Proposal Cover Page

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Title: Horizontal and Vertical Fluxes of Carbon in River Corridors of the Amazon Basin

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Abstract

Our proposed research addresses the overall role rivers and periodically inundated environments play in the biogeochemical cycles of the Amazon Basin. Recent evidence suggests that outgassing of CO_2 is of comparable magnitude to the lower estimates of carbon sequestration by forests. We have two primary objectives:

Objective 1. Complete research on the question of landuse change and its consequences for water chemistry in the Ji-Paraná River Basin

Objective 2. Expand research on the fluxes of gases between wetlands and the atmosphere, by testing the working hypothesis 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 and riparian forests to fluvial environments is the primary source of carbon that is eventually respired in rivers and evaded as CO_2 ."

We propose to address our objectives by (1) Conducting fieldwork in characteristic subbasins to complete water chemistry and to obtain an extensive suite of pCO_2 distribution measurements over the hydrologic regime, and to use proven geochemical techniques (gas flux measurements, isotopic tracers, 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) Using a terrestrial source/river transport and reaction model to synthesize and extrapolate the site-specific CO₂ evasion rate measurements to a basin-wide estimate of CO₂ evasion rate. The overall research here is relevant to a series of the LBA-ECO Science questions. The work considers explicitly the effects of changing land use, the relation of surface water chemistry to regional flow patterns, and the role of the extensive wetlands and temporarily inundated or saturated areas in Amazônia.

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Summary of Past Work and Accomplishments

Our LBA Ecology Phase 1 project was: Biogeochemical Dynamics in River Corridors of the Amazon Basin and their Response to Anthropogenic Change (ND-09; joint CD-06). Our perspective was (and continues to be) that the periodically or permanently flooded areas play important roles in the hydrology and biogeochemistry of the Amazon basin, and are particularly subject to changes in land cover and land use. As land cover changes, with concomitant alterations in hydrology and vegetation, significant changes in the partitioning between aqueous and gaseous species are be expected in river corridors. Accordingly, our research objectives for river corridors were to: 1) Establish the geographic and geochemical sources of C, N, and P species, 2) Define the biogeochemical consequences for the gas emissions and water chemistry associated with these species of anthropogenic perturbations against the background of natural environmental variability, and 3) Determine the distance that sediments, nutrients, and organic matter travel downstream before they are taken up, decomposed, temporarily stored, permanently buried or degassed, as mediated by the transport properties of the river system and the reactivity of the materials themselves. Our focus is the mesoscale Ji-Parana River Basin, in the State of Rondônia, Western Amazônia. The basin is important as both a focus of landuse activities in the Amazon, and as a "model" for regional dynamics. Our progress is as follows.

Technical Work

1. Development of Spatial Model of the Ji-parana Basin. We are developing an integrated analysis of the landscape characteristics of the Ji- Paraná river, based on the spatial analysis of various spatial patterns, including soil properties, river network, topography, and land use/cover (Ballester et al in review). This physical template is a GIS-based comprehensive tool to support the understanding of the biogeochemistry of surface waters. We divided the Ji-Paraná river basin into 14 drainage units, organized according to the river network morphology and degree of land use impact. Each sector corresponds to a sampling point where our group is determining river biogeochemistry. To delineate sub basin boundaries of the sampling sites, a 50 meter vertical resolution Digital Elevation Model (DEM) and river network were derived from 1:100000 maps from the Brazilian Institute of Geography and Statistics. Soil units were derived from a 1:500.000 map that was manually digitized. A series of soil profiles derived from the SIGTERON data set are under processing to derive soil property maps. A land use/cover map for 1999 was produced by the digital classification of eight Landsat 7 ETM+ scenes already geocorrected and georeferenced, acquired from the Tropical Rain Forest Information Center (TRFIC) at Michigan State University. A time series of land use and land cover change is under development. To access the spatial distribution of human interference we are also working on the following data sets: roads, settlement projects and legal reserves (national parks and Indian reservations). These data sets were obtained from the Planaflora Project. The geology and geomorphology maps were also obtained from the same source. It is important to point out that these data are available only for this project due to restrictions imposed by the data provider. We are working on the possibility to make these data public domain at least for the Ji-Paraná river basin. We are also working on the demographic and agricultural census data from IBGE. We have already compiled a 20 year data time series. A series of socioeconomic and agricultural indicators were chosen and made spatially-explicit using the county as a study unit. These data are under analysis to develop a socioeconomic and agricultural diagnosis of the study area.

2. Ji-parana Field Transect Measurements. Our fieldwork is based on two sets of transects through the Ji- Paraná basin. The first set involved sampling the main river channel and tributaries, covering the whole basin in expeditions that lasted 20-30 days. The second approach was designed to compare two sub-basins with contrasting land use/cover. For this, we sampled the upper Ji-Parana river at the city of Cacoal and the Urupa river at the city of Ji-Parana both weekly during the rainy season, and monthly during the dry season. A total of 7 expeditions were conducted along the whole basin, providing detailed spatial information. The sub-basin dataset consists of 25 expeditions, focusing on acquiring valuable temporal coverage to facilitate in the fast response to storm runoff events. During the last two years, a total of around 200 days were spent in the field.

