Still, J.Kaduk and J.T. Randerson, 2001: Seasonal and spatial variations in carbon isotopic ratios of plant biomass, terrestrial CO_2 fluxes and atmospheric CO_2. Submitted to *Global Biogeochemical Cycles*.

NSF ATM-9906568: Linking Biogeochemistry and Atmospheric Transport in the NCAR CSM $24,943, 05/01/1999 – 09/30/2000

With NSF support, the transport characteristics of the NCAR CSM were investigated and compared top those of other models and to observations of sulphur hexafluoride (SF_6) in the atmosphere. These comparisons are undertaken to evaluate the suitability of the model for investigations of biogeochemical cycles using atmospheric inverse modeling in the future. The NCAR-MATCH transport model was used, which duplicates the transport characteristics of NCAR CCM3 (the atmospheric component of CSM1). In the first simulation, winds and other meteorological fields were prescribed from CCM3 output. In the second simulation, meteorological fields were prescribed from NCEP reanalyses. Concentrations for the final year (1993) were archived and compared to other transport models and to observations, following the methods described in Denning *et al* (1999) exactly. A comparison of the simulated surface SF_6 to both observations and to 11 other model results on a north-south transect in the Atlantic Ocean and a west-east transect along the Trans-Siberian Railroad shows that the NCAR results lie within the "consensus" pack of models, and agree quite well with the observations. The simulation driven by CCM3 meteorology performs among the very best models in the northern hemisphere, but both simulations underestimate the surface concentrations slightly in the southern hemisphere.

Spatial and temporal variations of atmospheric CO_2 concentrations contain information about surface sources and sinks which can be quantitatively interpreted through tracer transport inversion. Previous CO_2 inversion calculations obtained very different results from one another due to differences in data, methods, and transport models used. We conducted a set of annual mean inversion experiments in which 16 different transport models or model variants were used to calculated sources and sinks from the same data with a standardized method, to isolate various contributors to uncertainty in the calculations. Model-mean retrieved fluxes for most regions were quite insensitive to the prior fluxes or their uncertainties. We found that simulated tracer transport is one of the dominant sources of uncertainty in the retrieved regional fluxes, particularly as it is manifested in the response to prescribed "background" fluxes due to fossil fuel combustion, the balanced terrestrial biosphere, and air-sea gas exchange. Transport uncertainty has the largest effect on retrieved surface fluxes in the northern middle latitudes, partly because of relatively high station density there, and partly because of differences in the strength and shape of the rectifier response among the models in this region. Tropical fluxes are largely unconstrained by data, and the retrieval reflects the priors and the global mass-balance of the atmosphere. Regional ocean fluxes are relatively well determined by the inversion in most regions. Analyses of annual mean results is essentially complete. Inversions for seasonal cycles and interannual variability are now being undertaken. We have produced a large body of experimental output which will be analyzed by all major inverse modeling groups in the world over the next several years.

Engelen, R.J., G.L. Stephens, and A.S. Denning, 2001: The effect of CO_2 variability on the retrieval of atmospheric temperatures. *Geophysical Research Letters*, **28,** 3259-3262.

Engelen, R.J., A.S. Denning, K.R. Gurney and G.L. Stephens. Global observations of the carbon budget: I, 2001. Expected satellite capabilities in the EOS and NPOESS eras. *Journal of Geophysical Research*, **106,** (D17), 20055-20068.

Gurney, K.R., R. M. Law, A. S. Denning, P. J. Rayner, D. Baker, P. Bousquet, L. Bruhwiler, Y.-H. Chen, P. Ciais, S. Fan, I.Y. Fung, M. Gloor, M. Heimann, K. Higuchi, J. John, T. Maki, S. Maksyutov, K. Masarie, P. Peylin, M. Prather, B.C. Pak, J. Randerson, J. Sarmiento, S. Taguchi, T. Takahashi and C.-W. Yuen, 2002: Towards robust regional estimates of CO_2 sources and sinks using atmospheric transport models. *Nature*, **415**, 626-630.

Denning, A. S., Gurney, K. R., Law, R. M., Rayner, P. J., and TransCom 3 modelers. TransCom 3 Inversion Intercomparison: Part 1. Annual mean control results and sensitivity to transport and prior flux information. Submitted to *Tellus*.

Law, R. M., Y.-H. Chen, K. R. Gurney, and TransCom 3 modelers. TransCom 3 CO_2 inversion intercomparison: 2. Sensitivity of annual mean results to data choices. Submitted to *Tellus*.

C.2 Background

The spatial and temporal distribution of CO_2 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) (Enting et al, 1995; Fan *et al*, 1998; Rayner *et al*, 1999; Bousquet *et al*, 2000; Gurney *et al*, 2002). 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 as seen by the present observational network, which cannot be distinguished on the basis of CO_2 concentrations alone. A sink resulting from nitrogen fertilization of the Boreal forest, for example, might produce the same depression in observed CO_2 concentration in the marine boundary layer at 50° N latitude as a somewhat weaker sink resulting from uptake by enhanced phytoplankton productivity in the North Atlantic Ocean. In other words, the matrix relating fluxes and concentrations, which must be inverted to estimate these sinks, is nearly singular.

Observations of the stable isotopic ratios, $\delta^{13}C$, of atmospheric CO_2 may provide important additional constraints on the carbon budget inversion problem. Photosynthesis discriminates against carbon-13. By contrast, atmospheric is $\delta^{13}C$ is nearly unchanged by the uptake of CO_2 into the surface oceans, because the atmosphere is near equilibrium with the surface ocean with regard to the isotopic composition of CO_2. Therefore, it should be possible to use the $\delta^{13}C$ ratio of CO_2 to distinguish terrestrial from marine fluxes through a process known as "double deconvolution" (e.g., Keeling *et al*, 1989). Weekly atmospheric samples are collected routinely from about 75 sites in the remote troposphere and compiled by the NOAA/CMDL Carbon Cycle Group into a single consistent database (Masarie and Tans, 1995). Analysis of the stable isotopic composition of these samples is performed at the University of Colorado (Trolier *et al*, 1996). A carbon budget inversion calculation that used observations of both atmospheric parameters (CO_2 and $\delta^{13}C$) would be better constrained than those using only one or two.

