Proposal for a European Science Foundation Scientific Program

"Stable Isotopes in Biospheric-Atmospheric Exchange"

1. Context

Terrestrial ecosystems play an important role in the global carbon (C) budget. The C amounts released by anthropogenic activities are almost a factor of two higher than the observed increase of atmospheric CO_2 concentrations measured globally (IPCC 1996). After accounting for a large oceanic sink, models predict a large C sink to be located in the Northern Hemisphere, particularly in the terrestrial biosphere (Tans et al. 1990; Ciais et al. 1995; Enting et al. 1995; Francey et al. 1995). However, the annual partitioning among different terrestrial carbon sinks, the effect of land use change, the human socio-economic impacts and the future development of the global C budget are still under debate (budget for 1980 to 1990; IPCC 1996; Keeling et al. 1996; Schimel et al. 2000). Furthermore, European politicians are increasingly faced with the consequences of the Kyoto convention, seeking ways to decrease European C sources and to increase C sinks, e.g. by C sequestration in the terrestrial biosphere. Thus, ecosystem physiology, specifically the CO_2 gas exchange between terrestrial ecosystems and the atmosphere as well as the carbon sink strength of various ecosystem types, is of primary interest for global change research (Walker and Steffen 1996) and European societies.

Scientists from various disciplines (usually from different countries), ranging from atmospheric physics to micrometeorology, from plant ecophysiology to biogeochemistry, using site-specific to global models, address the diverse aspects of biospheric-atmospheric gas exchange. However, the communication among these disciplines and joint research projects are still scarce, partly due to the increasing complexity of the aspects under investigation, partly due to the (necessarily) growing specialization within the individual disciplines. Thus, efforts to advance the science on biospheric-atmospheric interactions in Europe and to provide answers and recommendations to European politicians are gaining increasing importance. Consequently, we propose to develop and provide a platform that (1) will bring together European researchers, post-docs and students from different disciplines, (2) will allow exchange of methods and data, (3) will privide opportunities to train young researchers in new and advanced research methods, and (4) will allow the design of new, innovative experiments that cover multiple aspects (e.g., different organizational levels, time scales or spatial dimensions).

The analysis of carbon and oxygen isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) in plant and soil material as well as CO_2 proved to be a useful tool to address global change research questions at various temporal and spatial scales. The use of ^{13}C analysis in atmospheric CO_2 research provided a scientific breakthrough by allowing the partitioning of atmospheric CO_2 exchange between the ocean and the terrestrial biosphere (Tans et al. 1993). It is anticipated that the use of ^{18}O in CO_2 will bring the next breakthrough by allowing the partitioning of terrestrial CO_2 exchange between photosynthetic uptake and soil respiration (Farquhar et al. 1993; Yakir and Wang 1996). Atmospheric CO_2 concentrations and their corresponding carbon isotope ratios fluctuate seasonally, mainly due to changes in the terrestrial C fluxes (Conway et al. 1994; Trolier et al. 1996). Measurements starting in the early 1980s showed that atmospheric $\delta^{13}C$ ratios decreased by -0.025 ‰ per year during the 1980's, but that this rate of change approached almost zero between 1990 and 1993 (Trolier et al. 1996). Understanding such changes in the isotopic signatures of tropospheric CO_2 requires detailed knowledge about the ^{13}C signature of different compartments and fluxes in terrestrial ecosystems and the ^{13}C fractionation taking place during the biospheric CO_2 exchange with the atmosphere as well.

In this new research field on biospheric-atmospheric interactions, there is still a great number of open scientific questions such as: Which biotic and abiotic processes control the isotopic signatures of terrestrial ecosystems and the biospheric-atmospheric CO_2 exchange? Which environmental factors determine the temporal and spatial variability of stable isotopic signal in the terrestrial biosphere? How can stable isotopes help to separate flux components (assimilatory or respiratory) of net ecosystem fluxes measured with eddy covariance techniques? How can we scale up stable isotopic signatures from leaves and soils to the canopy, ecosystem and to regional scales? Can we use the currently available mechanistic understanding of C assimilation and respiration to simulate $^{13}C^{18}O^{16}O$ exchange in models? How can we link ecosystem scale measurements of $^{13}C^{18}O^{16}O$ exchange to atmospheric measure-ments of the convective boundary layer? These are some of the questions that are fundamental for the themes of this proposed ESF program.

The proposed program relies on existing, national and international European and global projects and initiatives in which several members of the Scientific Steering Committee already participate. But it also aims to enhance and fill in gaps in those programs. In the future, there might also exist the great opportunity for close collaboration with another ESF program on "The Role of Soils in the Terrestrial Carbon Balance", which has been submitted to ESF-LESC by Dr. Mark Rayment (University of Edinburgh, UK) in winter 2000. This complementary program aims to increase our understanding of soil carbon pools and fluxes, including issues like method development for soil carbon stock estimates or the potential for mitigating CO_2 emissions by soil carbon sequestration, aspects not covered within this proposed program. Two already existing European research networks offer good opportunities for the acquisition of information, vital for a biosphere-atmosphere interaction research initiative: (1) The new EU cluster CARBO-EUROPE (http://www.bgc-jena.mpg.de/ public/carboeur/index.html) with several large European research networks, and (2) the EU project NETCARB (http://www.PIK-Potsdam.DE/%7Ebadeck/netcarb/) with its objectives representing specific areas of plant eco-physiology. Complementary, there are the following global programs: GCTE (**G**lobal **C**hange and **T**errestrial **E**cosystems; http://gcte.org/), BAHC (**B**iospheric **A**spects of the **H**ydrological **C**ycle; http://www.pik-potsdam.de/~bahc) or FLUX

NET (http://daacl.ESD.ORNL.Gov/FLUXNET/). However, these programs have their specific research questions, are often limited to neighboring disciplines, and all are restricted to a tight time schedule. Therefore, an explicit European research program is needed to allow scientists interested in the application of stable isotopes, whether from the above projects or not, to step out of the relatively narrow focus of their projects and take a more holistic approach to discuss the development of the European stable isotope research area.