In the field, we measured discharge, pH, dissolved oxygen, electrical conductivity and temperature. Respiration rates were calculated from the consumption of dissolved oxygen in bottles incubated in the dark. Within a month from the period of sampling, the concentrations of the anions Cl⁻, SO₄²⁻, NO₃⁻, NO₂⁻ and PO₄³⁻ and cations Na⁺, K⁺, NH₄⁺, Ca²⁺ and Mg²⁺ were determined, along with the concentrations of dissolved inorganic and organic carbon, and suspended sediments were determined gravimetrically. Large volume (100 L) samples were ultrafiltered in the lab to separate the coarse (>63 µm) fine (0.1-63 µm) and ultradissolved (1-100 nm) organic matter. These fractions were analyzed for C and N concentrations and isotopic signatures, and organic matter fractions were further analyzed with the alkaline cupric oxide reaction procedure to geochemically characterize lignin and other biopolymers. Resulting interpretations include Bernandes et al. (in review), Krusche et al (in review), Ballester et al. (in review)

3. Analytical. We have conducted a number of experimental studies designed to aid in our interpretation of field observations. Although over 90% of organic matter (OM) transported by rivers of the Amazon is either sorbed to fine minerals or has remained dissolved, the compositions of these two fractions are quite different. These biochemical and isotopic differences have long been used to infer differences in the sources, degradation and transport of dissolved versus fine particulate OM, which in turn define the carbon cycling characteristics of the watershed. However, because it is known that sorptive exchanges of OM are important between dissolved and particulate phases (Hedges et al. 1997), we asked whether sorptive processes might be masking or enhancing these compositional signatures that are used to infer other processes (diagenesis, transport or source). Our findings were startling. Preferential sorption of certain biomolecules appeared alone to be responsible for all biochemical signatures related to nitrogen (Aufdenkampe et al. 2001) and for stable carbon and nitrogen isotopic signatures (Aufdenkampe et al., in prep). Specific compositional differences between dissolved and fine particulate OM - even in the absence of differences in diagenesis, transport or source – has had a substantial impact on our interpretations of carbon cycling processes. For instance, with this knowledge, we can now confidently conclude that conversion of forest to pasture in the Ji-Parana watershed has already resulted in measurable changes in the composition of organic materials reaching aquatic systems (Bernardes et al., in review).

In an effort to determine the possible influence of burning on the composition of organic matter in rivers, we analyzed samples for the presence of black carbon (BC), in the form of soot and char residues of combustion. We worked to adapt the commonly used cupric oxide oxidation method to the quantification of BC. This technique separates and quantifies certain molecules that may be used as molecular tracers. Using a set of charcoals prepared in the laboratory, we identified a suite of 21 molecules that are yielded by charcoals, but absent from the source wood and a set of potentially interfering samples. We also found these molecules in samples of natural charcoals and several sediment samples. Recently, however, we found another significant source of these molecules that may interfere with their use as molecular tracers for charcoal. Work is continuing to determine the feasibility of this methodology.

In another field-based study, we employed radiocarbon dating techniques to constrain the characteristic turnover times of organic matter fractions within rivers of the Amazon. Samples collected as part of the LBA-funded field campaigns were analyzed at the Center for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratories through a CAMS mini-grant. By showing that the average age of riverine organic and inorganic carbon decreases downstream (Aufdenkampe et al., in prep; Mayorga et al. in prep.), these results have provided firm evidence of the magnitude of carbon flows through rivers to the atmosphere as hypothesized by Richey et al. (in press). These samples (over 100) will dramatically increase the number of Δ^{14} C samples available, with concomitant increase in understanding.

4. In situ Measurement and Analysis of Trace Gas Fluxes. In our original proposal we hypothesized that the role of wetlands in the overall carbon cycle of the Amazon may be very important, but is very underdetermined. Hence we launched two sets of complementary activities. The first was direct trace gas measurements using floating and embedded chambers at a study site on the Urupá River near the confluence with the Ji-Paraná River (K. Balster, thesis in progress). The farm at this site has a wide range of landcover types as well as different land uses. A transect from the river bank to the edge of the water was sampled from late March to early June 2001 during the receding water stage. The 500 gas samples from the 5 flooded forest sites, 2 flooded pasture sites and 7 dry sites are being analyzed for methane and carbon dioxide concentrations. Flasks for isotope analysis were also taken from the sampling sites. Preliminary results suggest methane fluxes are positively correlated with water depth.