Following Tans et al [1993], the instantaneous effects of surface carbon fluxes on the isotopic composition of atmospheric CO_2 are given by

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

(1)

Here F_{FF}, F_{BB}, F_{OA}, F_{pho}, and F_{resp} are the instantaneous fluxes of CO_2 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 CO_2, 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.

Standard double deconvolution techniques use variations in both concentration and carbon isotopic ratio of atmospheric carbon dioxide to determine changes in global carbon sources and sinks. Because of a paucity of high-precision $\delta^{13}C$ analyses and uncertainties about the correct isotope ratios to use, these analyses have most often been performed only on the annual mean concentration and isotope ratio, at the global scale (Keeling *et al*, 1995; Francey *et al*, 1995; Battle *et al*, 2000). More information is available in the seasonal and spatial variations of $\delta^{13}C$ of the atmosphere (Keeling *et al*, 1989; Ciais *et al*, 1995, see Fig 1), but is difficult to interpret reliably because of variations in isotopic fractionation during photosynthesis, carbon turnover in ecosystems, and the isotopic disequilibrium between the atmosphere and the oceans. In general, the models used in these inversions assume that carbon isotope discrimination of the terrestrial

Figure 1: Zonal mean carbon exchange with the atmosphere (dark line) by the ocean (medium) and land surface (light), estimated by deconvolution of CO_2 and $\delta^{13}C$ (J. Miller, personal communication)

biosphere is constant in time and varies only by latitude, even though there is ample evidence for variation on diurnal, seasonal and interannual time scales (e.g., Lloyd and Farquhar, 1994; Lloyd et al., 1996; Flanagan et al, 1996, 1997; Buchmann *et al*, 1997a,b, 1998, Ehleringer and Cook, 1998; Miranda *et al*, 1997).

A recent analysis by Randerson *et al* (2002) pointed out that assuming invaraiant isotopic discrimination may produce systematic bias in deconvolution calculations. The advantage of making this simplifying assumption is that the influence of the terrestrial isotope disequilibrium, i.e. the isotopic difference between assimilated and respired fluxes, is multiplied by the *net* terrestrial CO_2 flux, which is only in the range of 2 to 4 Gt of carbon (Fung *et al*, 1997). If, on the other hand, carbon isotope discrimination changes over time, then subsequent respiration acts on organic matter with the new isotope ratio and therefore the disequilibrium must be applied to the *gross* respiration flux (typically 20 to 50 times greater!). As a result, a change of *0.2 per mil* in the global isotope discrimination factor can be interpreted as a *0.85 Gt-C* shift in the land versus ocean carbon sink. Of particular interest are the questions of whether interannual variations in discrimination and net assimilation are systematically related, and if they can be correlated with other environmental phenomena, such as El Niño Southern Oscillation (ENSO) or major volcanic activity. If discrimination and primary productivity do covary, then it may be
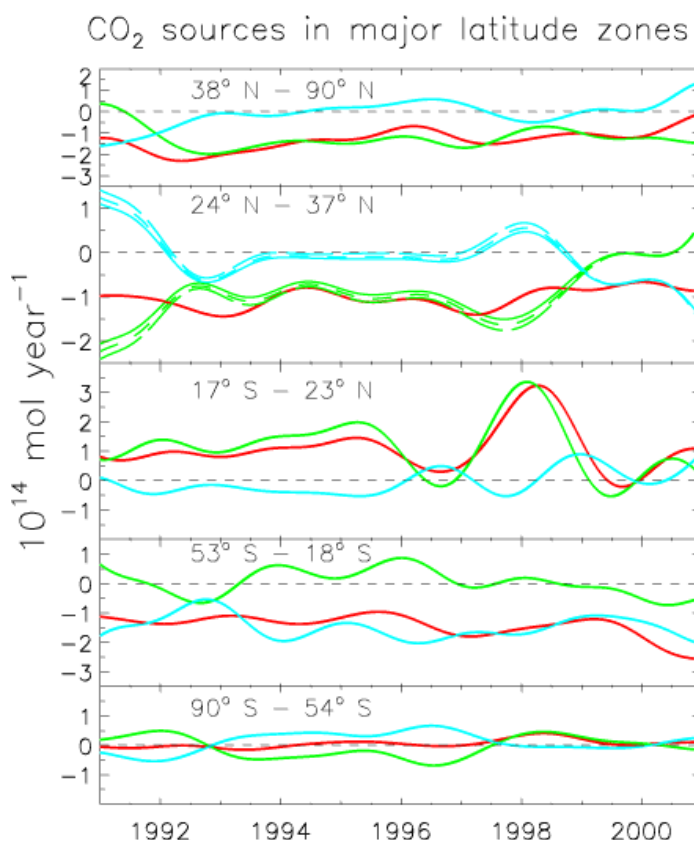
possible to write a linear equation relating discrimination anomalies to productivity anomalies, which would simplify the solution to the inversion problem.

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.

In addition to the $^{13}C/^{12}C$ ratio of CO_2, there is considerable interest in interpretation of variations of the isotopic composition of oxygen in CO_2. Photosynthesis acts on CO_2 dissolved in water, which is enriched in ^{18}O near evaporation sites in the leaves of terrestrial plants (Francey and Tans, 1987). The $\delta^{18}O$ of CO_2 can therefore be used to distinguish changes in photosynthesis (with a leaf $\delta^{18}O$ signature) from changes in respiration (with a soil $\delta^{18}O$ signature) [Farquhar et al., 1993; Yakir and Wang, 1996; Ciais et al., 1997a,b, Peylin *et al*, 1996, 1997]. Research on the controls on the $\delta^{18}O$ of atmospheric CO_2, including efforts to parameterize them in the NCAR CCSM are underway (Noone *et al* , 2000, 2002; Riley *et al* , 2001; Inez Fung and James Randerson, personal communication). The research proposed here is complementary with those efforts, and it is hoped that the overall carbon budget constraint will be considerably strengthened by the combined work.

