Proposal to:
NSF Program: Division of Environmental Biology, Ecosystems Studies

Carbon Dioxide Evasion from Fluvial Environments of Amazônia: A Major Sink for Terrestrially Fixed Carbon and Tracer of Ecosystem Processes

Request: September 1, 2002 – August 31, 2005

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A. PROJECT SUMMARY

The overall question we are addressing in this proposal is, *"What role does the evasion (outgassing) of CO_2 from the river system to the atmosphere play in the carbon cycle of moist tropical forests?"* Recent evidence suggests that the Amazon may be a net sink of atmospheric CO_2 of 1-9 Mg C ha^{-1} y^{-1} (depending on the technique used). We have made recent calculations that suggest that the evasion of CO_2 from the river system of the central Amazon basin is on the order of 1.2 ± 0.3 Mg C ha^{-1} y^{-1}. A flux of this magnitude suggests that the ecosystem processes involved in river corridors represent a significant pathway for the export of carbon fixed on land in the humid tropics at a globally-significant level.

Our working hypothesis is that: *CO_2 evasion returns as much carbon to the atmosphere as is sequestered in upland forests on an interannual basis. Export of organic material from upland forests to fluvial environments is the primary source of carbon that is eventually respired in rivers and evaded as CO_2*. We propose to test our hypothesis by conducting fieldwork in characteristic sub-basins of the Amazon (to determine the spatial and temporal distributions of $p\mathrm{CO}_2$ and to use geochemical techniques to quantify the rates of transfer of water and bioactive organic matter) and to use a terrestrial source/river transport and reaction model to synthesize and extrapolate the site-specific CO_2 evasion rate measurements to a basin-wide estimate of CO_2 evasion rate. We propose eight specific tasks to do this work (find and characterize representative sampling environments, determine distributions of $p\mathrm{CO}_2$, assess gas exchange rates, evaluate the source strength of terrestrial and river margin organic matter and CO_2, determine *in situ* respiration rates and substrates, characterize the isotopic and organic composition of dissolved organic and inorganic carbon, determine the seasonality of inundation and terrestrial runoff, and synthesize observations and modeling in computing downstream fluxes). This three-year project will be done jointly between the University of Washington and the Centro de Energia Nuclear na Agricultura, together with collaborating institutions in Amazônia.

C.1. CO_2 Evasion from Rivers and Wetlands of Amazônia

The overall question we are addressing in this proposal is,

"*What role does the evasion (outgassing) of CO_2 from the river system to the atmosphere play in the carbon cycle of moist tropical forests?*"

The deceptively simple expression of dissolved CO_2 gas (pCO_2) in surface waters of tropical river systems (usually at concentrations far exceeding equilibrium with the atmosphere) is the product of a long sequence of complex biological, hydrological, and geochemical processes. If we can explain the sequence of processes that eventually lead to the observed pCO_2, we will gain significant insight into how bioactive elements are spiraled down a continuum of rivers under the influence of flood-pulses (*sensu* Newbold et al. 1982, Vannote et al.1980, Junk et al. 1989). A likely and surprising outcome of these dynamics is that evasion may have important consequences for the role of fluvial systems in the overall carbon budget of the tropics, and of the tropics in the global carbon cycle.

The humid tropics play an important but ambiguous role in the global carbon cycle. While deforestation has been estimated to release about 1.6 Gt C y^{-1} (Houghton 2000), mature Amazon rainforests appear to sequester carbon (act as a sink), but of an uncertain magnitude. Current estimates of sequestration have wide variation between different types of measurements, from ~ 1.3 Mg C ha^{-1} yr^{-1} based on the accumulation of biomass and soils (Phillips et al. 1998, Chambers et al. 2001, Trumbore 2000) to 1.0 to > 5.9 Mg C ha^{-1} y^{-1} based on eddy covariance measurements (Fan et al. 1990; Grace et al. 1995; Malhi et al. 1998). However, recent calculations from global atmospheric inverse modeling imply that the net carbon exchange of the tropics with the atmosphere is about zero (Schimel et al. 2001). Discrepancies between these estimates of carbon sequestration rates may be due in part to methodological issues and integration times of methods. However, an issue often overlooked is terrestrial carbon "…that leaks out of the forest in forms that are not usually measured, such as gaseous emissions of hydrocarbons or dissolved C in groundwater flows. Although this carbon leakage is thought to be relatively small, surprises cannot be ruled out" (Malhi and Grace 2000).

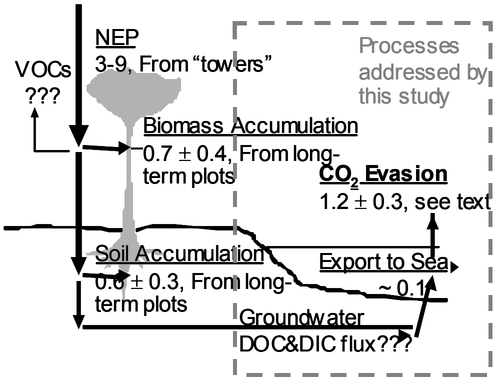

Fig. 1. Estimated C fluxes in the Amazon, Mg C ha^{-1} y^{-1}. (Adapted from Mahli and Grace 2000, Richey et al in review)

The major biogeochemical role of river systems is typically considered to be the "carbon leakage" (*sensu* Mahli and Grace 2000) - primarily the fluvial export of total organic (TOC) and dissolved inorganic carbon C (DIC) to the ocean of ~0.4 Gt C y^{-1}, respectively (Degens et al. 1992, Stallard 1998). While these fluxes are significant compared to the net oceanic uptake of anthropogenic CO_2 of ~2 Gt C y^{-1} (Sarmiento and Sundquist 1992), they are small components of the global C cycle. Fluvial carbon exports are not limited, however, to discharge. Richey et al. (1980) suggested that global riverine carbon fluxes, including both transport and evasion, exceed 1 Gt C y^{-1}. Gas evasion from water to the atmosphere has been shown to constitute a significant fraction the net annual carbon accumulation for the tundra (Kling et al. 1991) and for peatlands (Hope et al. 2001). If all rivers evaded 30% of their dissolved inorganic carbon (DIC) as CO_2, as does the Ottawa River, then the global evasion flux would be an order of magnitude higher than previous estimates (Telmer and Veizer 1999). Based primarily on surveys of temperate rivers, Cole and Caraco (2001) estimated that global CO_2 evasion of ~0.3 Gt C y^{-1} was comparable to export of organic carbon to the ocean (~0.4 Gt C yr^{-1}). Hope et al. (2001) cautioned that direct measurements of land-atmosphere CO_2 gas exchange that ignore water-borne fluxes might significantly overestimate terrestrial carbon accumulation.

We have recently computed that the evasion of CO_2 from surface waters to the atmosphere in the central Amazon basin is 1.2 ± 0.3 Mg C ha^{-1} y^{-1}, and hypothesized that it is driven primarily by in-stream respiration of organic carbon fixed originally on land and along river margins and mobilized into flowing waters (Richey et al. in review[1]). This flux is comparable to the (lower) estimates of forest sequestration and, if extrapolated across Amazônia, is over 10 times the fluvial export of organic carbon to the ocean. If the Amazon basin CO_2 evasion flux is representative of world wide humid tropics, CO2 evasion from all fluvial environments of humid tropics would total about ~ 0.9 Gt C y^{-1}, or three times the Cole and Caraco (2001) estimate for current global CO_2 evasion. Based on our initial estimates of CO_2 evasion from the central Amazon, this carbon loss could partially resolve the apparent dichotomy between significant carbon sequestration derived from Amazon eddy correlation measurements, regional deforestation releases, and the near-zero net CO_2 exchange with the atmosphere inferred by the global atmospheric inverse modeling.

Direct evasion of CO_2 of such magnitude from drainage waters would force us to revise our concept of the mechanisms coupling terrestrial and aquatic environments at regional scales. Linkages between land and water would be stronger than previously thought, with river corridors (*sensu* Richey et al. 1998) representing a significant downstream translocation of carbon (in both space and time) originally fixed by the forest. The intent of this proposal is to determine the overall magnitude, dynamics and consequences of CO_2 evasion by evaluating our:

> *Working Hypothesis. CO_2 evasion returns as much carbon to the atmosphere as is sequestered in upland forests on an interannual basis. Export of organic material from upland forests to fluvial environments is the primary source of carbon that is eventually respired in rivers and evaded as CO_2.*

We propose to test our hypothesis by the following. (1) Conduct fieldwork in characteristic sub-basins to obtain an extensive suite of $p\mathrm{CO}_2$ distribution measurements over the hydrologic regime, and to use proven geochemical techniques (gas flux measurements, isotopic tracers, molecular organic biomarkers, remineralization rates) to quantify the rates of the lateral transfer and cycling of water and bioactive organic matter from the land, through riparian environments and to the river system. (2) Use a terrestrial source/river transport and reaction model to synthesize and extrapolate the site-specific CO_2 evasion rate measurements to a basin-wide estimate of CO_2 evasion rate. The work will be done in the Amazon, as both a significant percentage of and model for the overall humid tropics. The proposed work will contribute to a "unifying theory," melding two important areas in ecosystem studies – the carbon cycle and the classic models of riverine dynamics, including the River Continuum (Vannote et al, 1980), nutrient spiraling (Newbold et al. 1982), and river flood-pulse (Junk et al. 1989).