5. Analysis of Existing pCO_2 Data and Floodplain Inundation Patterns: Our second activity related to gas fluxes was to assess what the potential role of periodicallyinundated environments may be in the overall basin C cycle by computing the evasion (outgassing) of CO_2 as a function of the seasonality of inundation of both large-scale (>100 m in width, detectable by radar) and small scale (<100 m in width) hydrographic environments (Richey et al, in press). As will be discussed further in the Background section of the proposal, this work has the startling conclusion that outgassing is much greater than previously thought, and may be of comparable magnitude to the lower estimates of sequestration. If so, this will change how we think about land-water coupling in the humid tropics. 6. Model Integration. To provide overall coherence and integration of the sources, transport and fate of carbon, we started the development of the "River Basin Organic Matter and Biogeochemistry Synthesis" model (ROMBUS, 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 a tropical river basin over an annual cycle, when coupled to the hydrologic model. The model partitions the carbon reservoirs within a river into measurable dissolved and particulate organic carbon pools (DOC and POC, respectively; each exhibit distinct dynamics and compositional traits that hold over a very broad range of geological, hydrological and climatic conditions). 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). The ROMBUS design is more consistent with newer initiatives in the soil carbon modeling community. Unique to ROMBUS is the explicit parameterization of organomineral interactions, which are increasingly acknowledged as fundamental to OM stabilization.

Training and Education

1. University Cooperation in Rondonia. We have established cooperation with the Lutheran University (ULBRA) and the Federal University of Rondonia (UNIR) at the city of Ji-Paraná. Groups of students and professors from these universities are being trained in the techniques of field sampling and analysis. Additionally, the students receive the necessary literature and explanations about the biogeochemistry of river basins, and are prepared to enroll in graduation programs. Nei Kavaguichi Leite (UNIR) is an example of this setup. He was trained in the field for a year, and is now a MSc student at CENA. Upon finishing his MSc, he will return to UNIR, where he will be responsible for the new chemistry laboratory, which we are installing there.

2. Students Supported:

- Aufdenkampe, Anthony. Univ. of Washington. Ph.D. USA. The Role of Sorptive Processes in the Organic Carbon and Nitrogen Cycles of the Amazon River Basin.
- Ballester, Maria Victoria Ramos. CENA. Post-doctoral. Chilean (Permanent resident in Brazil). From patterns to process: land use and land cover changes and its effects on the biogeochemistry of surface waters of tropical rivers in western Amazônia (Ji-Paraná, Rondônia)
- Balster, Kellie. Univ. of Washington. Masters. USA. Trace gas emissions from a periodically inundated reach of the Urupa River.
- Bernandes, Marcelo. CENA. Post-doctoral. Brazilian. Organic matter composition of rivers of the Ji-Paraná basin
- Bolson, Marcos Alexandre. UNIR-JP. Undergraduate Intern (iniciação científica). Brazilian. *Carbon dynamics in two rivers of Rondônia with different land use/cove.*
- Bonelle, Nilton. ULBRA-JP, Brazilian, PhD, The biogeochemistry of the Urupá River (Rondônia, Brazil).
- Coburn, Rebekkah. Univ. of Washington and CENA, undergraduate intern at CENA-USP from UW. Canadian. *Land use and Land cover mapping of the Ji-Paraná river basin.*

- Gouveia Neto, Sergio Candido de. UNIR-JP. Undergraduate Intern (iniciação científica). Brazilian. *Temporal variability of the water quality of two rivers of Rondônia with different land use/cover*.
- Hanada, Lais. CENA (Ecologia de Agroecossitemas). Masters. Brazilian. Land use and land cover changes at the agricultural frontier in western Amazônia, the Ji-Paraná River Basin, Rondônia.
- Leite, Nei Kavaguichi. CENA (Centro de Energia Nuclear na Agricultura). MSc. Brazilian. Land use/cover changes in the Ji-Paraná basin and its effects on the river biogeochemistry
- Macedo, Gelson de, ULBRA-JP. PhD. Brazilian. Biogeochemical effects of land use/cover changes at the interface land-water in the Urupá river, Ji-Paraná, RO.
- Marcondes, Renata, CENA (Economics). Undergraduate Thesis. Brazilian. Occupation and land use in the Ji-Paraná River basin (Rondônia): socio-economic and agricultural survey.
- Remington, Sonya. Univ. of Washington. Masters. USA. Carbon transport through the Ji-parana River system, using the VIC hydrology model.
- Toledo, Andre Marcondes, CENA. Ph.D. Brazilian. Environmental diagnosis of the Ji-Paraná river basin, Rondônia.
- Victoria, Daniel de Castro, CENA (Agronomy). Undergraduate thesis. Brazilian. Using GIS and the Thornthwaite hydric balance to estimate the potential evapotranspiration in the Ji-Paraná river basin (RO)

Data and Metadata Submissions to LBA-DIS.