This proposed program to the ESF has its US counter-proposal "Biosphere-Atmosphere Stable Isotope Network, BASIN" (http://gcte-focus1.org/basin.html), organized by Prof. Jim Ehleringer (University of Utah, USA), that is being funded by the National Science Foundation (NSF) of the United States of America for the next five years. Both proposals are complementary to each other, the goals of BASIN and the proposed ESF network are common and were developed after consultations, ensuring adequate opportunities at both national and international scales for research advancement, network development, cross-site training, field campaign interactions and joint workshops. To our knowledge, this is the first initiative that joins scientific efforts from the very beginning of the research process in a new research field, ensuring strong cooperative links and early developments of a common communication platform, not only across nations, but also across continents. This becomes even more relevant to the scientific community world wide, because global change is affecting terrestrial and aquatic ecosystems globally, not nationally, thus asking for a truly integrated and multi-disciplinary effort to understand biospheric-atmospheric CO_2 exchange.

2. Scope and scientific objectives of the program

Within the proposed ESF program, we aim to integrate the very different perspectives on stable isotopes in biospheric-atmospheric trace gas exchange research, particularly of CO_2 and H_2O. We strive to reach scientists working on different scales (e.g. in micrometeorology or global atmospheric circulation), using different methods (e.g. experimentalists or modelers) and investigating different organisms (e.g. microbes, plants or animals) or ecosystems (from tropical to boreal, grasslands to forests).

The following objectives will be the unifying mechanisms within the program:

- to provide a platform for European researchers of different disciplines for promoting and integrating stable isotopes to biospheric-atmospheric exchange research,
- to initiate new research activities using stable isotopes in the field of biospheric-atmospheric gas exchange in Europe, crossing discipline boundaries,
- to provide means, including exchange visits, conferences, workshops, summer schools, common databases and an interactive webpage, for the development and promotion of common approaches for measurements of stable isotopes in ecosystem gas exchange studies and for flux measurements,

- to provide opportunities for training young investigators in latest advances in experimental and modeling methodology of stable isotope fluxes in biospheric-atmospheric exchange projects, and
- to join with the BASIN program in the US and form a global network for the exchange of methodology, reference materials and data.

3. Program themes

The program will be focussed around the following three themes:

1. Understanding stable isotopic signals of the terrestrial biosphere,
2. Partitioning net ecosystem gas exchange into its component fluxes, and
3. Interpreting spatial and temporal variability of terrestrial and atmospheric isotopic signals.

3.1 "Understanding stable isotopic signals of the terrestrial biosphere"

State of the art

The CO_2 exchange of the biosphere with the atmosphere is influenced by the interactions of the turbulence regime and ecosystem physiology. The turbulence regime will influence the mixing of CO_2 with different isotopic compositions between the biosphere and the atmosphere. Ecosystem physiology will affect the carbon and oxygen isotopic signatures ($\delta^{13}C$ and $\delta^{18}O$) of the biospheric flux and the magnitude of this flux. Strong feed-back mechanisms exist such as the effect of high turbulence on ecosystem assimilation or low ecosystem gas exchange rates on the CO_2 concentrations. The main ecosystem processes that alter the isotopic signature of canopy CO_2 are assimilation, autotrophic and heterotrophic respiration, evaporation and transpiration, each carrying ^{13}C and ^{18}O signals integrated over different time spans.

Isotopic composition of organic materials
Isotope ratios are expressed in δ units according to $\delta(‰) = [(R_{sample}/R_{standard})-1] \cdot 1000$, where R is the ratio of heavy to light isotope of the sample and standard, respectively. Foliar $\delta^{13}C$ ratios are influenced by two key factors: (1) by the $\delta^{13}C$ of canopy CO_2, the source air for photosynthetic assimilation and (2) by carbon discrimination (Δ_{leaf}) during photosynthesis. Large fractionation against ^{13}C is usually observed in C_3 plants during CO_2 fixation (O'Leary 1988), therefore determining the isotopic imprint during biological CO_2 exchange. It is now well established that C_4 or CAM plants discriminate less against ^{13}C during photosynthesis than C_3 plants, but even within these photosynthetic groups, there can be considerable variation in Δ_{leaf}. Any factor such as light or vapor pressure deficit that may alter the stomatal resistance will affect the isotopic discrimination by photosynthesis and plant biomass. Internal recycling of CO_2 from respiration and photorespiration influencing the $\delta^{13}C$ value of

the substrate CO_2 inside the leaf as well as variations in the $\delta^{13}C$ values of atmospheric or canopy air CO_2 outside the leaf, are further factors affecting $\delta^{13}C_{leaf}$ values. However, despite this detailed process knowledge, the problem of how to scale up single leaf measurements to obtain a canopy isotopic signal remains unsolved.

The plant foliage, stems and roots are subsequently input pools for the large pool of soil organic matter (SOM). The $\delta^{13}C$ values of SOM reflect these varying contributions, but are also altered during decomposition processes. One of the most common observations in C_3 ecosystems is a progressive enrichment in $\delta^{13}C$ values associated with litter decomposition and soil organic matter oxidation (Ehleringer et al. 2000). It is common within a forest ecosystem to see enrichments of 1 to 3 ‰ between leaf litter and older (deeper) soil organic matter. The exact reasons for this pattern are still unclear and researchers from a variety of disciplines, microbiology, chemistry, physiology and soil science, will be needed to solve and test the different hypotheses that are available.

Isotopic composition of water

Soil water and leaf water are the sources of evapotranspiration that transfer large quantities of water and energy (as latent heat) between the land surface and the atmosphere. Evaporation also modifies the oxygen and hydrogen isotopic composition of water, creating a natural isotopic signal for different water reservoirs and fluxes ($\delta^{18}O$ and δD, respectively). The isotopic identity of leaf and soil water affect the $\delta^{18}O$ of ambient carbon dioxide through extensive oxygen exchange between these two constituents.