The work will be done as a full partnership between colleagues at the University of Washington (UW, Seattle, USA) and the Centro de Energia Nuclear na Agricultura (CENA, Piracicaba, Brazil), together with collaborating institutions in Amazônia, including the Instituto Nacional de Pesquisas da Amazônia (INPA, Manaus). We are building on the long history (starting 1982) of our NSF, NASA, and FAPESP (Brazilian) - supported project CAMREX (Carbon in the AMazon River EXperiment).

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[1] At the time of proposal submission, *Nature* has provisionally accepted the paper, pending final editorial details.

C.2. CAMREX: from Field Measurements to Synthetic Models

Our overall perspective in CAMREX is that the Amazon is a test case for developing extendable models of how hydrologic and biogeochemical cycles are coupled at regional to continental scales in the humid tropics. Our studies serve the dual purposes of gaining a broad mechanistic understanding, and of establishing data baselines needed to assess anthropogenic perturbations to these globally critical and ecologically complex systems. As documented in over 120 publications, the CAMREX dataset represents a time series unique in its length and detail for very large river systems. Of particular relevance to the work proposed here is a set of papers on gas fluxes, within river respiration, and organic matter sources in the basin (Hedges et al. 1986; Devol et al. 1987, 1988, 1990, 1995; Richey et al. 1988, 1990; Quay et al. 1989, 1992; Bartlett et al. 1990; Martinelli et al. 1994). Most recently, we published a "state-of-the-Amazon" book (McClain et al. 2001). Richey et al. (in press) and Mayorga and Aufdenkampe (in press) have developed syntheses of the hydrological and biogeochemical cycles. Aufdenkampe et al. (2001) and Hedges et al. (2000) have investigated the chemical control on organic matter cycling, including the presence of highly resistant black carbon (Dickens et al. in review). We have been using spatial models and remote sensing data to examine the landscape patterns that influence the chemical signals we detect in the river waters (Rosenqvist et al. in press; Mayorga et al. in review, Wilhelm et al. in review), including the effects of landuse change on river chemistry in Rondônia (Ballester et al. in review, Bernandes et al. in review). We are now extending this work to Southeast Asia (Richey et al. 2000) and the Pacific Northwest (PRISM, Richey 2001; http://www.prism.washington.edu).

Results from Previous NSF Support: NSF DEB-98-15912, $275,000, 1999- 2000. (J.E. Richey, P.I.; J. Hedges, A. Devol, P. Quay, R. Victoria, co-I's), Towards a model of the biogeochemistry of continental-scale river basins: an Amazon case study. Within the immediate past funding period, we focused on model-based synthesis of previous field measurements.

Carbon Dioxide Evasion from Amazon River Corridors to the Atmosphere.

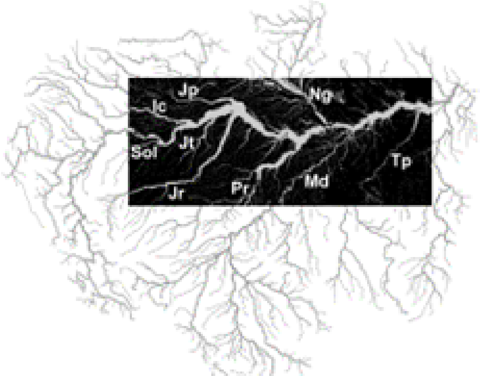

Fig. 2. High-water flooded area of the central Amazon, by radar (JERS-1), on GIS river network. Rios Negro (Ng), Japurá (Jp), Içá, (Ic), Solimões (Sol), Jutaí (Jt), Juruá (Jr), Purús, (Pr), Madeira (Md), Tapajós (Tp).

We evaluated the evasion of CO_2 from the fluvial environments of a 1.77 million-km^2 quadrant (Fig. 2) of the low-gradient central Amazon basin Richey et al. (in review). The problem was to determine the spatial extent of inundated areas across the full scale of Amazonian environments, from first order streams to the mainstem and its floodplain, and then the rates of CO_2 evasion for the respective areas. Newly available remote sensing datasets made it possible to quantify seasonal water coverage for representative low and high water periods, showing that up to 20% of the quadrant is flooded at high water. When we combined the areal extent of flooding and measurements of the distributions of pCO_2 with a gas evasion model, we observed a pronounced seasonality in evasion fluxes, corresponding to the annual hydrograph and the elevated CO_2 concentrations (Fig. 3). Integrating over the year and over environments, we computed that the surface waters of the central Amazon basin export 1.2 ± 0.3 Mg C ha^{-1} y^{-1} of CO_2 to the atmosphere over the entire quadrant. If these findings extend to other humid tropical river systems that drain weathered soils, they would contrast previous findings from temperate river systems, where lower drainage density, higher alkalinity waters and cooler temperatures lead to lower evasion (Cole and Caraco 2001, Telmer and Veizer 1999).

A critical ecological question is, where does the carbon come from that ultimately is evaded? From estimates of potential source strengths, we hypothesized that evasion is driven primarily by in-stream respiration of organic carbon fixed originally on land and to a lesser extent along river margins and mobilized into flowing waters, and not just by dissolved CO_2 in groundwater. This presents us with a problem. Despite negligible measured downstream gradients in dissolved and particulate organic matter, and constituent biochemicals that appear in general quite refractory, measured respiration rates in Amazonian waters are sufficiently large to recycle essentially all organic matter in a parcel of river water well before it reaches the ocean (Richey et al. 1990; Hedges et al. 2000). Thus we have either overestimated the *in situ* respiration rates or have left unmeasured a labile component to the organic matter pool that is fueling respiration.

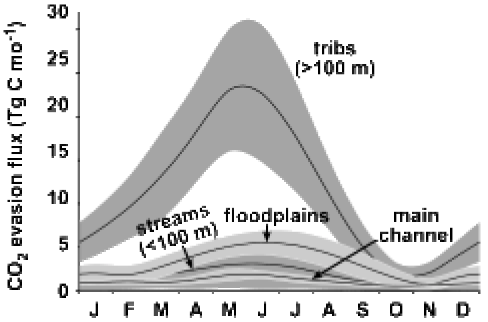

Fig 3. Spatially integrated sequences of CO_2 evasion for hydrographic environments. Lines are long-term means, shaded regions represent the 67% C.I. likely in a particular year.

Reaction and Advection of Organic Matter, Nutrients, and Biogenic Gases through the Amazon River System. The framework for quantifying the role of evasion from rivers in the basin was developed by Richey and Victoria (1996). They implemented a Lagrangian transport-reaction model that tracked parcels of water and its constituents as they moved downstream. With this past grant, we worked at extending the model from the mainstem to include tributaries and floodplains interacting with the mainstem. In part with NASA support, we initiated application of the grid-based hydrological model Variable Infiltration Capacity (VIC, Liang et al. 1994; Wood et al. 1997) that parameterizes the dominant hydrometeorological processes taking place at the land surface - atmosphere interface. The objective is to quantify the main characteristics of soil moisture and runoff production that move water and subsequently chemical species across the basin (Fig. 4). Richey et al. (in press) demonstrated that pCO_2 and other species could be systematically organized on the rising and falling limbs of the discharge hydrograph. The next step in this synthesis will be to couple hydrological and biogeochemical models to predict seasonal distributions of dissolved and particulate carbon concentrations in rivers.

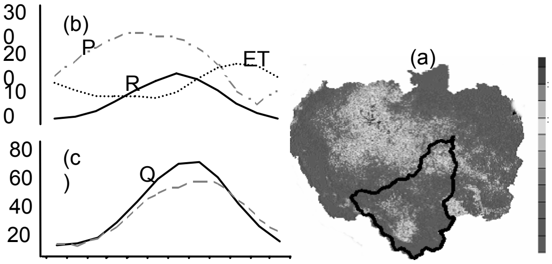

Fig. 4. Hydrological model: (a) Computed runoff fields, e.g.,Aug-Sep Rio Madeira: (b) runoff (mm/mo (gauges), Evapotranspiration (ET, computed), (c) discharge (Q, $m^3/s \times 10^3$) observed (-) vs computed (--),

Field Studies of Organic Carbon Dynamics. If labile carbon is exported from land to aquatic systems, then it is critical to identify the processes controlling organic matter composition and dynamics over the full range of aquatic environments in the Amazon watershed. The physical size fractions coarse particulate (CPOM), fine particulate (FPOM) and dissolved (DOM) organic matter each exhibit distinct dynamics and compositional traits that hold over very broad range of geological, hydrological and climatic conditions (Hedges et al. 1994). To further examine these traits, CAMREX launched a series of major expeditions in the last several years to extend the range of our original mainstem focus. These include surveys of Andean headwaters in Bolivia at low and high water and in Peru at low water, and a series of transects of the Rio Ji-Paraná system (Rondônia) over a range of hydrographic conditions.