C.2 Objectives and Hypotheses

Broadly, the objectives of the proposed research are to develop and test a state-of-the-art coupled simulation model of exchanges of CO_2 and $^{13}CO_2$ in the Earth system, and use it to better quantify sources and sinks of atmospheric CO_2 and understand the processes that control their variability.

Specifically, we identify the following hypotheses:

1. Isotopic discrimination against ^{13}C in terrestrial ecosystems is a function of physiological stress as expressed in stomatal conductance, and can be predicted by tracking ecosystem states (water balance, temperatures) to predict isotopic effects on the atmosphere and the composition of organic matter;

2. The isotopic composition of organic pools in terrestrial ecosystems varies over time in response to the changing atmospheric $\delta^{13}C$ and to changes in discrimination; these changes can be used to predict isotopic disequilibrium between land biota and the atmosphere;

3. Spatial and temporal variations in discrimination and disequilibrium can be calculated by a process-based model to estimate their magnitude and uncertainty in such a way that the inverse problem of estimating sources and sinks of CO_2 will be significantly better constrained using $\delta^{13}C$ observations than by CO_2 alone.

Hypotheses (1) and (2) will be addressed by comparison to data collected at the ecosystem scale and in the atmosphere, respectively. Hypothesis (3) will be addressed by uncertainty estimation in inversion calculations on both synthetic and real data.

C.3 The Community Climate System Model (CCSM)

The Community Climate System Model (CCSM) is a fully-coupled, global climate model that provides state-of-the-art computer simulations of the Earth's past, present, and future climate states (Boville and Gent, 1998). Development and maintenance of the model and its components is coordinated at the National Center for Atmospheric Research (NCAR). A cooperative and well-organized community effort is underway to develop and improve the model, with working groups for the atmosphere, ocean, and land-surface component models co-chaired by NCAR scientists and outside members of the wider climate modeling community. Other working groups coordinate applications of the coupled system such as biogeochemistry, polar climate, paleoclimate, and climate change. The community involvement in the design, implementation, testing, and application of the modeling system is unique and powerful. The research proposed here is intended to develop important functionality to the biogeochemistry and land surface components of the modeling system, with benefits to many other complementary projects being performed by other users and developers.

Community Land Model

The Community Land Model is the land surface model for the Community Climate System Model (CCSM). Much of the scientific development of this model over the past few years has focused on improved parameterization of energy (latent heat, sensible heat, longwave radiation, albedo), water vapor, and momentum fluxes required by the atmospheric model and freshwater runoff required by the ocean model. These new parameterizations grew out of work by the CCSM Land Model Working Group with the BATS (Dickinson et al. 1993), NCAR LSM (Bonan 1996), and IAP94 (Dai and Zeng 1997) land models and provide significant improvement to the simulated surface climate (Zeng et al. 2002; Bonan et al. 2002b).

While the new biogeophysical parameterizations were being developed, the biogeochemistry of the NCAR LSM also continued to be advanced. In particular, the NCAR LSM was developed to link the exchanges of energy, water, and CO_2. Global simulations of the NCAR LSM coupled to CCM3 showed that simple physiological and ecological assumptions result in reasonable simulation of land-atmosphere CO_2 exchange over a wide range of climates and ecosystems (Bonan 1995; Craig et al. 1998). Two ecological concepts are central to inclusion of CO_2 in the model. First, leaf photosynthesis, transpiration, and stomatal conductance are explicitly linked through a combined photosynthesis-conductance model. Integration of leaf stomatal conductance and photosynthesis over all the leaves in the canopy determines total carbon uptake during photosynthesis and water loss during transpiration. Second, the model represents vegetation not as biomes (e.g., savanna) but rather as patches of plant functional types (e.g., grasses, trees). This is because many of the leaf physiological and whole-plant allocation parameters used in terrestrial carbon parameterizations cannot be measured for biomes but can be measured for individual plants. Plant functional types reduce the complexity of species diversity in ecological function to a few key plant types and provide a critical link to ecosystem processes and vegetation dynamics (Woodward and Cramer 1996; Smith et al. 1997). To better interface with

ecosystem models and to take advantage of high resolution satellite land cover and leaf area data products, the NCAR LSM was re-coded to allow specification of plant types, their abundance, and their leaf area to be direct input to the model for each grid cell (Oleson and Bonan 2000; Bonan et al. 2002a). These concepts have been included in the Community Land Model.

These developments have lead to a prototype coupling of the NCAR LSM with a dynamic global vegetation model (Bonan et al. 2002c). The vegetation model simulates: the seasonal emergence and senescence of leaves; allocation of carbon uptake during photosynthesis to the growth of new foliage, stems, and roots; loss of carbon to the atmosphere during plant respiration; litterfall and decomposition of soil carbon; fires; and changing vegetation biogeography. It links physiological processes at the scale of seconds-to-minutes with longer-term ecosystem processes at the scale of day-to-weeks and vegetation dynamics over periods of years to centuries. The model simulates net primary production and global biogeography consistent with observations. It also simulates the dynamics of tundra, boreal forest, temperate forest, tropical forest, and savanna ecosystems that is consistent with observations. The vegetation dynamics code has subsequently been migrated to the Community Land Model.

Terrestrial Biogeochemistry Model

The global cycles of carbon and nitrogen have important interactions in the terrestrial biosphere, producing feedbacks between biogeochemistry and climate that operate on multiple time scales. At the shortest time scales, the fixation of atmospheric CO_2 by plants requires a substantial investment of nitrogen in enzymes and other proteins. Changes in the availability of mineral nitrogen resources from the soil affect the synthesis of these proteins, with direct impacts on carbon fixation and the production of new plant tissues. This same pathway also produces indirect effects on the surface partitioning of energy between latent and sensible heat, through rapid linkages between stomatal conductance and carbon assimilation, and through the slower mechanisms of seasonal leaf area dynamics. The availability of mineral nitrogen in the soil is controlled at short time scales by soil temperature and moisture conditions, at intermediate time scales by the supply of new organic matter from plant litter, and at longer time scales by changes in litter quality due to changing plant community composition. On very long time scales (centuries and longer), the existence and composition of natural plant communities depends on the balance between accumulation and loss of fixed forms of nitrogen, with accumulation from deposition of NO_x formed by lightning and from the symbiotic and asymbiotic fixation of mineral N from atmospheric N_2, and loss due to leaching and transport in outflow, microbial dentrification, and denitrification during biomass burning.