The principles underlying variations in the isotopic composition of water vapor and the water surface undergoing evaporation were first described by Craig and Gordon (1965) and good agreement has been observed between theoretical predictions and experimental results for soil water undergoing evaporation. Soil water becomes gradually enriched in the heavy isotope, ^{18}O, and a highly enriched 'evaporation front' usually develops at 0.1 - 0.5 m below the dry soil surface. Below such fronts, the isotopic enrichment decreases exponentially with depth, to the value of the source water in the system. The time required for the development of a steady state isotopic profile can be quite long, and depends on various edaphic and climatic factors. Thus, detailed soil science and climatic knowledge about the specific environment is needed before e.g. a plant ecophysiologist can use soil water isotopic information to infer water sourcing of local vegetation.

Leaves are usually treated as thin, well-mixed and isotopically uniform water pools to which the Craig and Gordon model can be applied. In the past, it was generally assumed that leaf water is always near isotopic steady state with respect to ambient environmental conditions. However, it was noted in numerous studies that the observed $\delta^{18}O$ of bulk leaf water is usually less enriched than that predicted (e.g., Yakir et al. 1989, 1990; Farquhar and Lloyd 1993; Roden and Ehleringer 1999). Various explanations have been proposed. The most realistic one is based on a one-dimensional advection-diffusion model that considers a continuous isotopic gradient within the leaf (Farquhar and Lloyd 1993). This gradient is the result of the shifting balance between the convective evaporation flux of unfractionated water through the leaf, and the back diffusion of isotopically enriched water away from the evaporating sites. Roden and Ehleringer (1999) suggested that isotopic composition of bulk leaf water can be corrected by an empirical, species-dependent factor to obtain estimates of isotopic composition of the water at the evaporating surfaces that are in good agreement with predicted values. Thus, further scientific advancement will need close collaborations of ecophysiologists and modelers to design, carry out and analyze the necessary experiments together.

Carbon isotope ratios of carbon dioxide

The carbon isotope ratio of ambient CO_2 is determined by (1) the $\delta^{13}C$ values of respiratory CO_2, (2) the discrimination during photosynthesis, and (3) the rates of these processes relative to turbulent mixing with the atmospheric CO_2 pool (Sternberg 1989; Lloyd et al. 1996). It is generally assumed that there is little or no isotopic fractionation associated with respiration processes (Lin and Ehleringer 1997). The $\delta^{13}C$ values of respired CO_2 are often determined by the mean isotopic composition of plant biomass and soil organic carbon, relatively rarely by direct measurements of soil respired CO_2 (e.g., Buchmann et al. 1997). However, just recently, new experimental results fueled the discussion about potential fractionation during heterotrophic respiration (Duranceau et al. 1999; Ekblad and Högberg 2000). Thus, carefully designed experiments are needed to answer this critical question in the future since many global models do not consider this effect when using isotopes to partition among global C sinks and sources.

Ecosystems having variations in the isotopic composition of biomass across spatial gradients also present a problem in deciphering the isotopic composition of respired CO_2. For instance, tropical forests exhibit heterogeneous isotopic signatures throughout their vertical profiles with upper canopy tissue having $\delta^{13}C$ values in the range of -28 to -26 ‰, and understory tissue exhibiting $\delta^{13}C$ values in the range of -36 to -32 ‰ (Medina and Minchin 1980; Sternberg et al. 1989). Since it is nearly impossible to determine the respiratory contribution by each component of these ecosystems, the isotopic signature of respired CO_2 is determined by "Keeling type" plots and CO_2 concentration measurements carried out at night (see below). However, there exists no common protocol to collect this kind of data although the information is most relevant to understand the isotopic signals of biospheric-atmospheric CO_2 exchange.

Oxygen isotope ratios of carbon dioxide

The ^{18}O of CO_2 from both root respiration and soil organic matter decomposition is strongly influenced by the oxygen isotopic composition of the water with which it is in contact. With the presence of carbonic anhydrase, ubiquitous in leaves and microorganisms, equilibrium is reached nearly instantaneously. The quantity of water usually involved is many orders of magnitude greater than that of the CO_2 present, so isotopically equilibrated CO_2 will take on the oxygen isotopic ratio of the water in which it is dissolved (modified by the temperature-dependent equilibrium fractionation), regardless of its initial $\delta^{18}O$ value. In the simplest case,

$\delta^{18}O$ of rainwater directly translates to the $\delta^{18}O$ of soil water, and after equilibrium and kinetic fractionation are taken into account, $\delta^{18}O$ of CO_2 production by respiration can be calculated. However, in reality, this calculation can be wrong, e.g. when fast CO_2 diffusion rates allow only partial equilibration, or when atmospheric CO_2 diffuses into and back out of the top soil, affecting both $\delta^{18}O$ of soil water and soil CO_2 by this invasion. Only a few field studies are available to date to test the theoretical model and tune it to many different soil types and soil moisture regimes (Tans 1998; Miller et al. 1999; Sulzman 2000).

Although, many studies assume soil water $\delta^{18}O$ to be constant and equivalent to rainwater, in fact, large variation in the $\delta^{18}O$ of soil water is observed. Soil water may become enriched near the surface relative to water deeper in the soil profile by evaporation. The extent to which this enriched water affects the $\delta^{18}O$ of respired CO_2 diffusing out of the soil is highly variable and not well understood. Local soil water may also change seasonally because of changes in precipitation, groundwater sources or vegetative cover. In addition to actual changes in the $\delta^{18}O$ of the source water, the water content of the soil or soil cover (e.g., lichens, mosses) influences the effective hydration rate, and seasonal and spatial changes in temperature will affect both the equilibrium and the hydration rate constants. Clearly, some knowledge of the isotopic composition of the local hydrologic cycle is necessary to predict $\delta^{18}O$ values of soil or plant water. Global sampling networks such as GNIP from IAEA might help here, joining in with efforts to model soil water depth profiles and determine plant water uptake zones.

Combining isotopic composition and concentration measurements

Stable isotopic signatures of CO_2 along with CO_2 concentration measurements provide the basis for "Keeling type" plots (Keeling 1958, 1961). The linear, two-ended mixing equation used in the Keeling plot (where $1/[CO_2]$ is plotted against the respective $\delta^{13}C$) is derived from the basic assumption that the atmospheric concentration and the isotope ratio of a substance (e.g. CO_2) in an ecosystem (i.e., the mixing pool) reflects the mixture of some background amount of this substance that is already present in the atmosphere (pool 1, atmospheric CO_2) and some amount of this substance that is added or removed by sources or sinks in the ecosystem (pool 2, ecosystem CO_2). The intercept of the equation ($\delta^{13}C_{ecosystem} = m + b * 1/[CO_{2,ecosystem}]$) reflects the isotopic ratio of the net sources/sinks in the ecosystem.