The following data sets have been registered for the last year:

Data Set Title: River Biogeochemistry data

Parameters: For sampling conducted in May '99, Sep '99, Nov '99, Feb '00, Jun '00, Sep '00: major ions, nutrients (NO₃⁻, suspended solids, dissolved inorganic and organic carbon , total carbon and nitrogen and isotopic composition, respiration rates, water characteristics (temperature, pH, conductivity, dissolved oxygen) URL: http://juruti.cena.usp.br/rondonia/data.html

Data Set Title: Land Use/ Land Cover Map 1999 Parameters: forest, water, pasture, riparian/regrowth, savanna, crops, urban, bare/burned soils, clouds

URL: http://juruti.cena.usp.br/rondonia/data.html

Data Set Title: River Network

Parameters: altitude, slope, stream order

URL: <u>http://juruti.cena.usp.br/rondonia/data.html</u>

Data Set Title: Soil Map

Parameters: cation saturation, soil texture (clay, sand and silt content) URL: <u>http://juruti.cena.usp.br/rondonia/data.html</u>

Datasets that are in preparation include:

Ji-Parana Basin river biogeochemistry data for 2001

Amazon Basin river biogeochemistry data from previously funded work (1980-1996).

Technical Description of Proposed Work

1. Statement of Research and Research Relevance

The Amazon basin is a region defined by its abundance of water, culminating in the world's largest river system (Fig. 1). Our original perspective was and continues to be that these periodically or permanently flooded areas play important roles in the hydrology and biogeochemistry of the Amazon basin, and are particularly subject to changes in land cover and land use.

In our original proposal, the primary question we asked was, What are the changes in the pathways and fluxes of organic matter, nutrients, and associated elements through river corridors (riparian, floodplain, channels, wetlands) as a function of land cover and land use change? The secondary question we asked was, How are the fluxes of trace gases between wetlands and the atmosphere of Amazônia affected by forest conversion and land use? As summarized above under Past Accomplishments, we focused on fieldwork in the Ji-Paraná River Basin of Rondônia, and the use of previous collections and the literature to develop a broader perspective on these questions.

With the research here, we have two primary objectives

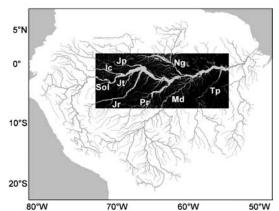


Fig. 1. Flooded area of the central Amazon basin (light areas in dark inset) at high water, as mapped from JERS-1radar data, underlain by a digital river network. Major tributaries are: Negro(Ng), Japurá(Jp), Içá(Ic), Solimões(Sol, Amazon mainstem exiting Peru), Jutaí(Jt), Juruá(Jr), Purus(Pr), Madeira(Md), Tapajós(Tp).

Objective 1. Complete research on the question of landuse change and its consequences for water chemistry in the Ji-Paraná River Basin

Objective 2. Expand research on the fluxes of gases between wetlands and the atmosphere, by testing the working hypothesis 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 and riparian forests to fluvial environments is the primary source of carbon that is eventually respired in rivers and evaded as CO_2 ."

The rationale for expanding the research on gas evasion is that our Phase 1 calculations on gas evasion (outgassing) suggested that this process was much greater than previously expected, to the extent that it may help resolve the current "imbalances" in the estimates of carbon sequestration (documented in the Key Background section). 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. We propose to address our objectives by (1) Conducting fieldwork in characteristic sub-basins to complete water chemistry and to obtain an extensive suite of pCO_2 distribution measurements over the hydrologic regime, and to use proven geochemical techniques (gas flux measurements, isotopic tracers, 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) Using 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.

More specifically, we will:

Task 1. Complete the studies of landuse change and its consequences for the water chemistry of the Ji-Parana River basin.

Task 2. Determine Spatial (Multiple Environments and Soil Types) and Temporal (Seasonal) Distributions and Potential Sources of Dissolved Gases

Task 3. Evaluate models of gas exchange and CO2 accumulation in the lower boundary layer.

Task 4. Determine Seasonality of Inundation and Terrestrial Runoff.

Task 5. Modeling regional dynamics of flow regimes and gas transfer

The overall research here is relevant to a series of the LBA-ECO Science questions. The work on Landuse in Rondonia is relevant to questions LC-Q1 and LC-Q2. The evasion work bears directly on CD-Q1, CD-Q3, TG-Q1, and TG-Q2. The water chemistry works is relevant to ND-Q4 and particularly ND-Q5. In the aggregate the work is very focused on regional-scale integration and synthesis. The work considers explicitly the effects of changing land use, the relation of surface water chemistry to regional flow patterns, and the role of the extensive wetlands and temporarily inundated or saturated areas in Amazônia. If proven true, the flux of CO_2 via riverine systems will impact considerations of the Amazon and ultimately 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.

Key Background

Current estimates of the magnitude of carbon sequestration in the Amazon are uncertain, depending on whether they are derived from measurements of gas fluxes above forests (Grace *et al.* 1995, Mahli *et al.* 1998) or of biomass accumulation in vegetation and soils (Phillips *et al.* 1998; Mahli and Grace 2000). It is also possible that methodological errors may overestimate rates of carbon uptake. Another explanation from Malhi and Grace (2000) involves carbon "...that leaks out of the forest in forms that are not usually measured, such as gaseous

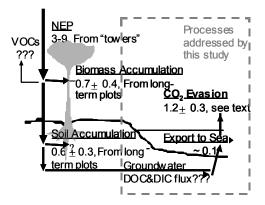


Fig. 2. Estimated C fluxes in the Amazon, Mg C ha⁻¹ y⁻¹ (adapted from Mahli and Grace 2000, Richey et al. in press)

emissions of hydrocarbons or dissolved C in groundwater flows. Although this carbon leakage is thought to be relatively small, surprises cannot be ruled out."