A project is currently underway to modify and extend the Community Land Model (CLM) component of CCSM to incorporate these interactions between the energy, water, carbon, and nitrogen cycles. The project is supported by the Biogeosciences Initiative at NCAR and includes regular collaboration with both the Biogeochemistry and Land Model Working Groups of the CCSM project. The most important changes to the existing CLM structure are improved treatment of litter and soil organic matter dynamics, incorporation of nitrogen constraints for carbon assimilation and allocation to different plant tissues, explicit competition between plants and soil biota for soil mineral nitrogen resources, explicit competition between multiple plant functional types for common soil water and mineral nitrogen resources, and interactions between plant community disturbance processes and age structure. In the spirit of community model

development embodied by the CCSM project, the details of these modifications have either been recommended or reviewed by the Biogeochemisty and Land Model Working Groups. The objective of this effort is to produce a new version of CLM that can be coupled within CCSM to perform simulations with prognostic atmospheric concentrations of CO_2 and reactive nitrogen species. Forcing for these simulations will include historical and projected future rates of fossil fuel burning and agricultural nitrogen deposition, as well as observed and projected anthropogenic modifications to land cover and land use.

The new version of CLM will borrow as much as possible from components that have been successfully evaluated in other projects. Once a first prototype of the new model is in place, additional intensive and extensive evaluation will be required to assess the interactions between newly coupled components. For example, the logical core for carbon and nitrogen cycle interactions between soils and plants will be derived from the treatments in version 4.1.1 of the Biome-BGC model (Thornton et al., 2002). The seasonal, interannual, and decadal signals in net ecosystem exchange of carbon for this model have been tested across a wide range of climates and stand structures using eddy covariance observations and biometric analysis (Kimball et al., 1997, Law et al., 2001, Thornton et al., 2002). An advantage of reducing the number of simulation constraints by coupling the carbon and nitrogen cycles with the physical climate is that new data sources are made available for evaluation of the coupled system – for example the predicted atmospheric concentrations of CO_2 and reactive nitrogen species can be compared against observations of these quantities from global networks.

NCAR CCSM Ocean Model (NCOM)

A simple, full-depth carbon biogeochemical model with diagnostic surface production in the NCAR CSM Ocean Model (NCOM, Gent *et al* , 1998). A fully prognostic version is also under development. The model includes full carbonate chemistry, transport, and biological production. The diagnostic model has been favorably compared to observations of anthropogenic CO_2 (Doney and Sabine, 1999). Doney and their co-workers have incorporated the C-13 cycle into the NCOM carbon model (Balle et al., 2000). The model includes temperature-dependent fractionation due to gas exchange as well due to carbonate chemistry.   Phytoplankton is assumed to be C_3 and have a photosynthetic discrimination of 18 permil, while no fractionation is associated with the remineralization of organic carbon. No fractionation is assumed to be associated with the formation and dissolution of particulate inorganic carbon.

C.4 Stable Isotope Systematics in SiB2

The simple biosphere model (SiB2) was developed as a land-suráface parameterization for climate models (Sellers *et al* , 1996a,b), and has been extended to predict ecosystem metabolism on a time step of seconds to minutes at local, regional, and global scales (Denning *et al*, 1996a,b; 2002). We propose to implement the stable isotope systematics from SiB2 into CLM3 and the CCSM. This will include modification of the existing logic in CLM2 to include multistep isotopic discrimination, storage and recycling of carbon species in the canopy air space, and isotopic disequilibrium between respiring organic matter and the atmosphere (Suits *et al*, 2002). The model is quite successful at predicting spatial and temporal variations of CO_2 and $\delta^{13}C$ in the atmosphere when coupled with a tracer transport code.

In an approach similar to Lloyd and Farquhar (1994), transport of CO_2 and water vapor in C_3 plants is divided into 4 separate steps: (1) diffusion of canopy CO_2 and H_2O across the laminar leaf boundary layer, (2) molecular diffusion through the stoma, (3) dissolution of CO_2 into mesophyll water, and finally (4) aqueous phase transport to the chloroplast:

$$\Delta_{C3} = \Delta_s \; C_{ca}/C_{ca} + (\Delta_i - \Delta_s) \; C_s/C_{ca} + (\Delta_{diss} + \Delta_{aq} - \Delta_i) \; C_i/C_{ca} + (\Delta_{rbsco} - \Delta_{diss} - \Delta_{aq}) \; C_{cc}/C_{ca}$$

Δ_s, Δ_i, Δ_{diss}, Δ_{aq} and Δ_{rbsco} are kinetic isotope effects associated with transport through the leaf boundary layer, into the stomatal cavity, into solution, aqueous phase transport and fixation by rubisco, respectively. C_{ca}, C_s, C_i and C_{cc} are the corresponding CO_2 concentrations in the canopy, at the leaf surface, within the stomatal cavity and chloroplast. Figure 2 shows this schematicallyC_4 photosynthesis also discriminates against ^{13}C, but to a much lesser extent. Currently, SiB2 assumes that carbon isotopic discrimination in C4 plants is constant at -4.4‰.
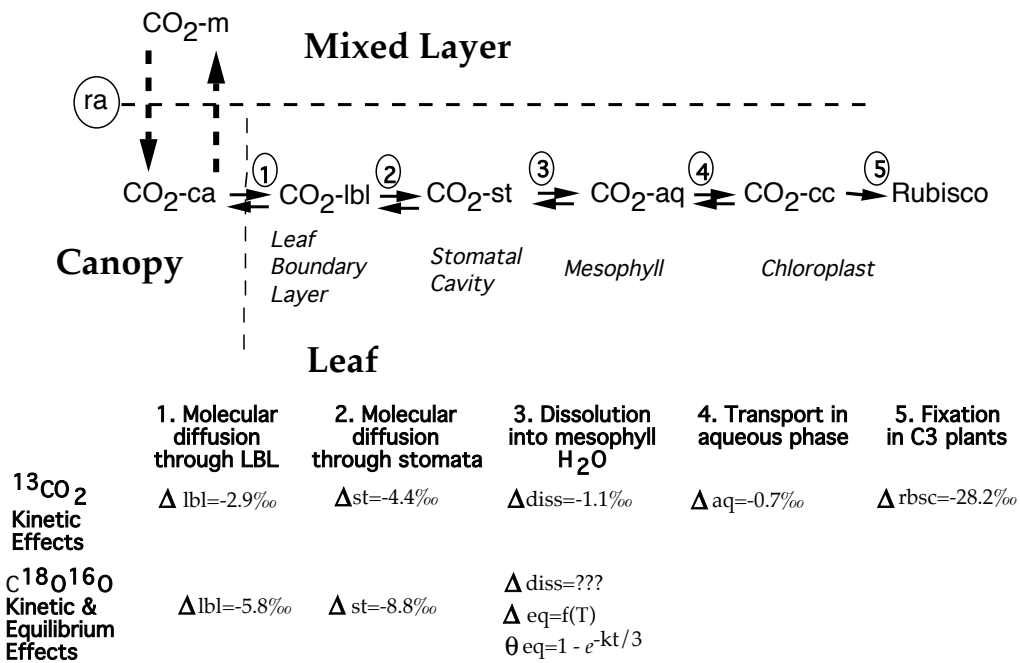