This relationship was first used by Keeling to interpret carbon isotope ratios of ambient CO_2 and to identify the sources that contribute to increases in atmospheric CO_2 concentrations at a regional basis. Later, researchers used this expression to identify the isotopic composition of respired CO_2 in forest ecosystems. More recently, the derivation of the isotopic composition of respired CO_2 has been used to determine ecosystem carbon isotope fractionation (Δ_e; Buchmann et al. 1997; Flanagan et al. 1996). A modified equation was also used by Bakwin et al. (1998) to estimate regional scale biological discrimination. Whole ecosystem discrimination was also assessed by relating the isotopic composition of CO_2 in the convective boundary layer (CBL), which integrates the effects of photosynthesis, respiration and turbulent transport to the isotopic composition of tropospheric CO_2 (Lloyd et al. 1996; Nakazawa et al. 1997). Whole ecosystem discrimination and CBL measurements can increase the window of observation to landscape or regional scales, e.g. for quantifying the contribution of C_3 or C_4 vegetation to productivity or in providing landscape to regional scale discrimination parameters required as inputs for global scale studies. However, only a limited dataset is available to date, which is, in addition, biased towards higher northern latitudes and forest ecosystems (Buchmann and Kaplan 2000).

Several open questions still exist in regard to the Keeling plot approach, such as the precision of the Δ_e estimates, the effect of CO_2 recycling within canopies and the appropriate reference CO_2 pool (i.e., CBL or free troposphere). Since this approach is also used to identify the source of water vapor to the evapotranspiration flux of ecosystems, these questions need to be resolved among scientists from various fields that do typically not cooperate in regular European projects.

Research Goals

Thus, the goals within theme 1 of the proposed program are

- to synthesize current knowledge on isotopic patterns within Europe,
- to provide a framework to European researchers that will allow easy and fast information exchange,
- to help selecting the best methodology and its uniform application for determining the isotopic signature of soil or ecosystem respired CO_2 and evaporated water as well as the isotopic signatures of important C pools,
- to develop scaling protocols from the leaf, canopy, region to the continent,
- to investigate underlying principles of isotopic patterns, particularly to test hypotheses on fractionation during heterotrophic respiration,
- to identify the source of respired CO_2, e.g., the proportions of root respiration vs. microbial organic matter decomposition,
- to advance our understanding on processes determining $\delta^{18}O$ signals in soil and leaf waters and their interactions with atmospheric and soil CO_2,
- to initiate further model development for predicting $\delta^{18}O$ of soil CO_2 in soil types under varying moisture regimes,
- to extend our database on isotopic signatures for representative European ecosystems, particularly taking into account different land use management.

Expected outputs

- recommendations for optimal methodology, experimental protocols, cross calibrations and scaling issues for stable isotopes in biospheric-atmospheric exchange,
- web-based data bases and user-friendly data sharing mechanisms,
- improved temporal and spatial resolution for isotopic patterns in terrestrial ecosystems.

3.2 "Partitioning net ecosystem gas exchange into its component fluxes"

State of the art

Several micrometeorological techniques, such as the flux-gradient method or the eddy covariance technique, offer the potential to measure net fluxes of water vapor, CO_2 and other trace gases exchanged between ecosystems and the atmosphere with high temporal resolution. Subsequent data analyses allow the calculation of net ecosystem CO_2 exchange. The need to understand CO_2 fluxes into and out of terrestrial ecosystems and to determine their carbon budgets resulted in numerous studies around the globe. Measurements at isolated field sites, along transects or as part of larger continental networks provided a first step for the spatial integration of processes within an ecosystem, including soils and vegetation (e.g., projects within FLUXNET).

These net fluxes, however, reflect the balance between different component fluxes. In the case of CO_2, two opposing fluxes contribute to this net flux: CO_2 uptake during photosynthesis and CO_2 release during respiration. For water vapor, leaf transpiration and soil evaporation are the major contributors to the combined net flux. Studies of these fluxes are complicated by CO_2 recycling within canopies (i.e., refixation of respiratory CO_2 before it leaves the system), or redistribution of water among ecosystem reservoirs. Distinguishing among these components is critical to obtain insights into the processes underlying ecosystem responses to climate forcing. This is because environmental parameters, such as temperature and soil moisture, differentially affect biological activities. Observing a net annual increase in CO_2 uptake of a forest, for example, is not sufficient to determine whether this is due to an increase in ecosystem photosynthesis or to a decrease in ecosystem respiration.

Oxygen and carbon stable isotope compositions of different ecosystem components provide a powerful tool towards quantifying the contribution of different components to the ecosystem exchange. When this tool is used in conjunction with concentration or flux measurements, an even greater amount of information is derived (e.g., Harwood et al. 1998; Wang et al. 1998). Deciphering the individual fluxes of an ecosystem using stable isotopes can be approximated by knowledge of the isotopic identity of the major ecosystem components as summarized above (see Chapter 3.1) or can be inferred by direct measurements that are currently being developed. These new measurements include combining isotopic and flux measurements or by applying relaxed eddy accumulation or hyperbolic relaxed eddy accumulation (Bowling et al. 1999a,b). However, to date, there are still many difficulties in precisely estimating those individual components. Further studies are needed that provide validations to earlier results and that advance our technology and theory. But the first results are very promising and estimates of independent contributions to gross ecosystem fluxes are anticipated to evolve within the next five years. Further efforts will also be put in advancing mechanistic models at various scales, from stands to regions to continents. This is particularly important for Europe since our landscape is very diverse and research results from one vegetation or land use type cannot necessarily transferred to neighboring areas with a different type.