In our work in Phase I of LBA, we evaluated the magnitude and dynamics of the "dissolved C leakage" down river corridors. We evaluated the evasion of CO_2 from the fluvial environments of a 1.77 million-km² quadrant of the low-gradient central Amazon basin (Fig. 1) as a function of seasonal inundation patterns and surface pCO_2 concentrations. We partitioned the quadrant into hydrographic environments – the Amazon mainstem channel, the mainstem floodplain, tributaries (channels and floodplains >100 m in width, as constrained by the pixel dimensions of JERS-1 radar mosaics), and streams (channels and riparian zones <100 m in width). Data from the Japanese Earth Resources Satellite-1 (JERS-1) L-band synthetic aperture radar were used to estimate the areal coverage and inundation status of rivers and floodplains >100 m in width. Data were compiled into mosaics for periods of high water (May-June 1996) and low water (October 1995) (Siquera et al. 2000). For each mosaic, the study area was

classified into either flooded or non-flooded areas based on radar backscatter intensities as delineated by image segmentation (Barbosa et al. in press). The area was divided into 25 tributary sub-basins from the river network (Fig. 1). To account for river corridors <100 m in width, we computed an area density function by extending a geometric series relating stream length and width to stream order from the river network for the whole basin (Fig. 1), and applied it to the study area. Mean monthly stage data from multivear hydrographic records within each tributary sub-basin (Richey et al. in press) were used to estimate tributary flooding sequences by assuming a temporal correspondence between stage height and areal extent of inundation. The temporal sequence of inundation within the mainstem and its floodplain was computed from multi-year monthly composite Scanning Multichannel Microwave Radiometer (SMMR) data (Sipple et al. 1998).

As computed from the radar mosaics, the flooded area of the mainstem and tributaries rose from 79,000 km² (about 4% of the quadrant area) in October 1995 to 290,000 km² (16% of the quadrant area) by May-June 1996. The low (21,000 km²) and high water (51,000 km²) areas estimated for streams were comparable to the area of the mainstem floodplain and greater than the area of the mainstem channel itself. Scaling to river stage height records and integrating over all sub-basins by hydrographic environment

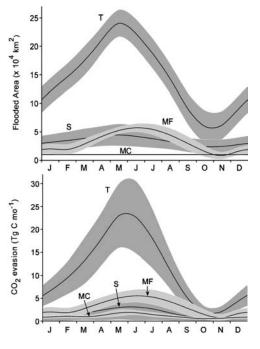


Fig. 3. Spatially integrated annual sequen ces of (a) surface water area by hydrographic environments (MC: Amazon mainstem channel, MF: mainstem floodplain, T: channels and floodplains of tributaries>100 m, S: streams and riparian zones <100 m), from JERS-1 radar data and multiyear hydrographic records. (b) CO_2 E vasion. Lines represent the best estimate of long-term means, whereas shaded regions represent the 67% confidence interval for the range of values likely in a particular year, determined by Monte-Carlo error propagation of both measurement uncertainties and interannual variability in river stage data.

yielded the monthly extent of inundation for a typical year (Fig. 3a). Tributaries south of the Amazon mainstem typically reached peak stage in April or May, whereas those to the north peaked in June or July. The result is that the region was most flooded in May ($350,000 \text{ km}^2$ inundated, or 20% of the quadrant), with an annual mean flooded area of 250,000 km². A non-trivial outcome of these computations is that there may be significant consequences for the water and energy budgets of the basin.

River and floodplain waters of the central Amazon basin maintain partial pressures of dissolved CO₂ (*p*CO₂) that are supersaturated with respect to the atmosphere (Richey et al. 1990). High partial pressures of CO₂ translate to large gas evasion fluxes from water to atmosphere. By combining the areal extent of flooding and the distributions of *p*CO₂ with a simple but widely used gas evasion model, we observed a pronounced seasonality in evasion, corresponding to both the elevated water levels and the increased CO₂ concentrations (Fig. 3b). Integrating over the year, the surface waters of the central Amazon basin (the 1.77 million km² quadrant) export 210 ± 60 Tg C y⁻¹ to the atmosphere. This corresponds to a flux of 8.3 ± 2.4 Mg C ha⁻¹ y⁻¹ over the annual mean flooded area of the central basin, or 1.2 ± 0.3 Mg C ha⁻¹ y⁻¹ over the entire quadrant. Extrapolating across Amazônia, the total basin evasion is ~ 470 Tg C y⁻¹. That is, the waters of the Amazon export ~13 times more carbon via CO₂ evasion to the atmosphere than via the export of total organic carbon (36 Tg C y⁻¹) or of DIC (35 Tg C y⁻¹) to the ocean (Richey et al. 1990).