	1. Molecular diffusion through LBL	2. Molecular diffusion through stomata	3. Dissolution into mesophyll H_2O	4. Transport in aqueous phase	5. Fixation in C3 plants
$^{13}CO_2$ Kinetic Effects	Δ lbl=-2.9‰	Δst=-4.4‰	Δdiss=-1.1‰	Δaq=-0.7‰	Δrbsc=-28.2‰
$C^{18}O^{16}O$ Kinetic & Equilibrium Effects	Δlbl=-5.8‰	Δst=-8.8‰	Δdiss=??? Δeq=f(T) θeq=1 - $e^{-kt/3}$		

Figure 2: Schematic of $^{13}CO_2$ exchange logic in SiB2

To treat exchanges of CO_2 and its stable isotopes in SiB2, we introduced a new prognostic calculation of scalar quantities in the canopy air space. Traditional land surface parameterizations (e.g., Bonan, 1996) typically diagnose the temperature and water vapor pressure of the canopy air space from mixed-layer temperature and heat flux through a resistance network. The current NCAR CLM2 follows an analogous strategy to diagnose CO_2 concentrations in the canopy:

$$\rho \Delta z \frac{C_a - C_m}{r_a} = R_H + R_A - A \qquad (2)$$

where C_a is the canopy air space CO_2 concentration, C_m is the mixed-layer (or measurement) CO_2, R_H is heterotrophic respiration, R_A is autotrophic respiration, A is the assimilation of CO_2 by photosynthesis (GPP), r_a is the aerodynamic resistance, ρ is the air density, and Δz is the height increment. This approach has the disadvantage that there is no "memory" or "storage" of previous conditions. At local scales, this approach was found to lead to unrealistic behavior in early morning and late afternoon as the sign of the net CO_2 flux reverses, producing instantaneous changes of CO_2 concentration of hundreds of ppm (Denning *et al*, 2002). We have therefore introduced prognostic equations for energy, water, and carbon species in the canopy air formulated as a flux divergence that is solved using implicit time differencing:

$$\rho \Delta z \frac{\partial C_a}{\partial t} = R_H + RA - \frac{C_a - C_m}{r_a} \qquad (3)$$

Canopy storage of CO_2 allows the signals of photosynthetic assimilation (enriched in ^{13}C) and respiration (depletes ^{13}C) to mix in the canopy reservoir. Depending on the relative timing of light penetration into plant canopies and the onset of turbulence in the morning, some recycling of respired carbon into new photosynthate may occur. In the model, this effect tends to deplete $\delta^{13}C$ of organic matter in very productive ecosystems (e.g., tropical forests) by as much as 0.75‰ (Suits *et al*, 2002).

One advantage of the approach taken in SiB2 is that it allows CO_2 and stable isotope simulations to be directly evaluated with data collected during field experiments. We have
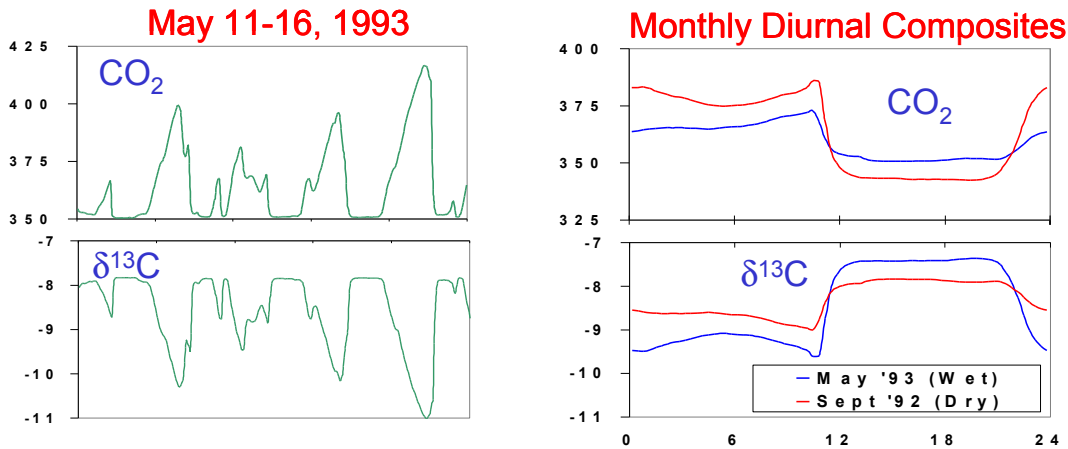