Research Goals

Thus, the goals within theme 2 of the proposed program are

- to integrate carbon and oxygen isotope measurements to flux measurements,
- to compare and develop different experimental approaches, including relaxed eddy accumulation, conditional sampling and flask sampling for isotopic analyses,
- to initiate joint studies that aim at partitioning fluxes into their component fluxes in relevant European terrestrial ecosystems,
- to stimulate new approaches for determining isotopic signatures of individual flux components,
- to improve our theoretical understanding and modeling of isotopes in biospheric-atmospheric exchange.

Expected outputs

- prototype model dataset using different methods for partitioning ecosystem fluxes,
- database on contributions of component fluxes to net ecosystem fluxes for representative European ecosystems,
- advanced regional and continental scale model using isotopes.

3.3 "Interpreting spatial and temporal variability of terrestrial and atmospheric isotopic signals"

State of the art

Recently, an increasing number of studies have evaluated the $^{13}CO_2$ exchange of terrestrial ecosystems. Estimates of the carbon isotope ratio of ecosystem respiration ($\delta^{13}C_{ER}$, estimated using the Keeling plot approach) varied globally between -29.4 ‰ and -20 ‰, averaging -25.3 $\pm$ 2.2 (SD) ‰ (Buchmann and Kaplan 2000). Tropical forests and agricultural stands exhibited very low $\delta^{13}C_{ER}$ values, while agricultural C_4 stands in Mediterranean and temperate regions showed the highest $\delta^{13}C_{ER}$ values. Physiological constraints of C_3 photosynthesis as well as the expression of the C_4 photosynthetic pathway probably resulted in this large global spread of $\delta^{13}C_{ER}$ values, but necessary additional information were not available to solve this question. Greatest variability was found for agricultural stands, particularly in Europe, illustrating the pronounced effects of land use change (Buchmann and Ehleringer 1998). Under these circumstances, irrigation or changes in the photosynthetic pathway of vegetation cover from C_3 to C_4 (and vice versa) result in a mixture of organic matter in the soil that is being respired carrying a mixture of both ^{13}C signatures. However, to date, scaling these measurements to larger scales, e.g. to European regions, remains impossible because the necessary spatial resolution of isotopic measurements is still lacking for a landscape composed by such a mosaic of different land uses as in Europe.

Atmospheric boundary layer measurements of concentrations and isotopic composition of trace gases have just emerged recently and might offer a new approach to this problem (Raupach et al. 1992; Culf et al. 1999; Levy et al. 1999; Lloyd et al. 2000). Aircrafts are used to measure vertical profiles within the convective boundary layer (e.g., up to 3000 m) and intensive modeling is used to estimate regional flux rates of various substances. However, validation of these estimates are still scarce. In one example, the boundary-layer budget flux measured over a patchy forested area in Siberia was somewhere within the range of flux values measured over different surface types using eddy covariance techniques (Lloyd et al. 2000). These discrepancies might be attributed to a number of either technical, meteorological or conceptual reasons, but no clear pattern has emerged yet.

In addition to these spatial variations, large temporal variations in the isotopic signatures in pools and fluxes typically occur at different time scales: daily, seasonally, annually. For example, carbon isotope ratios and concentration of canopy CO_2 may well be above (for $\delta^{13}C$) or below (for $[CO_2]$) the atmospheric background value if the rate of photosynthesis is high relative to turbulent mixing. This has been observed in tropical forests (Quay et al. 1989) and in agricultural crops (Yakir and Wang 1996; Buchmann and Ehleringer 1998). Because photosynthetic discrimination is subject to diurnal and seasonal environmental influences, it is hypothesized that the photosynthetic imprint by the ecosystem will also vary on these time scales and that ecosystem discrimination may fluctuate as well. However, to date, the database on temporal variations is very limited and cannot be used to reject or accept this very plausible hypothesis.

At longer time scales (annual or decadal) further factors come into play. The relative proportion of C_3 plants (having average $\delta^{13}C$ values of about -26 ‰) to C_4 plants (having average $\delta^{13}C$ values of about -12 ‰) in ecosystems has important influences on the isotopic identity of respired CO_2. It is expected that European ecosystems, such as grasslands or arable lands, which might have a high proportion of C_4 plants, should have respired CO_2 with a less negative $\delta^{13}C$ value than those having a greater proportion of C_3 plants such as temperate forests. However, numerous complications can confound these expectations. Different photosynthetic types may dominate some ecosystems, such as croplands and deforested areas at different time periods. Soil organic carbon may retain the isotopic signal of the previous vegetation for several years due to the long residence times of organic matter in the soil, contributing to differences between the isotopic composition of respired CO_2 and that of the biomass present at the time of sampling (Buchmann and Ehleringer 1998). This phenomenon is usually referred as isotopic disequilibrium. Disequilibrium can also arise from soil organic matter being derived from photosynthesis that occurred at a time when the carbon isotopic ratio of atmospheric CO_2 was different than the present day (Enting et al. 1995; Fung et al. 1997). The continuous increase in the concentration of atmospheric CO_2 over the past hundreds years is due to the addition of ^{13}C-depleted CO_2 from organic sources (fossil fuels and biomass burning), a process that has progressively changed the isotopic composition of the atmosphere (Trolier et al. 1996) and all biomass produced from atmospheric CO_2. This, in turn, results in a small difference between the mean $\delta^{13}C$ values of current biomass production and of soil respiration that is derived from older biomass (Enting et al. 1995; Fung et al. 1997). Thus, the $\delta^{13}C$ of soil respiration carries this long-term 'ecosystem memory', dependent on the turnover rates of soil organic matter. Using innovative experimental designs or using additional isotope analyses such as of radiocarbon (^{14}C), will be necessary to deconvolute these overlying processes and will need a group of researchers from very different disciplines.

Research Goals

Thus, the goals within theme 3 of the proposed program are

- to initiate joint projects among CBL researchers and ecosystem ecologists to obtain model datasets, including stable isotope analyses at various spatial scales,
- to improve our understanding of isotopic signatures of ecosystem CO_2 and H_2O exchange and their temporal and spatial variability,
- to include the effects of human land use change in experimental studies on isotopic signals of net ecosystem exchange,
- to address questions of isotopic disequilibrium using stable isotopes and radiocarbon analyses.