Building on our previous work, the data from these collections are beginning to reveal important processes in the evolution of organic matter from small streams to the biggest of rivers (Hedges et al. 2000; Aufdenkampe et al. 2001; Devol and Hedges, 2001; Mayorga and Aufdenkampe, in press; Bernandes et al. in review). As part of our quandary of understanding the sequence of processes leading to CO_2 evasion, we have been considering how carbon species might be exported by groundwater from the landscape to the drainage basin (OM "downwelling"). Observations point toward a substantial and somewhat continuous input of labile organic substrates that are then rapidly remineralized somewhere within the river or its hyporheic zone. However, if the substrates fueling respiration are so labile, how do they persist long enough to be transported to the river? Previous observations of methane gradients in the river (Devol et al., 1996) and of substantial concentrations of volatile organic acids (VOAs) such as formate, acetate, and glycolate in Amazon waters (Skoog, unpublished) point toward oxygen-poor groundwaters as perhaps the most likely source. The key concept is that although fermentation of DOM is possible after groundwater reaches anoxia, net electron loss is not. Thus, any water that percolates into the soil carrying more moles of DOC than dissolved O_2 (which is likely in sandy soils throughout the basin; McClain et al. 1997) should be an efficient transporter of reduced carbon to the first site where oxidizing agents again become available. In this manner groundwater can transport both an oxygen deficit to stream systems, as well as fermentation intermediates that are likely to react rapidly (and to be missed by most conventional organic analyses). All of these recent insights into organic processing within rivers have been critical to the formulation of our emerging biogeochemical model (below).

$\Delta^{14}C$ of Organic Matter and DIC. A grant from the Center for Accelerator Mass Spectrometry (CAMS), Lawrence-Livermore National Labs, has allowed us to dramatically expand the number and variety of $\Delta^{14}C$ measurements throughout the Amazon River system. The limited radiocarbon analyses of particulate and dissolved organic matter carried out in the mid-80's (Hedges et al. 1986) provided key insights into the distinct origins and cycling times of CPOM, FPOM, and DOM. However, no further measurements had been done since then in Amazonian rivers above the marine mixing zone. We have used archived samples from previous CAMREX expeditions to analyze more than 120 samples for $\Delta^{14}C$ at the CAMS facility. These samples span a wide range of environments, from high-altitude Andean streams to the mainstem Amazon (Fig. 5, Aufdenkampe and Mayorga, unpubl. data). More than 70 samples have already been processed, and the rest will be completed by May 2002. Showing large geographical, longitudinal, and seasonal variability, current results provide a unique and richer view of carbon residence times in DIC and several particulate and dissolved OC size fractions in a large river system. For example, preliminary results appear to support the view that DOM size fractions have different residence times, with low molecular weight (LMW, 1 - 10 kDa) fractions possibly having a mean age of around one decade, while high molecular weight (HMW, > 10 kDa) fractions may have a mean age of around 30 years. DIC-^{14}C measurements will allow us to estimate the replacement time of CO_2 downstream along elevation and environmental transects, and to constrain the range in age of CO_2 in lowland rivers. Taken together, these new ^{14}C results

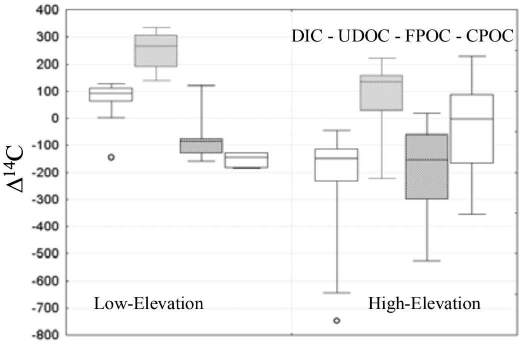

Fig. 5. $\Delta^{14}C$ for each primary fraction for lowland and Andean environments. Median values are represented by lines, 25th & 75th percentile by boxes and 10th and 90th by whiskers.

coupled to additional CAMREX measurements enable an integrated examination of organic and inorganic carbon cycling throughout the river system.

Developing a Model of Organic Carbon Transport and Dynamics in Rivers. Large rivers receive and transform inputs from heterogeneous landscapes, making it difficult to ascertain geographic origins and the role of small-scale riparian transformations on the resulting organic matter. The issue we face is trying to decompose this aggregate signal into its sources of origin. The previous two decades of research by the CAMREX group has built a solid foundation of understanding carbon cycling within the Amazon basin. We are now synthesizing this understanding into a "River Basin Organic Matter and Biogeochemistry Synthesis" (ROMBUS, Fig. 6) model (Aufdenkampe and Mayorga, in prep). The overall goal of this model development is to predict the concentration and flux of dissolved and particulate carbon in rivers throughout the Amazon basin over an annual cycle, when coupled to a hydrologic model.

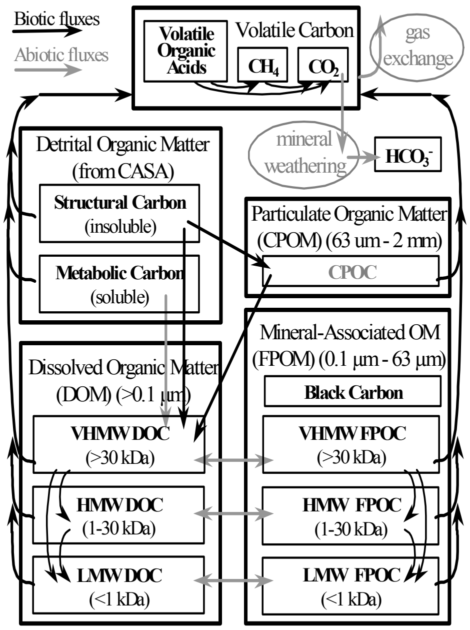

Fig 6. Schematic of the ROMBUS model; calculates biogeochemical reactions at each location and time-step within a spatially-distributed, integrated model framework.

The model partitions the carbon reservoirs within a river into measurable dissolved and particulate organic carbon pools (DOC and POC, respectively). The POC pool is divided in fine and coarse fractions because of their significantly different compositions, sources and degradation histories. Both the POC and DOC pools are further divided by molecular weight to account for the observed increase in degradation state as the molecular size of the organic matter decreases (Amon and Benner 1996a, 1996b) and to facilitate the parameterization of organo-mineral associations. In contrast, most land-surface carbon models divide OM into unmeasurable (conceptual) pools with characteristic turnover times that are difficult to verify (e.g., the CENTURY model, Parton et al. 1994). Our ROMBUS design is more consistent with newer initiatives in the soil carbon modeling community (Christensen 1996; Elliott et al. 1996). Unique to ROMBUS is the explicit parameterization of organo - mineral interactions, which are increasingly acknowledged as fundamental to OM stabilization (Hedges et al. 1995; Christensen 1996; Baldock et al. 2000).

The dissolved inorganic carbon pool, at the pH range for rivers in the Amazon basin, is composed of the HCO_3^- ion and dissolved CO_2 gas. Within ROMBUS there is a flux of CO_2 from the OM pools derived from the *in situ* respiration of labile organic matter. The controls on these respiration rates are not well constrained for the mainchannel of the Amazon River, for it's major tributaries, nor especially for smaller rivers in the basin. This transfer of carbon from OM to dissolved CO_2 gas is a critical step for our proposed research as the concentration of dissolved CO_2 and its air-water gas transfer rate will determine the CO_2 evasion rate from the rivers in the basin. Within ROMBUS each of the organic and inorganic carbon pools (rectangles in Fig. 6) are represented by state variables that characterize the nitrogen-to-carbon ratio (for the OM pools), $\delta^{13}C$ signature and age (via $\Delta^{14}C$). Within each pixel, the transformations between these pools are calculated by ROMBUS for three sub-pixel elements (surface water; riparian soils; and upland soils) each at three sediment/soil horizons. Horizontal and vertical transport between sub-pixel elements and from one pixel to the next are determined via the modified VIC hydrology model and our stream and river channel network (Mayorga et al. in review). Therefore, for a given sub-pixel element, the concentration of each individual chemical species (or state variable) is tracked by a mass balance. First order kinetics are used to parameterize transformation rates, with rate constants from the literature and previous work that are subsequently modified by environmental variables such a temperature and moisture. These key characteristics provide information about carbon sources and cycling times within the basin and, importantly, can be compared to direct measurements made by the CAMREX group over the last decade in rivers across the basin. This comparison of predicted and observed state variables will serve as a major test of whether our model predictions of OM cycling and respiratory input of dissolved CO_2.