Fig. 3 - Simulated CO_2 and ^{13}C in the canopy air space at a flux tower site in a tropical forest in Brazil. This simulation used prescribed meteorology and assumes constant mixed layer conditions of 350 ppm and ^{13}C + -7.8 ‰.
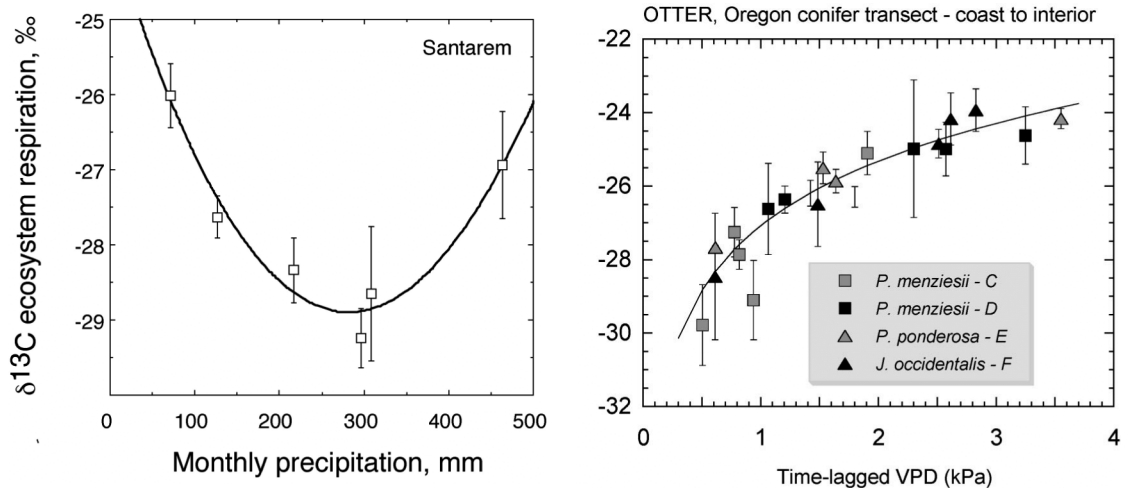
Fig 4: Variations of isotope ratio of respired CO_2 in response to soil moisture (left panel, for a tropical rainforest in Brazil; Ometto *et al*, 2002) and humidity stress (right panel, for a transect in Oregon; Bowling *et al*, 2002)

compared local-scale simulations of vertical structure and diurnal cycles of canopy air space CO_2 and $\delta^{13}C$ at a forested site in Wisconsin (e.g., Denning *et al*, 2002), an Oklahoma grassland/cropland (mixed C_3/C_4), and forests and pasture in Brazil (Fig 3).

Stable isotope ratios of ecosystem carbon fluxes have now been compiled for dozens of sites around the world, using the "Keeling plot" method (Keeling, 1958). These data are available through the Biosphere-Atmosphere Stable Isotope Network (BASIN, D. Pataki, pers. comm., see attached letter of collaboration). Most significantly, for many ecosystems, data are finally available on the variations in stable isotope ratios over time in response to changes in climatic forcing and physiological stress. (Fig 4). These data can help us evaluate the mechanisms by which the coupled model treats stable isotope exchange with the terrestrial biosphere. Clearly, the isotope ratio of the respiring pool of organic matter is more dynamic in nature than it has previously been modeled to be, responding on time scales of weeks to months to changes in discrimination related to environmental factors. These data contain information about both the physiological stresses under which the organic matter was formed and the residence time and possible pathways of photosynthate through the ecosystems. We propose a detailed evaluation of the results of the diurnal, seasonal, spatial, and interannual variability of isotopic ratios of CO_2 fluxes against these data, across as many types of ecosystems as possible.

The dependence of the kinetic isotope effect on C_i/C_a generally favors biochemical fractionation (more discrimination, lighter organic matter) when stomata are open, and diffusional effects when plants are stressed and stomates are closed. In simulations of interannual variability of isotope systematics in SiB2 driven by observed climate, we found substantial variation in isotopic discrimination of terrestrial ecosystems on a suite of temporal and spatial scales that was related to physiological stress. Locally, the relationships between physiological stress, though it is less pronounced than in the observations, and shows no sign of heavier CO_2 at very high precipitation rates as is suggested by the single month in the data (Fig 5). The offline simulation shown here does not include variations of $\delta^{13}C$ in the overlying atmosphere or recycling in the canopy, both of which will tend to amplify the stress effect. We
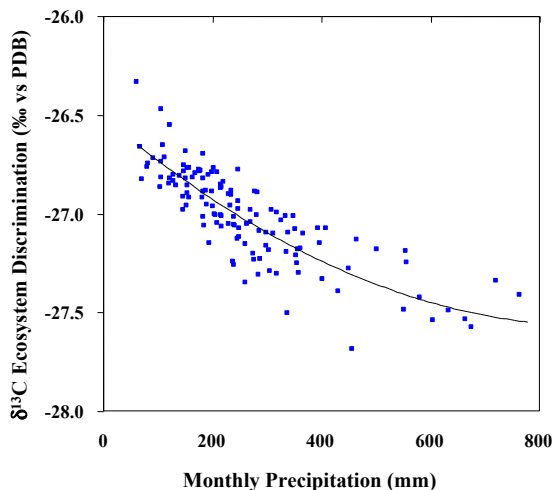
Figure 5: Simulated $\delta^{13}C$ of respiration *vs* precipitation from offline SiB2
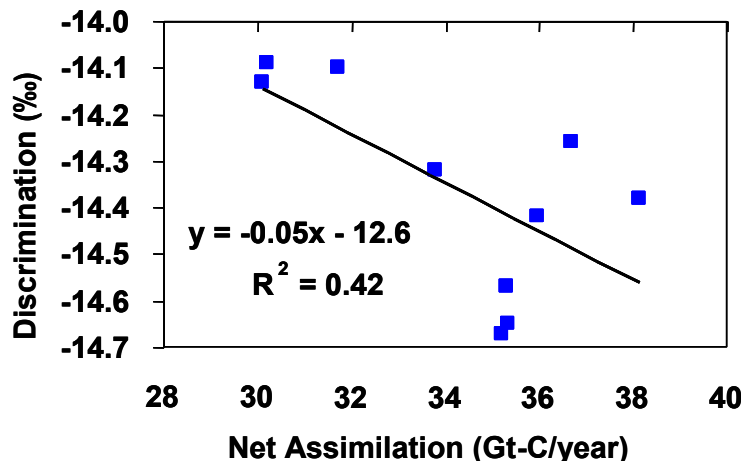
Figure 6. Correlation between annual Net Assimilation (GtC/year) and annual Net Assimilation-weighted Discrimination (‰) simulated by SiB2 over tropical South America for the years 1983 through 1993.

will repeat this calculation in the fully coupled model, and analyze this effect in detail as part of our model evaluation activities.