Expected outputs

- global maps of isotopic signatures of $^{13}CO_2$ exchange of terrestrial ecosystems,
- finer resolution biogeochemical model describing the inter- and intra-annual variability of ^{13}C net fluxes.

4. References

Bakwin PS, Tans PP, White JWC, Andres RJ. 1998. Determination of the isotopic ($^{13}C/^{12}C$) discrimination by terrestrial biology from a global network of observations. Global Biogeochemical Cycles 12: 555-562.

Bowling DR, Delany AC, Turnipseed AA, Baldocchi DD, Monson RK. 1999a. Modification of the relaxed eddy accumulation technique to maximize measured scalar mixing ratio differences in updrafts and downdrafts. J Geophys Res 104: 9121–9133.

Bowling DR, Baldocchi DD, Monson RK. 1999b. Dynamics of isotopic exchange of carbon dioxide in a Tennessee deciduos forest. Global Biogeochemical Cycles 13: 903-922.

Buchmann N, Ehleringer JR. 1998. A comparison of CO_2 concentration profiles, carbon isotopes, and oxygen isotopes in C_4 and C_3 crop canopies. Agricul and Forest Meteorology 89: 45-58.

Buchmann N, Guehl JM, Barigah TS, Ehleringer JR. 1997. Interseasonal comparison of CO_2 concentrations, isotopic composition, and carbon dynamics in an Amazonian rainforest (French Guiana). Oecologia (Berlin) 110: 120-131.

Buchmann N, Kaplan J. 2000. Carbon isotope discrimination of terrestrial ecosystems - how well do observed and modeled results match. *In:* ED Schulze, DS Schimel and IC Prentice (eds) Global Biogeochemical Cycles in the Climate System. Academic Press, London, New York. in press

Ciais P, Tans PP, Trolier M, White JWC, Francey RJ. 1995. A large northern hemisphere terrestrial CO_2 sink indicated by the $^{13}C/^{12}C$ ratio of atmospheric CO_2. Science 269: 1098-1102.

Conway TJ, Tans PP, Waterman LS, Thoning KW, Kitzis DR, Masarie KA, Zhang N. 1994. Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network. J Geophysical Research 99: 22831-22855.

Craig H, Gordon LI. 1965. Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. *In*: Tongiorgi E (ed) Proceedings of the conference on stable isotopes in oceanographic studies and paleotemperatures. Laboratory of Geology & Nuclear Science, Pisa, 9–130.

Culf AD, Fisch G, Malhi Y, Costa RC, Nobre AD, Filho AOM, Gash JHC, Grace J. 1999. Carbon dioxide measurements in the nocturnal boundary layer over Amazon forest. Hydrology and Earth Systems Sciences 3: 39-54.

Duranceau M, Ghasghaie J, Badeck FW, Deleens E, Cornic G. 1999. $\delta^{13}C$ of CO_2 respired in the dark in relation to $\delta^{13}C$ of leaf carbohydrates in *Phaseolus vulgaris* L. under progressive drought. Plant, Cell and Environment 22: 515-523.

Ehleringer JR, Buchmann N, Flanagan LB. 2000. Carbon isotope ratios in belowground carbon cycle processes. Ecological Applications 10: 412-422.

Ekblad A and Högberg P. 2000 Analysis of $\delta^{13}C$ distinguishes between microbial respiration of added C_4-sucrose and other respiration in a C_3-ecosystem. Plant Soil 219: 197-209.

Enting IG, Trudinger CM, Francey RJ. 1995. A synthesis inversion of the concentration and $\delta^{13}C$ of atmospheric CO_2. Tellus 47B: 35-52.

Farquhar GD, Lloyd J. 1993. Carbon and oxygen isotope effects in the exchange of carbon dioxide between plants and the atmosphere. *In*: Ehleringer JR, Hall AE, Farquhar GD (eds) Stable isotopes and plant carbon-water relations. Academic Press, New York, pp 47–70.

Farquhar GD, Lloyd J, Taylor JA, Flanagan LB, Syvertsen JP, Hubick KT, Wong S, Ehleringer JR. 1993. Vegetation effects on the isotope composition of oxygen in atmospheric CO_2. Nature 363: 439-442.

Flanagan LB, Brooks JR, Varney GT, Berry SC, Ehleringer JR. 1996. Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO_2 in boreal forest ecosystems. Global Biogeochemical Cycles 10: 629-640.

Francey RJ, Tans PP, Allison CE, Enting IG, White JWC, Trolier M. 1995. Changes in oceanic and terrestrial carbon uptake since 1982. Nature 373: 326-330.

Fung IY, Field CB, Berry JA, Thompson MV, Randerson JT, Malmstrom CM, Vitousek PM, Collatz GJ, Sellers PJ, Randall DA, Denning AS, Badeck FW, John J. 1997. Carbon 13 exchanges between the atmosphere and the biosphere. Global Biogeochemical Cycles 11: 507-533.

Harwood KG, Gillon JS, Griffiths H, Broadmeadow MSJ. 1998. Diurnal variation of delta13CO2, deltaC18O16O and evaporative site enrichment of dH218O in *Piper aduncum* under field conditions in Trinidad. Plant, Cell and Environment 21: 269-283.

IPCC. 1996. Climate Change 1995. The Science of Climate Change. Cambridge University Press, Cambridge. pp 572.

Keeling CD. 1958. The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. Geochimica et Cosmochimica Acta 13: 322-334.

Keeling CD. 1961. The concentration and isotopic abundances of carbon dioxide in rural and marine air. Geochimica et Cosmochimica Acta 24: 277-298.

Keeling RF, Piper SC, Heimann M. 1996. Global and hemispheric CO_2 sinks deduced from changes in atmospheric O2 concentrations. Nature 381: 218-221.

Levy PE, Grelle A, Lindroth A, Mölder M, Jarvis P, Kruijt B, Moncrieff J.B. 1999. Regional-scale fluxes over central Sweden by a boundary layer budget method. Agric. For. Meteorol. 98-99: 169-180.

Lin G, Ehleringer JR. 1997. Carbon isotopic fractionation does not occur during dark respiration in C_3 and C_4 plants. Plant Physiol 114: 391-394.