C.3. Proposed Research

Our research plan is focused on testing our working hypothesis, that 1) CO_2 gas evasion from Amazon rivers systems is of the same order as terrestrial carbon sequestration and 2) the CO_2 source is primarily a result of *in situ* respiration of terrestrially-derived labile organic matter (Fig. 7). There are alternatives to the hypothesis. While we are confident that our initial assessment of evasion (Richey et al. in review) is reasonably accurate in the aggregate over the Central Basin, there are much greater uncertainties (in flooding regimes, air-water gas transfer rates, seasonal variation of $p\mathrm{CO}_2$ especially in smaller streams) for each given place or time. To test our hypothesis we need a much better understanding of the controls on such temporal and spatial variability. While our initial estimates are able to roughly account for enough terrestrial organic carbon export to (potentially) fuel CO_2 evasion, we don't know what controls the relative contributions of terrestrial sources of carbon relative to along margins (macrophytes). It may be that the uplands and fluvial systems are more decoupled, and that the bulk of the river signal is derived from along stream and river margins and on floodplains. We don't know how riparian and hyporheic conditions might alter the input of terrestrial carbon to streams. Even if we establish that "enough" organic matter is introduced into river networks to augment dissolved CO_2 injections in supporting evasion, we still need to establish that this material is mineralized within the transit times of the rivers.

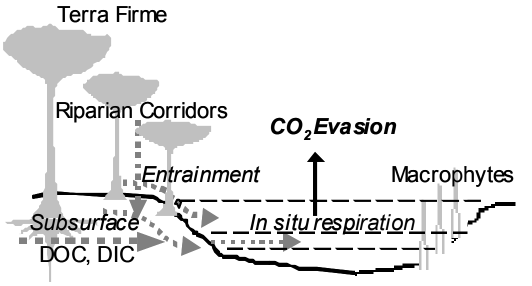

Fig. 7. Schematic of *processes* to be analyzed by proposed research. Δ = changing water level and redox conditions

Given the realities of Amazon logistics and our requirement to characterize diverse environments, we propose to pursue a nested sampling and modeling strategy. We will focus our sampling on sub- regions that are both representative of the diversity of Amazon environments, and feasible to sample (with collaborators). The fieldwork will be both intensive (more detailed studies on both patterns and processes at a smaller number of sites) and extensive (defining the variability of $p\mathrm{CO}_2$ by different habitat type in more survey mode at a wider variety of sites). The parameters measured are selected explicitly as those necessary to develop and validate the coupled biogeochemistry/hydrology model that will be used for basin-wide extrapolations and ultimately as the basis for a general model to be tested elsewhere Using this combination of techniques, we anticipate being able to quantify the CO_2 fluxes and identification of the mechanisms controlling them in humid tropical forests.

Task 1. Find and Characterize Representative Sampling Environments. We must first finalize site selection and make the logistical arrangements for sampling. For each experimental site (region) we will develop a spatial model of the area (including terrain, soils, drainage networks, and land cover) and incorporate it (nest it) into our existing regional model. For most of the sites under consideration, most relevant data already exist, either in whole or in part (for the latter case, we will augment it as necessary).

For the intensive studies we propose to focus initially on the Ji-Paraná river basin, a tributary of the Rio Madeira that crosses a zone of significant land use change. This basin is not atypical of the forested (and deforested) basins on the lower part of the Brazilian shield. We have an ongoing project based in the city of Ji-Paraná, through the NASA-funded LBA (Large-Scale Biosphere Atmosphere Experiment in the Amazon)-ECO program. This project focuses, in collaboration with several local universities and institutions, on the effects of landuse change on river chemistry, and will provide us significant background information and logistical support for the work proposed here. From here it is also feasible to access other sites in Rondônia, including the Rio Madeira itself. Because we are already set up there, we propose to start experimental work in Year 1, concentrating on the Fazenda Walter (a secured reserve close to the city with both intact forest down to river edge and pasture environments). As we find suitable sites representing different environment types elsewhere, we can expand our experimental base in Years 2 and 3.

We propose to develop a network for the extensive sampling in stages. Again, this work is necessary to characterize $p\mathrm{CO}_2$ distributions in multiple regions (without necessarily doing more detailed experimental work). Our target sites are summarized in Fig. 8. We intend to make final selections as soon as possible in Year 1, and then start sampling in the latter part of Year 1 or Year 2 (depending on logistics). For each region, we will adopt a "network" sampling strategy, based on the protocol we currently use for the Ji-Paraná, whereby the primary stream is sampled upstream to downstream, together with the progressively smaller affluents flowing into it (Ballester et al. in review).

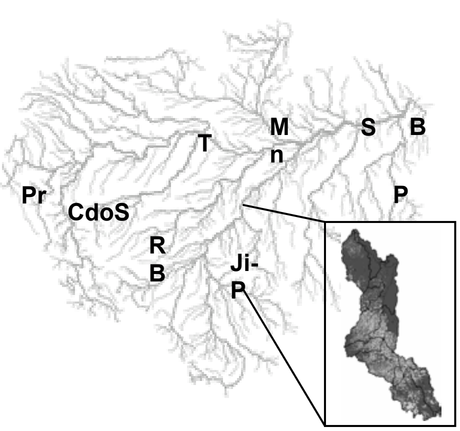

Fig. 8. Research sites (identified by nearest cities, potential facilities). The "intensive" site is Ji-Paraná (Ji-P, blow-up, light area is deforestation). Potential extensive sites: very elevated $p\mathrm{CO}_2$ rivers of the western Amazon - Rio Branco (RB, upper Rio Purús) and Cruzeiro do Sul (CdoS, upper Rio Juruá), Tefé (T, lower Japurá draining remote northwest sector and Juruá, extensive floodplains, Mamiraua research station). Black water rivers with a large area, but poorly-constrained $p\mathrm{CO}_2$ - Manaus (Mn, INPA), Large, poorly-characterized "clear water" rivers Tapajós, Xingú, Tocantins draining both forest and savannas of eastern Amazônia - Santarém and Palmas (S,P, -, LBA sites at Caxiuna, Bananal). Heavily impacted and drier eastern Amazon at Belém (B, LBA at Paragominas, others), lower $p\mathrm{CO}_2$ of more upland areas of Andean regions (Pr, colleagues in Lima, elsewhere).

Task 2. Determine Distributions of $p\mathrm{CO}_2$. We propose to conduct a field-sampling program of $p\mathrm{CO}_2$ and support measurements (dissolved O_2, routine chemistry) that resolves both spatial and temporal variability in the river system at our intensive and at our extensive sites. Such a $p\mathrm{CO}_2$ survey will provide the first order estimate, when combined with the CO_2 gas transfer rate measurements discussed below, of the CO_2 evasion rate for the basin and be used to validate model predictions. Downstream DIC trends provide insight into the effect of respiration and gas exchange of the carbon budget.

We propose to conduct two levels of sampling (recognizing practical constraints on access to specific sampling sites). The first is to characterize broader seasonal patterns on a synoptic basis by sampling at set intervals over a two-year time span covering the hydrograph. Our target is monthly transects, recognizing that at some sites we may not be able to do better than every several months, while at others even weekly may be feasible. We will also institute event sampling at intensive sites, to characterize the rapid response of streams to storm events (which we suspect to be the major force mobilizing terrestrial materials into the streams). An advantage of $p\mathrm{CO}_2$ surveys is that the sampling itself is easy (specifically not requiring the laborious depth-integrated sampling required for quantitative sampling of particulates), and the equipment is straightforward. We anticipate collecting literally hundreds of samples from different environments. In addition to concentration measurements, we will preserve on the order of several hundred samples for $\delta^{13}C$ analysis and about 20 samples per year for $\Delta^{14}C$ of DIC, DOC, and POM (Task 6).

Accurate analysis is critical for pCO_2. Given that the entire CO_2 system can be characterized by measurement of any two of its components (Stumm and Morgan, 1996), these variables are frequently calculated from other system variables such as pH and alkalinity as we have done previously (Devol et al., 1995). However, although alkalinity samples are easily stored for precise lab measurement, field measurements of pH are often not precise enough for accurate calculation of pCO_2 and DIC. Differences of 0.05 pH units can cause 10-20% errors in the calculation of pCO_2. In contrast both pCO_2 and DIC can be determined directly with an infrared gas analyzer (IRGA) (Cole and Caraco 1998). We will evaluate which combinations of measurements are most appropriate for which sampling situations. For example, in instances where survey samples are to be collected, poisoned and stored for analysis back at the laboratory the best combination of measurements might be alkalinity and DIC. On the other hand, for experiments where instrumentation is available in the field the best combination might be pCO_2 and DIC. The measurement of pH will be done by electrode with a meter capable of 0.005 pH unit resolution and alkalinity will be done by micro-Gran titration, as described in Devol et al. (1995). We will employ an Infrared Gas Analyzer (IRGA) for both the pCO_2 and DIC measurements. pCO_2 will be measured by a head space equilibration as described by Cole and Caraco (1998), with the extracted CO_2 determined in the field with a battery-operated Li-Cor LI-800 IRGA.