The large evasion raises an important ecological question: what are the carbon sources that support such a flux? We evaluated potential terrestrial and aquatic sources of CO₂, both as CO₂ and as organic carbon that would be subsequently respired. While the following estimates have considerable uncertainty because of large temporal and spatial variability in the attributes of the respective environments, they do indicate the relative importance of the pathways leading to evasion. The partial pressure of CO_2 in the soil atmosphere is very high (Davidson et al. 1995), resulting from root respiration and the decomposition of organic matter. Dissolution of this CO₂ and its subsequent export to streams (using a typical water through-flow rate 1.25 m y^{-1}) is ~25% of evasion. Dissolved organic carbon (DOC) concentrations in groundwater vary from 100 µM draining clav-rich Oxisols to over 3000 µM in groundwater draining sand-rich Spodosols (McClain et al. 1997). Assuming that Oxisols predominate, groundwater DOC flux (computed as the product of the through-flow rate and DOC concentrations) is $\sim 15\%$ of evasion. Litterfall, either directly into water or via entrainment by rising waters (estimated by applying litterfall rates for flooded forests (Melack and Forsberg 2001) to the rivers and for upland forests (Chambers et al. 2000) to the streams), is $\sim 35\%$ of evasion. Root respiration and decomposition from floating and emergent macrophytes, which can fix atmospheric CO_2 directly and return some of that production to water, is $\sim 25\%$ of evasion (computed from annual net production and the area of habitat from a classification of the JERS-1 images). Organic matter and CO₂ derived from the algal (phytoplankton and periphyton) and submerged macrophyte production/respiration cycle are strictly aquatic, and thus cannot be considered as potential sources.

In total, the estimate of carbon nominally available for evasion is consistent with the computed evasion. Of this amount, $\sim 80\%$ is of terrestrial upland and near-channel origin and $\sim 20\%$ is aquatic. Furthermore, $\sim 75\%$ originates as organic matter that would have to

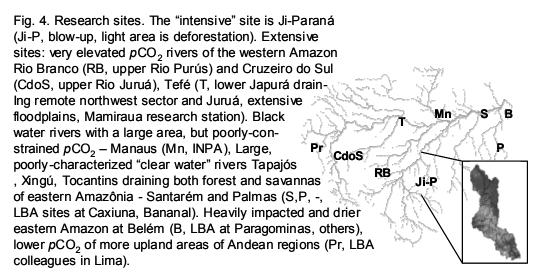
be respired in transit. This possibility is supported by our previous work showing that DIC turnover time due to *in situ* respiration is 10-14 days for the large rivers of the Amazon (Devol et al. 1995). Hence we hypothesize that evasion is driven primarily by in-stream respiration of organic carbon fixed originally on land and along river margins and mobilized into flowing waters. If true, linkages between land and water would be stronger than traditionally thought, with river corridors representing a significant downstream translocation of carbon originally fixed by the forest.

Assuming that the fluxes computed for the Amazon are representative of fluvial environments of lowland humid tropical forests in general, surface water CO_2 evasion in the tropics may help explain an anomaly in the current balance of the global carbon cycle. Estimates that the tropics are a net carbon sink are not consistent with recent calculations from global inverse modeling, which imply that the tropics are at least in balance with the atmosphere if not a net source (Schimel et al. 2001; Gurney et al. 2001). Extrapolating over the global area covered by humid tropical forests¹ with our estimate of areal evasion rates for the Amazon basin yields a flux of roughly 0.9 Gt C y⁻¹ (three times larger than previous estimates of global evasion). A return flux from water to the atmosphere of this magnitude comes closer to reconciling independent carbon budgets for the tropics. From these findings, we suggest that the overall carbon budget of rainforests, summed across terrestrial and aquatic environments, is more in balance than would be inferred from studies of uplands alone.

Technical Approach

Our research plan is focused on (1) completing our previous aquatic nutrient dynamics work in the Ji-Parana, and (2) testing our working hypothesis on the importance of CO_2 gas evasion Functionally these problems are closely related, and can be broken into their respective constituents. The nutrient dynamics is part of the sequence of processes that are ultimately expressed as excess CO_2 . Sampling is done on the same expeditions. The CO_2 evasion is the product of the areal extent of open water (which is the product of the hydrologic regime and landscape), surface CO_2 concentrations (the product of a complex series of biological and transport processes), and the gas exchange rate (controlled by dynamic processes across the air-water interface).

Given the realities of Amazon logistics and our requirement to characterize diverse environments, we propose to pursue a nested sampling and modeling strategy (Fig. 4). 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 (involving more detailed studies on both patterns and processes at a smaller number of sites, primarily in the Ji-Paraná) and extensive (involving defining the variability of pCO_2 by habitat type at a wider variety of sites). For the extensive sites, we will focus on areas of other LBA investigations, particularly in the Tapajós and lower Negro/greater Manaus regions. We also hope to work in collaboration with LBA colleagues at Mamiraua, Rio Branco, Paragominas, the Bananal, and Caxiuna. The parameters to be 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. Complete the studies of landuse change and its consequences for the water chemistry of the Ji-Parana River basin.