Lloyd J, Kruijt B, Hollinger DY, Grace J, Francey RJ, Wong CS, Kelliher FM, Miranda AC, Gash JHC, Vygodskaya NN, Wright IR, Miranda HS, Farquhar GD, Schulze ED. 1996. Vegetation effects on the isotopic composition of atmospheric CO_2 at local and regional scales: theoretical aspects and a comparison between rain forest in Amazonia and a boreal forest in Siberia. Aust J Plant Physiol 23: 371-399.

Lloyd J, Francey RJ, et al. 2000. Vertical profiles, boundary layer budgets and regional flux estimates for CO_2, its $^{13}C/^{12}C$ ratio, and for water vapour above a forest/bog mosaic in central Siberia. Global Biogeochemical cycles. in press.

Medina E, Minchin P. 1980. Stratification of $\delta^{13}C$ values of leaves in Amazonian rain forests. Oecologia (Berlin) 45: 377-378.

Miller JB, Yakir D, White JWC, Tans PP. 1999. Measurement of $^{18}O/^{16}O$ in the soil-atmosphere CO_2. Global Biogeochemical Cycles 13: 761-774.

Nakazawa T, Sugawara S. 1997. Aircraft measurements of the concentrations of CO_2, CH_4, N_2O, and CO and the carbon and oxygen isotopic ratios of CO_2 in the troposhere over Russia. J Geophysical Research 102: 3843-3859.

O'Leary MH. 1988. Carbon isotopes in photosynthesis. BIOSCIENCE 38: 328-336.

Quay P, King S, Wilbur D. 1989. $^{13}C/^{12}C$ of atmospheric CO_2 in the Amazon Basin: forest and river sources. J Geophysical Research 94: 18327 - 18336.

Raupach MR, Denmead OT, Dunin FX. 1992. Challenges in linking atmospheric CO_2 concentrations to fluxes at local and regional scales. Aust J Botany 40: 697-716.

Roden JS, Ehleringer JR. 1999. Observations of hydrogen and oxygen isotopes in leaf water confirm the Craig-Gordon model under wide-ranging environmental conditions. Plant Physiol 120: 1165-1173.

Schimel D, Melillo J, Tian HQ, McGuire AD, Kicklighter D, Kittel T, Rosenbloom N, Running S, Thornton P, Ojima D, Parton W, Kelly R, Sykes M, Neilson R, Rizzo B. 200. Contribution of increasing CO_2 and climate to carbon storage by ecosystems in the United States. Science 287: 2004-2006.

Sternberg LSL. 1989. A model to estimate carbon dioxide recycling in forests using $^{13}C/^{12}C$ ratios and concentrations of ambient carbon dioxide. Agricul and Forest Meteorology 48: 163-173.

Sternberg LSL, Mulkey SS, Wright SJ. 1989. Ecological interpretation of leaf carbon isotope ratios: influence of respired carbon dioxide. Ecology 70: 1317-1324.

Sulzman E. 2000. Soil carbon and water dynamics: ^{13}C and ^{18}O as system tracers. PhD thesis. Colorado State Universitry, Fort Collins, CO, USA.

Tans PP. 1998. Oxygen isotopic equilibrium between carbon di-oxide and water in soils. Tellus 50B:163–178.

Tans PP, Fung IY, Takahashi T. 1990. Observational constraints on the global atmospheric CO_2 budget. Science 247: 1431-1438.

Tans PP, Keeling RF, Berry JA. 1993. Oceanic ^{13}C data. A new window on CO_2 uptake by the oceans. Global Biogeochemical Cycles 7: 353-368.

Trolier M, White JWC, Tans PP, Masarie KA, Gemery PA. 1996. Monitoring the isotopic composition of atmospheric CO_2: measurements from NOAA global air sampling network. J Geophysical Research 101: 25897-25916.

Walker B, Steffen W. 1996. Global Change and Terrestrial Ecosystems. Cambridge University Press, Cambridge. pp 619.

Wang XF, Yakir D, Avishai M. 1998. Non-climatic variations in the oxygen isotopic compositions of plants. Global Change Biology 4: 835-849.

Yakir D, DeNiro MJ, Rundel PW. 1989. Isotopic inhomogeneity of leaf water: evidence and implications for the use of isotopic signals transduced by plants. Geochimica et Cosmochimica Acta 53: 2769-2773.

Yakir D, DeNiro MJ, Gat JR. 1990. Natural deuterium and oxygen-18 enrichment in leaf water of cotton plants grown under wet and dry conditions: evidence for water compartmentation and its dynamics. Plant Cell Environ 13: 49–56.

Yakir D, Wang XF. 1996. Fluxes of CO_2 and water between terrestrial vegetation and the atmosphere estimated from isotope measurements. Nature 380: 515-517.

5. Proposed activities

5.1 Exchange visits

Exchange visits of young researchers are considered a major backbone of the program. These research visits provide a unique opportunity to young graduate students, postdocs or young faculty to learn the latest advances in the field of experiments or models, to make contacts to other European laboratories outside their home country and to work on collaborative, interdisciplinary research within the themes of the program. These exchange visits further allow the establishment of a strong network of common approaches for measurements of stable isotopes in ecosystem gas exchange studies throughout Europe.

Exchange visits will be funded up to nine months. The estimated average allowance per month of visit is about 1.65 kEuro plus travel costs. Calls for applications will be published in international journals as well as distributed through relevant e-mail listservers, e.g., via CarboEurope, FluxNet or the ecophys and isogeochem server, and posted on the ESF and the program's webpage. Applications will be granted based on the suitability and the quality of the submitted proposal to the program as well as on past research performance and letters of recommendation. Exchange visits will only be funded for stays outside the respective home country of the applicant; priority will be given to candidates of countries supporting the program.

5.2 Workshops, schools

Workshops and summerschools are regarded as major tools to achieve the program's goals. Workshops serve a critical need to bring together scientific communities with different expertise and scientific experiences to address and promote the program's efforts. They are also important opportunities for young researchers (graduate students and postdocs) to interact with more established investigators in a common setting. In addition, summerschools provide the chance to learn new techniques and approaches "hands-on" as participants are exposed to a certain topic during an intensive short course. Graduate students and postdocs are often not aware of the "isotopic" potentials in biospheric-atmospheric exchange studies since courses covering stable isotopes are not within the regular curriculum of university programs.