We will use two methods to determine oxygen concentration. For routine measurement of oxygen concentration in samples from stream waters we will use polarographic oxygen electrode techniques. This is the technique we have used to make most of our previous dissolved oxygen measurements and it has proved sufficiently precise to estimate the degree of disequilibrium in most waters. However, at times there will be a need for more accurate dissolved oxygen measurement. In these instances we will use a scaled down version of the standard Winkler titration. Samples will be taken more selectively for DOC, basic nutrients, and isotopes.

Task 3. Gas Exchange Rates. A significant amount of the error in our overall assessment of evasion was derived from uncertainties in computing the actual gas exchange rates. While the problem of gas exchange has been recognized literally for decades, it is still not resolved. Gas fluxes between surface waters and the overlying atmosphere can be calculated from: (1) saturation gradients such as Flux = $K(C_{sat}-C)$, where K is an exchange coefficient, C_{sat} is the atmospheric equilibrium concentration, and C is the measured aqueous concentration, (2) measurement of gas concentration change over time in "domes" free-floating on water surface (Devol, et al., 1990; Bartlett et al.1990), (3) purposeful tracer addition (e.g., SF_6 and ^3He, Clark et al., 1996) or from 4) eddy correlation studies (McIntyre et al. 2001)

Given the importance of the exchange coefficient, we propose to further evaluate gas exchange models for the different environments we are dealing with, from the flowing waters of the big rivers to streams to floodplains. We will focus on the saturation gradient model, continue to make measurements with domes, and initiate purposeful tracers. We will not pursue the eddy correlation approach (due in part to expense and logistics). For these experiments we will target a spectrum of rivers with different hydraulic characteristics, width, depth and velocity in order to be able to extrapolate across the range of rivers in the basin. This work will be done primarily at the Ji-Paraná site (with its range of river types and ready access), and elsewhere as appropriate.

For lakes and other quiescent waters there are a number of well-established relationships between wind speed and the gas exchange coefficient (MacIntyre et al., 1995; Wanninkhof and McGillis, 1998) or surface renewal rates (MacIntyre et al., 2001; Soloviev and Schuessel, 1994). We will couple the predicted gas exchange rate with measured CO_2 gas gradients to calculate CO_2

fluxes. In flowing waters, we will take two approaches to estimate CO_2 gas fluxes. First, we will estimate gas exchange from a reach mass balance of O_2 and CO_2, as we have for the mainchannel of the Amazon River (Devol et al., 1987). This will require us to measure the transport into and out of the reach and the respiration rate within the reach. Second, under low wind conditions where the flowing water surface is smooth we will measure gas fluxes using the "floating dome" approach that we utilized previously for estimating O_2, CO_2 and CH_4 fluxes. We anticipate doing this at least quarterly over one hydrologic year (or more, if results are inconclusive).

In order to get an independent estimate of gas exchange and verify the dome experiments, we will also conduct dual tracer experiments. Previous dual tracer experiments have used SF_6 and ^3He (Clark et al., 1994, 1996) SF_6 is easily determined by gas chromatography, however ^3He is expensive, difficult to sample and requires a special mass spectrometer to analyze. Consequently, we will use SF_6 and an alternative tracer. For the second tracer we will evaluate H_2, CO, (we currently have the analytical capability for these) or a dye such as rhodamine or fluorocene. These experiments will be done on an experimental basis concurrently with the dome measurements, though probably less frequently.

Task 4. Evaluation of Source Strength of Terrestrial and River Margin Organic Matter and CO_2. To evaluate the relative source strengths and characteristics of terrestrial organic matter and CO_2 potentially fueling evasion, we propose a strategy focusing of focusing on experiments at the intensive sites, starting with the Ji-Paraná sites. We will also make take samples at the extensive sites that already have most of the infrastructure in place (Manaus, Santarém).

To evaluate the role of groundwater export it will be necessary to account for the forms of carbon occurring in oxic and anoxic groundwater and streams. We will sample DOC and CO_2 in ground water and the soil environments across transitions from uplands into the riparian zone and streams. We will collect the groundwater moving into the streams with PVC piezometers installed in the holes drilled by hand augers or by wells. Piezometers will be slotted over their lower meter. Soil water from upper horizons will be collected in both tension porous cup and zero-tension lysimeters on selected profiles. At well sites, we will collect soil gas samples using tubes installed in the walls (after Davidson and Trumbore 1995). Alternatively we will open an auger hole to the depth of the dry season water table, insert L-shaped tubes a few centimeters into the side of the hole at various depths with their tops extending to the surface, and then backfill the hole. Gases in solution from water samples collected from the saturated zone will be preserved following Davidson et al. 1988). We anticipate establishing 3-5 sites at our Ji-Paraná base site, and tracking it over the course of a hydrologic cycle, following initial setup. By the second year of the work we intend to initiate work at several other sites which present contrasting conditions to the Ji-Paraná; in particular the Rio Negro (with colleagues at INPA). In addition to being potentially important carbon forms, VOAs and methane should be useful indicators of *in situ* anoxic conditions and tracers for DOM components that are highly reactive once they reach oxic conditions in stream corridors. The NH_4^{+}/NO_3^{-} ratio also could be similarly used as an indicator of redox history. The O_2 content of groundwaters should be measured as an indicator of the extent of aerobic respiration that has occurred since percolating precipitation lost active contact with the atmosphere. The overall chemical parameters to be measured are discussed in Task 6. To approximate through-flow, the discharge of the local stream will be monitored, and, ultimately, modeled with the hydrology model (below).

A more problematic but potentially important source of organic matter is surface litter entrained by rising waters. A maximum estimate of the amount of material available is from studies of litterfall. But we need to know not so much the litterfall, but how much of it is exported by streams particularly by the very flashy, sudden downpours characteristic of the region. These events cause a sudden rising of waters in the "baixos" (low channel corridors) that can sweep the corridor clean of litter (pers. observation). We will conduct simple litter entrainment studies at several of the intensive sites, near to the groundwater sampling sites. We will start in Ji-Paraná, in Year 1, and then add at least Manaus (where we will attempt to select sites at locations of previous litterfall studies conducted by researchers of INPA) and hopefully Santarém and Tefé in Year 2 (to provide a diversity of habitat types). The studies will entail inventorying the stock of litter along transects from stream edge up the bank to *Terra Firme*. Each study will start at low water at the end of the dry season, and track the stock over a hydrologic cycle. Sampling frequency will focus on before/after storm events, when sheet wash or direct entrainment is most likely to carry away litter. To complement the before/after experiments, we will attempt to use a fine mesh net across a stream channel and trap material carried during a storm. Samples will be dried, weighed, and aliquots assessed for carbon composition (Task 6). To integrate across regions, we will develop empirical relations of litter yield as a function of drainage density (from GIS river networks) and the hydrology model. Fine sediments are also a potential source, but in the very low gradient lower basin where most of our work is being carried out, erosion is minimal. Therefore we will treat sediments directly as POM transported in particularly the larger rivers with Andean origin, where the vast majority of the sediment is derived.

While we believe that uplands are the predominant source of CO_2, the role of herbaceous macrophytes (floating plants which start out rooted, cover large expanses of floodplain waters, and exhibit a seasonal succession in synchrony with the annual flooding cycle) cannot be discounted, particularly in regions dominated by extensive floodplains. They can fix atmospheric CO_2 directly, and return some of that production to water via decomposition and also potentially through root respiration (Hamilton et al. 1995). A key aspect of macrophytes is that they are C4 plants, and are isotopically enriched ($\delta^{13}C$) relative to most of *Terra Firme* plants (except for C4 grasses in the savannas of the eastern Amazon). This $\delta^{13}C$ signature provides us with a robust tracer of macrophyte influence. It is beyond the scope of this project to measure directly the production, decomposition, and respiration of macrophytes. Rather, we propose to develop simple spatial model of macrophyte distributions (primarily from the literature, augmented by remote sensing; e.g. Wilhelm et al. in review), and estimate the potential for organic matter from decomposition and of respiration (Melack and Forsberg 2001; Piedade et al. 2001). We will particularly focus on the potential for overall riverine pCO_2 and DIC to be influenced by a C4 signal. We will work with colleagues W. Junk (Max Plank) and M. Piedade (INPA) on this problem, possibly including modest fieldwork on the isotopic signals, if necessary.