We will complete the set of expeditions covering the hydrograph in the basin. The next trip is scheduled for March-April 2002 (with the current grant). This will be a "high water" trip to 38 stations along the basin, sampling not only the mainstem and primary tributaries, but also upstream tributaries. Subsequent sampling expeditions include August 2002 (very low water), October 2002 (beginning of rainy season), and January 2003 (beginning of high water. In between these, there will be expeditions to Nova Vida (in collaboration with the Deegens/O'Neil project). Complementing the field work will be the completion of landuse change maps of the basin.

Task 2. Determine Spatial (Multiple Environments and Soil Types) and Temporal (Seasonal) Distributions and Potential Sources of Dissolved Gases

Task 2.1. Spatial and Temporal Distributions. We propose to enhance our fieldsampling program of pCO_2 and support measurements (dissolved O_2 , routine chemistry) that resolves both spatial and temporal variability in the river system across the Ji-Parana and at our extensive sites. Such a pCO_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, starting with the programmed Ji-Parana expeditions. Over the second year, we will try to expand these to monthly transects (of a reduced scope), recognizing that at some sites we may not be able to sample more than every several months, while at other sites even weekly sampling 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 pCO_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 hundreds of samples from different environments. In addition to concentration measurements, we will preserve several hundred samples for $\delta^{13}C$ analysis and about 20 samples per year for $\Delta^{14}C$ of DIC, DOC, and POM.

Accurate analysis is critical for pCO_2 . Given that the entire CO_2 system can be characterized by the 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 pCO₂ and DIC. Differences of 0.05 pH units can cause 10-20% errors in the calculation of pCO₂. 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 pCO₂ 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 CO₂ determined in the field with a battery-operated 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 2.2. Evaluate Processes Leading to the Evasion of CO₂

The deceptively simple expression of dissolved CO_2 gas (pCO_2) in surface waters 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 confidence in our overall conclusions, and we will gain better insight into how landuse change may affect these processes. As summarized above, we have hypothesized that groundwater export of CO_2 and DOC, entrainment of litter, and macrophytes are the respective sources of the CO_2 that is ultimately evaded. We have proposed elsewhere (to NSF) to examine these processes in more detail. If that proposal is successful, we will not need to repeat that work here. If it isn't, we propose a reduced set of experiments, primarily in Ji-Paraná, that will at least give us insight into the magnitude of the respective processes.

To evaluate the role of groundwater export it will be necessary to account for the different forms of carbon occurring in oxic and anoxic groundwater and streams. We will sample DOC and CO_2 in ground water and 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 them over the course of a hydrologic cycle, following initial setup.

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 determined from litterfall studies. However, we need to know not only litterfall, but how much of it is exported by streams, particularly by the sudden downpours characteristic of the region. We will conduct simple litter entrainment studies at several of the intensive sites, near to the groundwater sampling sites. The studies will entail an inventory of the litter stock 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.

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. We will particularly focus on the potential for overall riverine pCO_2 and DIC to be influenced by the C4 signal characteristic of these plants. We will work collaboratively with the Melack/Novo project on this problem, as they will be assessing the overall production potential of macrophytes. Possibly we will also include modest fieldwork on the isotopic signals, if necessary.

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.

Task 3. Gas Evasion and Boundary Layer Accumulation

A critical component of our overall working hypothesis is the direct measurement of CO_2 evasion and subsequent impact on the CO_2 in the ambient air. There is significant circumstantial evidence that the impact is very detectable. Concentrations of CO_2 increase from mid-day lows of ~340 µatm to in excess of 400 µatm at night, while $\delta^{13}CO_2$ goes from $-7 \, {}^{o}/_{oo}$ to $-12 \, {}^{o}/_{oo}$, due to the accumulation of gas as a relatively shallow nocturnal boundary layer is established (Bartlett et al. 1990, Quay et al. 1992). These patterns are sufficiently robust that gas evasion can be computed, assuming that a "flux box" can be established by the boundary layer (Bartlett et al 1990). The profile over the water is presumably due to outgassing, rather than simple dilution or spill over from the forest. Quay et al (1992) computed that the $\delta^{13}CO_2$ over rivers was consistent with a

mixed layer height of 75 m, and that a δ^{13} CO₂ of the rivers is considerably heavier than the forest and is consistent with CO₂ of a riverine source. Wofsy et al. (1988) observed that the small spatial scale of CO₂ variations observed by aircraft at 150 m are controlled mainly by local exchange between the atmosphere and surface. In one sample over the Tapajós River, J. Ehleringer (pers. comm.) observed enriched $\delta^{18}O_2$ over the water relative to forest and pasture samples. S. Denning (Colorado State University) recently found strong CO₂ gradients between forest and river consistent with those predicted by RAMS for a river evasion flux of 5 μ mol m⁻² s⁻¹ (stronger than our average signal) (Fig. 5, noting that an issue in such efforts is deconvolving river evasion from topographic drainage flow off the forest floor).