Coherent interannual variability in climate due to El Nino and other large-scale phenomena lead to substantial variation in simulated isotopic discrimination and the isotope ratio of newly formed organic matter (Fig 6). This in turn must produce variations in the isotope ratio of respired carbon in subsequent years, which affects the isotopic disequilibrium and the gross flux of ^{13}C from the biosphere (Randerson *et al*, submitted). These correlated interannual variations between GPP and Δ violate the basic assumptions of the double deconvolution method, and are crucial to model correctly if the promise of isotopic constraints for inverse modeling is to be realized. In the model, much of the interannual variability in regional and global discrimination arises because of changes in the fraction of C_4 photosynthesis on interannual time scales (Fig 7). The C_4 fraction of grid-scale vegetation is parameterized in SiB2 from physiological considerations and continuous fractional vegetation coverage derived from satellite imagery (Defries *et al*, 1999). C_4 plants account for approximately 20% of total terrestrial net assimilation. The regions in which they are the dominant flora tend to be warm and dry, and subject to seasonal and interannual variations in water availability, which in turn can lead to fluctuations in rates of net assimilation on the same timescales In the fully coupled CCSM calculation, competition between C_3 and C_4 vegetation will be modeled dynamically, as will the turnover of organic matter and its stable isotopes in vegetation and soils.

In addition to local evaluation of against ecosystem biogeochemical measurements, the coupled model can be tested by comparison to data collected by the global flask sampling network. We have used the ecosystem fluxes of CO_2 and $^{13}CO_2$ simulated by SiB2 as boundary conditions for a set of global tracer transport experiments using TM2 (Heimann *et al*, 1996). At most stations, the model successfully predicts the seasonal variations in both CO_2 and $\delta^{13}C$ (Fig 8).
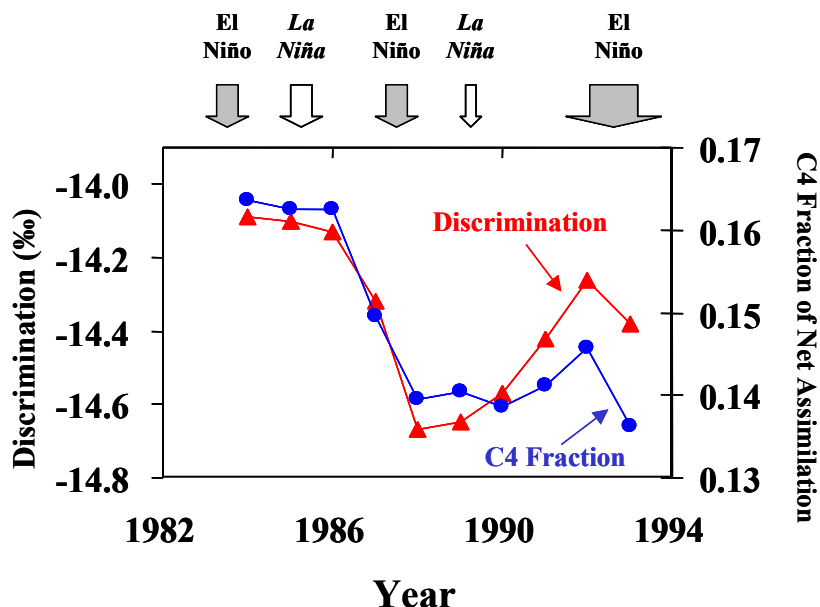

Figure 7. Annual Assimilation-weighted Discrimination (‰) and the fractional contribution of C4 plants to annual Net Assimilation.

These experiments were not consistent: ocean CO_2 and $^{13}CO_2$ fluxes were prescribed using output from the Princeton Ocean Model, as annual mean values only. Also, the winds and convective transports in TM2 were not consistent with the ECMWF meteorology used to drive the SiB2 ecosystem flux calculations. We will repeat the calculation in the fully coupled CCSM, this time with a self-consistent model. Ocean fluxes will be calculated by NCOM-BGC, and transport by CCM4. Precipitation, ecosystem drought stress, CO_2 flux, and isotopic discrimination will interact appropriately, and will be evaluated by comparison with observed CO_2 and $\delta^{13}C$.
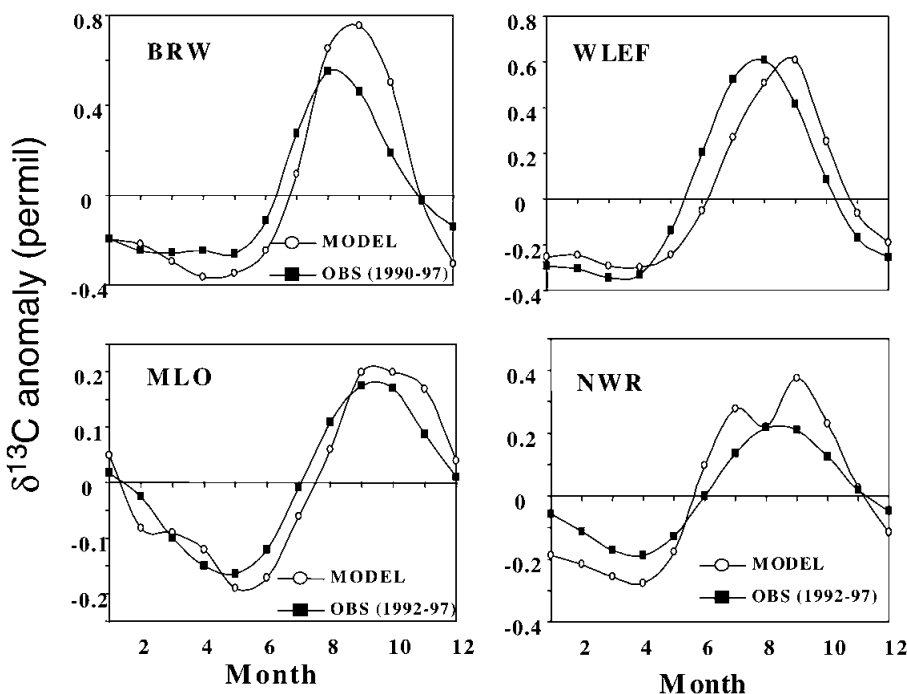

Figure 8. Simulated and observed $\delta^{13}C$ at 4 flask stations, as deviations fro the annual mean measured from 1992-1997 by NOAA CMDL.