Task 5. In situ respiration. The remineralization of organic carbon within streams and rivers is one of the key processes controlling CO_2 evasion from aquatic systems to the atmosphere. As such, we will need to measure rates of *in situ* heterotrophic respiration extensively in conjunction with our routine sampling of pCO_2. These rates will be determined from small-bottle incubations, as we have done previously, by measuring the difference in oxygen concentration between a triplicate set of poisoned controls and a triplicate set of unpoisoned samples (Devol et al., 1995). All incubations will be conducted in the dark at near *in situ* temperature for 6 to 10 hr. We intend to make these measurements at several sites on each of the pCO_2 transects.

In addition, a more intensive suite of large-bottle incubation experiments will be conducted to study the controls on respiration rates within stream and rivers. This work has been recently funded in part via a 15-month post-doctoral research fellowship for Anthony Aufdenkampe (a joint grant from NSF International Programs and NSF Division of Environmental Biology). We propose to collaborate with Dr. Aufdenkampe. These large-bottle incubations are specifically designed to constrain the biologically mediated fluxes within ROMBUS. Previous studies and analysis of data therein clearly suggests that bioavailability is a function of both size class (Amon and Benner 1996a,b; Volk et al. 1997) and elemental (thus biochemical) composition (Vallino et al. 1996; Sun et al. 1997; Volk et al. 1997; Hopkinson et al. 1998). For each sampling, three sets of large-bottles will be incubated in order to differentiate first-order rate constants for CPOM, FPOM, VHMW DOM, HMW DOM and LMW DOM. At the beginning and end of each incubation, we will analyze dissolved O_2, DIC, CH_4, NH_4, NO_2, NO_3, and PO_4 – in addition to the concentration and elemental composition of each organic size fraction. Making all of these measurements concurrently provides an extremely powerful set of data with which to evaluate the controls on the processing of organic matter in rivers.

To test our hypothesis that the respiration is derived primarily from allochthonous (external) organic matter, we need to determine the potential role of organic carbon photosynthetically fixed in or near the rivers (e.g., aquatic grasses) as a fuel for respiration and thus CO_2 evasion. That is, we need a method to identify the importance of *in situ* photosynthesis. We have employed the $^{18}O/^{16}O$ of dissolved oxygen as a unique tracer of the photosynthesis in Amazon rivers and lakes (Quay et al., 1995). The approach relies on the observation that the $\delta^{18}O$ of the O_2 photosynthetically produced is derived from water with a $\delta^{18}O$ (-5 ‰) that is very different from O_2 derived from air-water gas exchange ($\delta^{18}O$=+23 ‰). Combining measurements of the $\delta^{18}O$ and saturation level of dissolved O_2 yields estimates of the respiration/photosynthesis ratio (Quay et al., 1995). Our previous results indicates that rivers in the Amazon basin have a R/P = 2-4 and thus are strongly heterotrophic. We plan to perform a limited survey of small streams and floodplain waters for $\delta^{18}O$ of dissolved O_2 since our previous river measurements are limited to the mainchannel of the Amazon River and its primary tributaries.

Task 6. Characterize the Isotopic and Organic Composition of Dissolved Organic and Inorganic Carbon. Our ROMBUS model framework predicts a set of parameters that characterize the organic and inorganic carbon pools in rivers (as discussed above). We propose to measure the concentrations and elemental and isotopic compositions of the key carbon pools represented in the model on the samples collected under Tasks 2-5. We will utilize a set of tracer techniques to characterize materials of both river samples and to samples extracted from terrestrial sources. Combining measurements of both stable and radio- carbon isotopes provides particularly powerful constraints on the processes in question. Proportions of carbon fixed in forests versus grassy floodplains can be distinguished with $\delta^{13}C$. $\Delta^{14}C$ measurements yield characteristic turnover times for carbon pools, and in the case of CO_2, a further constraint on its likely OM source. Therefore, we propose to measure extensively the $\delta^{13}C$ and $\Delta^{14}C$ of each of the primary organic carbon size fractions and also of the dissolved inorganic carbon. We have extensive experience in making both $\delta^{13}C$ (at both CENA and the UW) and $\Delta^{14}C$ measurements of all these sample types in the Amazon (Hedges et al., 1986; Quay et al., 1992), and are now currently expanding our analytical capabilities via the mini-grant with CAMS.

The C and N content of suspended CPOM and FPOM will be measured via elemental CHN analyzers. Total DOC will be quantified via high-temperature combustion DOC analyzers, and DON via high intensity UV-oxidation (Aufdenkampe et al., in press). DOC size fractions will also be quantified by measuring DOC concentrations in the permeate of 1 kD and 30 kD molecular weight cutoff Centricon units (Millipore). These disposable ultrafiltration units only require 2-15 mL of sample and allow for the processing of 24 samples simultaneously in a centrifuge. Quantification of volatile organic acids (using the HPLC method of Albert and Martens (1997)), dissolved methane, nitrate and ammonium – all ROMBUS state variables – will provide proxies of *in situ* anoxic conditions and tracers for DOM components that are highly reactive once they reach oxic conditions in stream corridors. These measurements, combined with DIC, alkalinity, and dissolved O_2 will allow for the budgeting of processes that occur in waters no-longer exchanging with the atmosphere.

Task 7. Determine Seasonality of Inundation and Terrestrial Runoff. To complete the analysis of the overall carbon pathways, from terrestrial source to atmospheric evasion, we need to know the seasonality of inundation and the flow paths that produce it by segment of the river networks. There are several issues to resolve. River discharge observations from the national hydrological agency (Agência Nacional de Energia Elétrica – ANEEL) are very sparse, particularly in smaller rivers. We will augment these with our own discharge measurements, using both current meters and acoustic Doppler current profiling. For surface area, river systems (channel and floodplain) wider than about 100 m are quite readily detectable by remote sensing techniques (Siqueira et al. 2000; Sipple et al. 1998), but smaller systems are much more difficult to assess on a regional basis. We propose to use hydrological modeling validated locally to describe water flow across the river networks, then use those estimates to drive a surface area model. It should be noted that our requirements are not for state-of-the-art hydrology or precise flood-forecasting *per se*, but for a regional view of water movement that can be related to biogeochemical dynamics and CO_2 evasion.

The primary model we will use will be the VIC model we already have set up for the Amazon (above). If necessary to resolve finer-scale properties, we will be prepared to implement the full spatially distributed hydrological model DHSVM (Wigmosta et al. 1994) that we are using in the Pacific Northwest. The direct transfer of water and materials from *Terra Firme* to river systems will be implemented by modifying the VIC sub-grid parameterization scheme. We propose to partition each cell (which are sub-divided to handle sub-grid heterogeneity) into linked elements according to relative topography and dominant direction of flow towards streams. That is, each model cell will be sub-divided into distinct *Terra Firme*, riparian, and stream elements, and these elements will be connected through lateral surface and subsurface transport of water and materials. Lateral water movement may contribute to the saturation of the riparian element from below, influencing the redox state of this environment. Each terrestrial element will be composed of three to five soil horizons. Rates of flow between elements will be parameterized based on hillslope elevation gradient and soil transmissivity. ANEEL data will be used for validation of hydrological fluxes across the basins. It will operate at a daily time step and its temporal dynamics will be forced by climate and biophysical fields from available datasets derived from ground observations and remote sensing (through LBA). The river routing scheme used by VIC (Lohmann et al. 1998) will be modified to include inundation and exchanges with floodplains (e.g., Garbrecht and Brunner 1991); such interactions will be parameterized with floodplain measurements from JERS-1 and, if available, through a digital elevation model from the Shuttle Radar Topography Mission, Gesch et al. 1999). To determine the areal extent of larger scale inundation we will continue to explore the use of passive and active sensors with colleagues at UC Santa Barbara and the Jet Propulsion Laboratory, through LBA. For smaller streams, we will use higher resolution sensors where possible, but cloudiness is a significant problem for systematic work in these regions. Hence we will also incorporate field surveys, and further develop the geomorphic index approach used by Richey et al. (in review).

Task 8. Integration of Observations and Modeling in Computing Downstream Fluxes. In the previous tasks we assess the size and characteristics of the organic and dissolved inorganic carbon sources that could potentially be driving CO_2 evasion over a range of hydrologic regimes. We now need to integrate this information and compute the downstream turnover (“spiraling”) of organic matter and its effect on evasion. We propose to couple the ROMBUS with VIC models, following the advection-reaction structure of Richey and Victoria (1996). This proposed model will yield a spatially-explicit means to extrapolate our site specific measurements of CO_2 evasion and organic matter to basin-wide scales. Our objective is to quantitatively describe the downstream input and turnover of organic matter and CO_2 from the land to the river system and its eventual fate either via evasion to the atmosphere or export to the ocean.