At least one annual **workshop** is planned within the program dealing with the scientific aspects described above. Furthermore, a call for workshop proposals will be issued annually and reviewed by the Scientific Steering Committee (SSC) to encourage participation of a wide range of European researchers. Applications will be granted based on the relevance and the quality of the submitted proposal to the program as well as on past research performance. Workshops should be restricted to a maximum number of 40 persons; the participation of young scientists should be particularly promoted. If the US proposal to NSF by Prof. Jim Ehleringer (University of Utah, USA) is accepted and funded, one international workshop per year (alternatively in the US and in Europe) is planned. The primary reason for these workshops is to bring together investigators from North and South America and Europe to address the global perspective of the program's themes.

The following program workshops are tentatively scheduled:

- "Partitioning ecosystem CO_2 fluxes into their respiratory and assimilatory components", to be held in Jena, Germany. The eddy covariance measurements continuously monitor net ecosystem CO_2 exchange at many stations globally. However, these measurements do not allow partitioning into the different component fluxes what is critical to understand the variability of measured net CO_2 fluxes. Currently, several techniques are available to address this problem, ranging from scaling-up chamber measurements to new techniques such as eddy accumulation of one-way $^{13}CO_2$ fluxes. The workshop aims to synthesize these new developments and provide recommendations for the design of new experiments for direct comparison.

- "What can we learn from Keeling plots?", to be held in Rehovot, Israel. Stable isotope signatures of CO_2 along with CO_2 and H_2O concentration measurements provide the basis for "Keeling type" plots. One of the problems with the Keeling type plot is that the extrapolated intercept from the linear regression is many units away from the actual measurements. Therefore, small errors in measuring either the isotope ratios or the concentration of the component of interest can lead to large errors in the extrapolation (such problems apply to both water and CO_2 measurements). The requirements for steady state conditions during sampling poses another challenge in measurement that usually requires sampling around the diurnal cycle. Nevertheless, the Keeling plot approach is a very simple methodology that has a great potential in providing key information in many stable isotope application to ecosystem research, if properly applied. The workshop aims to advance the theory underlying the Keeling approach and discuss the potential complications and possible ways to address these issues, thus promoting a uniform and substantiated application of the Keeling approach.

- "The use of isotope tree ring analyses to study the impact of environmental changes on vegetation: potentials and weaknesses", to be held in Villigen, Switzerland. Dendrochronological data provide a means for climate reconstruction. But it is often difficult to discern between the different climatic factors impacting tree ring growth. Stable carbon and oxygen isotope ratios provide a good tool to distinguish whether tree ring width was increased or decreased because of changes in water availability or temperature. Tree ring width and the isotopic signature are also influenced by increased CO_2 concentrations or nitrogen depositions. The possibility to assess this impact of past and present changes, archived in tree rings is very promising. Yet, tree physiology impacts the isotopic signature in tree rings as well, to a degree, which is not well known yet. The workshop aims to discuss and evaluate both, the strengths and the weaknesses of stable isotopes in tree ring analyses in combination with dendrochronology.

The establishment of **summerschools** is planned. Summerschools should host about 20 European graduate students and postdocs. About 8 to 10 European lecturers, experts of their corresponding fields, will be invited to introduce summerschool participants in selected isotopic aspects, using lectures as well as discussion groups, computer labs, field trips, etc. Participants will be selected based on the application and the letters of recommendation with the goal to achieve a group with diverse scientific backgrounds and European nationalities.

The following summerschool is tentatively scheduled:

"Stable carbon and oxygen isotopes in net ecosystem CO_2 exchange studies" by Prof. Dan Yakir (Weizmann Institute, Israel) and PD Dr. Nina Buchmann (Max-Planck-Institut für Biogeochemie, Germany). This regular summerschool will be hosted alternatively in Israel or Germany. This initiative is based on two fundaments: (1) the "Stable Isotope Ecology Lecture and Laboratory Short Course" held annually at the University of Utah, USA, organized by Prof. Jim Ehleringer (http://ecophys.biology.utah.edu/Biology_5470/course_description) and (2) the summerschool "Isotopes in community and ecosystems ecology" organized by Prof. Joao Pereira (Universidade Tecnica de Lisboa, Portugal) and PD Dr. Nina Buchmann (Max-Planck-Institut für Biogeochemie, Germany). Close collaborations, also with the activities within NETCARB, are guaranteed. This summerschool aims to expose participants to most recent methodology and theory about $^{13}CO_2$ exchange of terrestrial ecosystems.

5.3 Conferences

Within the proposed program, two conferences are planned in the years 2 and 5. The goals of these conferences are to broaden the scientific outreach of the program, to review the results achieved so far and to point out new, promising areas of joint research efforts. The participation of young scientists will be particularly encouraged. International experts of the relevant disciplines will be invited to these conferences to give critical feedback on the program and suggest changes in direction, if necessary.

5.4 Committee meetings

The Scientific Steering Committee (SSC) will be responsible for all decisions concerning the proposed program. Since the research topics addressed by this program are still rather new (last five to ten years), the SSC also includes younger scientists (such as postdocs and young faculty). Smaller Executive Steering Committees (ESC, including the Chair of the program and three to four additional members of the SSC) will be formed when dealing with selected activities of the program. E.g., an ESC is anticipated supporting the SCC in the review process of proposals for exchange visits, workshops or conferences. The additional ESC members will rotate on an annual or bi-annual schedule. The ESC will report annually to the SSC.

The members of the SSC will meet once a year to coordinate the program's activities. The smaller ESC will meet according to activities' demand, e.g., once or twice a year following call for proposals.

5.5 Secretariat

To facilitate fast communication among participants and to provide secretarial support, a part-time assistant to the chair is requested. Further tasks will be the organization of SSC and ESC meetings, workshops and conferences, the organizational interaction with the US counter-program as well as the maintenance of a common database.