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C.5 Inverse Modeling with the CCSM

Forward simulations in the CCSM will be completely self-consistent, and will be compared in detail to the flask CO_2 and $\delta^{13}C$ record. This internal consistency is important to resolve atmospheric gradients which may arise from covariance of surface exchanges with atmospheric transport – the "rectifier effect" (Denning *et al* , 1995, 1999). In addition, we will use the isotope ratios of simulated CO_2 exchanges at the land and ocean surface as isotope emission scenarios to investigate the sensitivity of simulated CO_2 and $\delta^{13}C$ to ecosystem discrimination, isotopic disequilibrium, and atmospheric transport.

The inverse problem of estimating sources and sinks of CO_2 from variations in concentration is usually solved by discretizing variations in CO_2 fluxes in space and time into "basis functions," then prescribing the basis fluxes as emission scenarios in forward calculations of concentration with a tracer transport model. Linear combinations of the resulting conentration distributions in space and time are then optimized to match observations on annual mean (e.g., Fan *et al*, 1998), seasonal (Bousquet *et al* , 1999), or interannual time scales (Rayner *et al*, 1999; Bousquet *et al*, 2000). In the TransCom 3 experiments, basis vectors consisted of the concentration response to unit "pulses" of CO_2 released from each of 22 regions in each month (Gurney *et al* , 2002 reported the results of annual mean inversions among 16 tracer transport models; the monthy experiment is described in Gurney *et al*, 2001, see also http://transcom.colostate.edu). The entire suite of concentration response functions to monthly pulses of CO_2 from the TransCom regions is available to us from 11 different transport models.

Using the basis functions from such a calculation, we can decompose the concentration of CO_2 into components arising from each region in each month prior to the observation: $d = G\ m$, where d is a vector of observed concentrations, G is the Jacobian of the transport model response (ppm per Gt of emissions) to unit regional pulses in each month, and m is the (unknown) magnitude of each pulse. The inverse problem is to invert G to find m from d. For the $\delta^{13}C$ problem, we can simply multiply each element in m_{ij} by an isotope ratio R_{ij}, which is the $^{13}C/(^{12}C+^{13}C)$ ratio of the net CO_2 flux in or out of region i in month j. Multiplying the Jacobian G by this modified m, we obtain a vector of simulated isotope ratios at each flask station in each month which can be directly compared to the flask observations of $\delta^{13}C$. This calculation can be trivially performed for each of the 11 transport models which produced monthly mean output for TransCom.

If we had perfect confidence in the ability of the CCSM to predict the fractionation and disequilibrium exchanges of $^{13}CO_2$ we could simply augment the Jacobian of the transport model with columns modified by suitable isotopic ratios, and add extra elements to the data vector representing the observations of $\delta^{13}C$ at each station in each month. These augmented data and transport matrices would be used to estimate the regional monthly CO_2 fluxes with less uncertainty than for the case of CO_2 alone. But of course we will not have perfect confidence in the forward model, or we would not be doing the inversion at all! Also, the isotope ratio of the net fluxes represents a combination of the effects of fractionation on net fluxes and isotopic disequilibrium acting on much stronger one-way gross fluxes at the land and ocean surfaces.

We will use the CCSM with its mechanistic treatment of these fluxes and ratios to test methods to deconvolve the sensitivity of observed $\delta^{13}C$ to ecosystem-level processes. This will entail development of prior estimates of fluxes and isotope ratios and detailed error estimation for these priors, using the process model. We will investigate the possibility of separately estimating the stress response of discrimination and the turnover time of organic matter in various ecosystem pools from the atmospheric data. We will test these method with synthetic data produced by the forward coupled model, and test their sensitivity to transport error by comparing across the range of TransCom model responses. Finally, we will perform an inversion of the combined CO_2 and $\delta^{13}C$ record to estimate regional fluxes over the past 20 years with the stronger constraint afforded by the isotopic data. It is hoped that besides better estimates of CO_2 fluxes, this work will lead to better representations of the processes controlling CO_2 exchange in the coupled model as well.

C.6 Schedule/WorkPlan

In year 1, we will work with NCAR scientists and programmers to port our isotopic systematics logic into the CLM. In parallel with this effort, the ecosystem biogeochemistry model will also be implemented at NCAR, and both will be merged to form CLM3. Substantial collaboration and effort will be required at NCAR to accomplish this, though we do not seek support for personnel outside CSU (see attached letter of collaboration from NCAR scientists). We will also perform forward sensitivity tests of the $\delta^{13}C$ of atmospheric CO_2 using the TransCom response functions and our monthly isotope ratios from SiB2. These will be compared in detail to the flask record (see attached letter of collaboration with John Miller).

In year 2, we will test the forward process model, and evaluate it against available data. This will involve first running the land component of the model offline, forced with observed weather and vegetation distributions. Results from these uncoupled simulations will be compared with ecosystem isotope data compiled by the BASIN activity (see attached letter of collaboration from Diane Pataki). Coupled simulations will then be performed at NCAR including predicted physical climate, dynamic vegetation, and the ocean carbon cycle (including ^{13}C, see attached letter of collaboration with Inez Fung). Results of these simulations will be compared to the flask observations as well as the ecosystem data of BASIN.

In year 3, we will use the results of the offline and coupled experiments to develop improved inverse modeling of the sources and sinks of CO_2 from atmospheric data. This will include estimating monthly discrimination and disequilibrium from both land and ocean basis regions, and their uncertainties. We will use the forward model to test the new inverse method. Finally, we will perform the inversion over the period from 1985 to 2005, using CO_2 data only for the early part of the record and adding $\delta^{13}C$ information as it became available.

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