In order to deal with increased uncertainty about the system as river size decreases, the river system will be subdivided into three scales: the smallest streams at sub-grid scale receiving direct input from the land, medium-scale streams handled in a generalized fashion, and larger-scale rivers (drainage areas of ~ 100 km^2 and larger) treated explicitly. The focus of analysis will lie on the larger-scale rivers, but this hierarchical framework can be modified with finer resolution data. More realistic surface water routing and geochemical transport-reaction will be implemented only at the largest scale, and only here will the models be validated with data from specific rivers; model output from low-order streams at sub-grid scales will be evaluated primarily as regional ensembles. This scheme is a type of sub-scale parameterization from a river perspective.

In order to resolve the influence of different soil moisture regimes and flowpaths, ROMBUS will operate at each VIC soil horizon, in each VIC sub-grid landscape element. We will track a substantial number of biogeochemical species in each spatial compartment, including concentrations of dissolved and particulate size fractions of OM, concentrations of DIC and CO_2, the age (via $\Delta^{14}C$) of each carbon pool, its $\delta^{13}C$ and C/N, and O_2. The coupled models will predict concentrations, isotopic compositions, and fluxes of these carbon species in terrestrial and riverine environments. Redox conditions will be estimated directly via O_2 concentrations.

Comparison of model output against river observations will allow us to validate the coupled models and to improve the parameterizations. This will enable us to use the model for basin-wide extrapolations and estimate the total export of organic matter and CO_2 from *Terra Firme* to the river system and total CO_2 evasion from open waters. We have in hand an exploratory set of measurements from the Ji-Paraná sub basin (where we emphasized observations across contrasting catchments and in a longitudinal transect along the Ji-Paraná mainstem) that can be used for initial validation purposes.. This trial validation will serve to streamline the sample collection and analysis methods and develop relatively simple methods to maximize the number of measurements.

The final part of the quantitative assessment of evasion is to evaluate it relative to carbon sequestration by the forest (to put the relative magnitude into context). The sequestration and deforestation work itself is being done elsewhere (by the LBA project). Hence the only requirement here is to obtain those results. Similarly, river export from the basin has already been done.

C.4. Execution of the Proposed Work

Extensive work is proposed here, in geographically very disparate locations. What makes the project feasible is that it is a truly cooperative effort among institutions that are based in these regions and have extensive experience and logistic and personnel support. We will be able to take advantage of the infrastructure and capabilities of the NASA-funded LBA project in the Amazon. Of major significance is that Brazil, through CENA, will commit resources equivalent to that requested here from NSF. Thus the work force available is essentially double the investment that is requested from NSF.

Institutional Arrangements. CAMREX was conceived originally and continues to be a fully collaborative project between the UW and CENA. The project will function in Brazil under agreements between the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq) of Brazil and NSF. The Principal Investigators of the project will be Jeffrey Richey (UW, responsible to NSF) and Reynaldo Victoria (Director, CENA, responsible to Brazilian authorities). This collaboration will benefit each institution and the regions they represent. A letter from Dr. Victoria is attached under Facilities (Section H).

Timing and Logistics. We have proposed a three-year project (Table 1). While ambitious, we believe that we have sufficient experience and are well enough set up to carry it off, from initial setup to final synthesis. For the time sequencing of the work, we have proposed a starting date of September 2002. This timing coincides with the minimum low water of the dry season, and constitutes a perfect timing to launch field activities. The basic working personnel model will be

Table 1. Time sequencing of individual tasks (T). Site selection and setup (SS), set-up of collections and experiments, sample analysis, setup and running of models (continuous updating of models with field results). JiP is Ji-Paraná , ExS is Extensive sites, UW: JR = Richey, RV = Reynaldo Victoria, PQ=Paul Quay, AD = Allan Devol, JH= John Hedges; CENA: AK = Alex Krusche, VB = Victoria Ballester, MB = Marcelo Bernandes, AA = Anthony Aufdenkempe.

T	Sep'02	Jan'03	May'03	Sep'03	Jan'04	May'04	Sep'04	Jan'05	May'05	Personnel
T1	--JiP SS--	-------------------- Site maintenance --------------------------								JR, RV
		----- ExSt SS -----		-------------------- Site maintenance ----------						AK,VB
	---------------------------- GIS Spatial Modeling --									
T2	---------------------------- Ji -P Sampling --------------------------------									JR,AD
		-------------------- Extensive Sampling------------------------								AK,MB
T3		------------------ JiP, ExS Domes and Budgets -------------								AD,AK
			--------JiP SF_6 ----------							
T4		--- JiP install ---		-----------------JiP Experiments---------------------						JR,MB
			---ExS install ----- Collections ------------							
T5	-------------------------Small bottles: Jip--ExS -------------------------------									AK, AD
	-----------Big bottles (on AA post-doc)----------									AA
				---------------------$\delta^{18}O$------------------						PQ
T6		-------------------------------------- Analyses ---								AK,JH,
				($\delta^{13}C$: CENA, $\delta^{18}O$, $\Delta^{14}C$: UW)						PQ,MB
T7		-------------- Flow Measurements by Site -------------------------------								JR, AK
	------------------------------------ Modeling --									
T8	----- Setup----------------- Assimilation of Data ------------------- Validation -----------------									JR,PQ,
	------------------------------------ Overall Data System Execution ------------------------------									VB

to have graduate students (and local undergraduate students) working on the respective tasks, with the supervision and participation of (at least) one of the senior personnel. The extensive sites in particular will depend on students recruited from the respective region. Routine field samples (pCO_2 and supporting chemical measurements) will be analyzed in the field, or at near-by base labs. The more complex isotope and biomarker samples will be analyzed at both CENA and the UW, by professional staff (and by the students as they become sufficiently trained).

Education and Human Resources. CAMREX has and will continue to train and depend on students with a broad geographic basis. We have an extensive record of not only U.S. students but of supporting Brazilian students. The process will continue here in two primary ways. As noted above, we will involve students not only at the UW and CENA, but also from Amazonian institutions. We have been doing this with the LBA project in Ji-Paraná, with considerable success (including short courses). In this web-enabled world, results and word of such a project circulates rapidly. We maintain an Amazon (and overall "Rivers Research Group") website, which leads not only to frequent "hits" but frequent requests for "information about the Amazon." We will devote effort to upgrading the site, and making it as informative as possible. Part of the upgrade will be to use our PRISM technology to make sub-set versions of "virtual" river basins available to the classroom (including our own) and to the public.

Extension of Proposed Work to Society. If proven true, the flux of CO_2 via riverine systems will impact considerations of the global carbon cycle. We believe that this program addresses not only key multi-scaled aspects of river basins, but it has the potentially unique capability to address changes in river response due to anthropogenic impacts in globally important river ecosystems. CAMREX has led to several projects of immediate societal application in Brazil (the PiraCENA project), Southeast Asia (SEA/BASINS, which has a major resource planning and training role), and the Puget Sound region of the Pacific Northwest (PRISM). The investment in basic research made here is being leveraged directly into assessments of critical water resources elsewhere in the world.

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F. Budget Justification

The proposed budget is phased over three years. As shown under project management (C.4), we intend to ramp up and start sampling in Year 1 with (1) purchase of equipment and supplies, (2) fine-tuning and revamping of current models, and (3) analysis of samples on hand and initiate field collections. Year 2 will focus on fieldwork and model development. Year 3 will emphasize finishing up the fieldwork and data synthesis.

The proposed work is very challenging, both in its intellectual scope and its logistic realities. To be successful within the relatively short time horizon of 3 years, the work must be done efficiently and on time. This requires a very experienced team, while providing ample training opportunities for students. We propose to involve the senior UW faculty team that has been the UW core of CAMREX, together with their counterparts at CENA (at no cost to NSF). We propose the involvement of staff, to insure that the required samples are acquired and analyzed promptly. We propose two new graduate students at the UW (for NSF funding), to work with their Brazilian student colleagues at CENA and in the Amazon.

We request salaries for:

Senior Personnel. The UW does not cover "research" for its faculty; hence for grant purposes faculty must be considered as "soft money" and request support proportionate to their efforts. Jeffrey Richey (P.I., 3 mo/yr) will be responsible for overall project supervision and coordination, modeling and synthesis. He will lead the site selection team, and will supervise the set up of both the intensive and extensive sites. Allan Devol (2 mo/yr) will be responsible (along with Richey) for the field-sampling program, interpretation of results and model development. He will lead the gas evasion measurements (domes and purposeful injections). John Hedges (Co-I, 1 mo/y for 1st 2 years, then 2 mo/y for Year 3) will be responsible for the overall efforts for organic carbon analyses and interpretation. Paul Quay (Co-I, 1 mo/y for 1st 2 years, then 2 mo/y for Year 3) will responsible for the overall efforts for isotope analyses and interpretation, and for assisting in the modeling. The second month for Quay and Hedges in Year 3 is to provide time to devote to data analysis and writing. While no funds are requested here, CENA faculty will participate with each UW faculty. Reynaldo Victoria will work with Richey on project supervision. Victoria Ballester will lead the work on GIS modeling. Alex Krusche and Marcelo Bernandes will work with Richey and Devol on fieldwork planning and execution, and with Hedges and Quay on chemical analyses.

Professional staff. In a project with extensive remote fieldwork and logistics, staff support is important in making sure key tasks are accomplished. We request support for (1) a field logistics coordinator, to spend full time in Brazil, (2) a data and spatial modeling specialist who will be responsible for the development and maintenance of the spatial data bases, acquisition and processing of images, and preparing data for input to models, and running the models (with Richey), (3) a chemical support, covering organic geochemistry and isotopes.

Graduate students. We request NSF support for 2 (new) graduate students at the UW. We anticipate that one student will focus on organic matter/isotope dynamics, and the other on respiration and gas fluxes. Both will participate in modeling. The NSF-supported students will be augmented by students at CENA and at Amazonian institutions, supported by Brazilian funding.

Undergraduate students. We will involve undergraduate students in laboratory analysis and computer coding (a successful program we have worked out with the Dept. of Computer Sciences at the UW).

We request support for:

Equipment. We request (1) 2 portable infrared gas analyzers (equivalent to the Licor-800), for the pCO_2 analyses and (2) an ECD gas chromatograph, for measuring SF_6 for the evasion experiments.

Supplies and Materials. The fieldwork (and subsequent lab work) will require routine supplies of glassware, chemicals, filters, etc. We will require pH and O_2 meters and computers. We will establish field labs at the different sites, and support local participation. Our past experience in the Amazon has shown that the rate of consumption of supplies, and getting supplies to and from sites is high.

Travel to the field sites and to meetings is requested. Foreign travel covers 3 trips to Brazil in Year 1 and 4 trips per year during Years 2 and 3. Two trips per year to domestic meetings are included.

Analysis of isotopes are budgeted at $200 each. A budget in this first year is requested because we have samples on hand that we will analyze first.

Field expenses ($25,000/yr for year 1, $30,000 for the more intensive years 2 and 3) is requested to cover boat charters in the field (including personnel, local expenses, etc). This value is based on our extensive experience with the costs of fieldwork in the Amazon.

Other Contractual services. Publication, copying, shipping and other miscellaneous costs

Indirect costs. A split between on- and off campus rates is requested on the basis of how much time personnel are in the field.

The NSF budget will be complemented by two other sources. As noted elsewhere, Dr. Victoria (Director, CENA) has pledged support from Brazilian sources equivalent to what is being requested here from NSF. As participants in LBA, we will compete for NASA funding for the second phase of LBA. If successful we will be able to draw on considerable logistical and personnel support.

H. Facilities

The proposed analyses will be conducted at field sites and at laboratories at the University of Washington, and the Centro de Energia Nuclear na Agricultura (CENA) in Piracicaba, Brazil.

The UW Stable Isotope Laboratory has two Finnigan isotope ratio mass spectrometers, a MAT 251 and DeltaXL, the latter of which is about one year old. The MAT 251 has an automated multisample inlet device that allows 24 gas samples to be admitted sequentially to the mass spec. The MAT 251 has three collectors for masses 32, 33, and 34 for simultaneous measurement of the $^{17}O/^{16}O$ and $^{18}O/^{16}O$. The DeltaXL has an automated on-line Elemental Analyzer sample preparation system that measures the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ (and C/N) of particulate organic material. The DeltaXL also has an HP 6590 GC and Finnigan in-line combustion device (GC/C III) for compound-specific $^{13}C/^{12}C$ and $^{15}N/^{14}N$ analysis by the GC/C/IRMS method allowing isotopic measurements on picomolar size samples. The DeltaXL has a Finnigan in-line pyrolysis device coupled with the HP 6590 GC for measuring the D/H on individual compounds. The Stable Isotope Lab has high vacuum sample preparation lines for the following measurements: the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ of dissolved O_2, the $^{13}C/^{12}C$ of atmospheric CO_2, CO and CH_4, dissolved inorganic carbon (DIC) in seawater and particulate organic material, the D/H of atmospheric H_2 and CH_4 and particulate organic material, and the $^{15}N/^{14}N$ of NO_3 and particulate organic material. We have two GCs: one for the measurement of ambient atmospheric concentrations of CH_4, and CO_2 and the other for ambient atmospheric H_2 and CO measurements. There is a combustion furnace, drying oven, and glass blowing facilities for repair of the sample preparation lines. We moved into brand new laboratory space (~2200 sq. ft.) during Spring 2000. Importantly for the work proposed here, the new UW facility is housed in a "^{14}C-free building. No enriched ^{14}C studies are allowed in the building and the Stable isotope Lab is routinely checked by AMS swipes to verify that no contamination has occurred. The UW facility operates a Windows 2000/UNIX (NTFS) network with ~300 Gb of storage, including three Sun workstations and multiple PCs.

CENA has new laboratories. They are equipped with Dionex LC and HPLC modules, composed of GP40 and GS50 gradient pumps, EG40 eluent generator, ED40 electrochemical detector, UVD340s UV-Visible diode array detector and AS50 Autosampler. Interchangeable configurations allow analyses of anions (inorganic and organic) and cations, amino-acids, carbohydrates, pigments and other organic compounds. Also installed is a Shimadzu GC17A gas chromatograph, with autoinjector and FID and ECD detectors, for the analysis of gases (CO_2, N_2O and CH_4) and organic compounds (lignins). The Mass spectrometry laboratory has a Finnigan Delta E spectrometer, dedicated to the analysis of deuterium, a Finnigan DeltaPlus spectrometer, with interfaces for the elemental analyzer (to measure C and N isotope ratios in plants and soils) and the gas bench (to measure C and N isotope rations in gases) and a sencond Finnigan DeltaPlus spectrometer with interfaces for the elemental analyzer and the PreCon system, which allows preconcentration of gases for isotope measurements. Also installed are a Perkin Elmer AS700 Atomic Absorption spectrometer, with graphite furnace and a Shimadzu TOC5000A organic carbon analyzer. The CENA facility operates a Windows 2000/UNIX network. CENA is also extensively equipped for field research in the Amazon. They have a large, long-range 4-wheel drive expedition vehicle, equipped with field kits (Niskin bottles, sounders, etc), including trailer and boat(s). They have an acoustic Doppler current profiler (ADCP) for making current velocity profiles.

Auxiliary laboratories will be augmented in Porto Velho, Ji-Paraná, and Manaus. Through our LBA work, we have access to labs at the state universities in Porto Velho and Ji-Paraná, and have worked in collaboration with INPA (Manaus) for many years.

UNIVERSIDADE DE SÃO PAULO
CAMPUS "LUIZ DE QUEIROZ"
Centro de Energia Nuclear na Agricultura

Piracicaba, January 7, 2002.

To: the National Science Foundation.

As the current Director of the Centro de Energia Nuclear na Agricultura (CENA) of the Universidade de São Paulo (USP), I am writing this confirming "letter of support" for the proposal being submitted by the UW and CENA, "Carbon Dioxide Evasion from Fluvial Environments of Amazônia: A Major Sink for Terrestrially Fixed Carbon and Tracer of Ecosystem Processes." The subject of this project is of primary interest to CENA, and is of major interest to Brazil, because of its relevance to not only the land use change issues but to water resources. Because the project is of fundamental interest to our group, we will commit significant CENA resources to the project. This will include (at no cost to NSF):

(1) Commitment of the time of myself and the CENA co-Is, Moreira, Krusche, Ballester, Moraes, Bernardes, Ometto, Martinelli, and technician support, totaling at least 10-12 months/year. All salaries are paid for by the institution. As a prime platform for Education and Training, we will commit student support, based on fellowships to be made available in Brazil.

(2) Commitment of CENA analytical equipment to the project. CENA has extensive capabilities in mass spectrometry (3 mass specs, with two new Delta Plus on order capable of automated analyses for 13C, 15N, and 18O gas, liquid and solid samples). CENA has a major division for routine analytical chemistry, gas and liquid chromatography, including both organic and inorganic analysis.

(3) Commitment of the CENA GIS and Remote Sensing lab. Under V. Ballester, we have developed a lab capable of operating in the ArcInfo and Erdas environment, with hardware and software for remote sensing capable of handling data from various sources.

(4) We already have funds from FAPESP to help support the field activities, including transport between Piracicaba and Rondônia, up to the year 2003.

Overall, resource wise this commitment is similar to what is being requested from NSF by the UW, considering the differences in how salary costs and indirect costs are prorated. CENA is a full and equal partner in this project.

Sincerely,

Prof. Dr. Reynaldo Luiz Victoria
Full Professor – Isotope Ecology
Director – CENA/USP