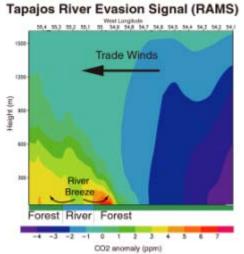


Fig. 5. CO_2 concentration anomalies (ppm) simulated on a 1 km grid centered over Flo-Na Tapajós from a cross section (2.9° S, 3 PM, 8-Aug-2000) consistent with a river evasion flux of 5 μ Mol m⁻² s⁻¹. (S. Denning, unpubl. results).

Accordingly, we propose a complementary approach to the problem of estimation of outgassing that will allow us to tie site-specific point measurements more directly to the broader regional scale perspective so important in LBA. We will examine alternative methods of outgassing, and we will take advantage of the properties of CO_2 and its stable isotopes $\delta^{13}C^{18}O_2$ in ambient air over the water. We will work explicitly with the Ehleringer, Denning, Bakwin, and Wofsy teams on these tasks.

Task 3.1. Assessment of Evasion Models. 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. But 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, and to floodplains.

Saturation Gradients and Floating Chambers. 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 CO₂ gas gradients to calculate CO₂ fluxes. In flowing waters, we will take two approaches to estimate CO₂ gas fluxes. First, we will estimate gas exchange from a reach mass balance of O₂ and CO₂, as we have done 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 O₂, CO₂ and CH₄ fluxes. We anticipate doing this at least quarterly over one hydrologic year (or more, if results are inconclusive). For these experiments we will target a spectrum of rivers with different hydraulic characteristics, widths, depths and velocities in order to be able to extrapolate across the range of rivers in the basin. We will do this in conjunction with Acoustic Doppler Current Profiling systems (ADCP), to relate measured evasion rates to current velocity (which will expedite measurements in other environments when not using the domes). This work will be done primarily at the Ji-Paraná site (with its range of river types and easy access), and elsewhere as appropriate.

Dual-Tracer Injections. In order to get an independent estimate of gas exchange and verify the dome experiments, we may also conduct dual tracer experiments (if we obtain NSF funding). Previous dual tracer experiments have used SF₆ and ³He (Clark et al., 1994, 1996) SF₆ 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 SF₆ and an alternative tracer. For the second tracer we will evaluate H₂, 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.

Eddy Co-variance. While widespread on land (and in LBA), eddy co-variance methods are only beginning to be applied to the problem of gas exchange over water (e.g., McIntyre et al. 2001). We propose to deploy a portable eddy co-variance system (consisting of a 3-D sonic anemometer, an open-path CO_2/H_2O analyzer, data logger, and supporting equipment), mounted on a boat. Because the waters are generally calm, canopy is minimal to non-existent, and fetch is considerable, the conditions to use the technique in this mode are met). This set-up can be readily moved to different environments.

Task 3.2. Assessment of CO_2 Concentrations in Ambient Air. Consistent with the above discussion, we propose to explore the properties of the ambient air over the water in multiple water environments, and relate resulting profiles to regional flux estimates. At all sites where we will take surface water samples for pCO_2 , we will measure ambient air CO_2 (either directly with a field IRGA or with syringes). Where atmospheric conditions permit, we will measure the profile of CO_2 and its isotopes $\delta^{13}C$ and $\delta^{18}O_2$ over the water, from at the water surface up to tens of meters (using tethered balloons, if necessary). As

we do not know what that profile will look like, we will experiment until we feel that we have it determined. If we can establish a consistent gradient and its change over time, we will be able to compute a flux. These latter experiments will be done as much as possible in concert with measurement campaigns at the Tapajós and Manaus sites and with other LBA teams.

Task 4. 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 for each by segment of the river network. 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 ADCP. 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, and 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 floodforecasting *per se*, but for a regional view of water movement that can be related to biogeochemical dynamics and CO_2 evasion.

Task 4.1. Terrestrial Runoff and Downstream Routing. A prerequisite to predicting the dynamics of riverine exchange of carbon with the atmosphere is the ability to predict the movement of water from the surface and subsurface into streams, and subsequently its movement into the channel system, at regional scales. To date, we have been working with the Variable Infiltration Capacity (VIC) model that was designed from such VIC (see Liang et al, 1994) is a physically based model, which applications. parameterizes small scale processes to allow application to large river basins, which typically are resolved at spatial resolutions from 1/8 degree latitude by longitude (e.g., where the resolution of the precipitation, temperature, radiative, and other surface forcings are available or can be derived), to coarser resolutions such as the 2 degree global application described by Nijssen et al (2002). The model has parameterizations to represent the vertical exchange of moisture and energy between the vegetation canopy and the atmosphere, similar in many respects to other Soil-Vegetation-Atmosphere Transfer Schemes (SVATS). Its main distinction from other SVATS is its representation of the effects of spatial variability in soil, topography, and vegetation, and their effects on runoff generation, which is assumed to occur dominantly via the saturation excess mechanism (which is usually a defensible assumption in humid environments). The model also represents a "slow," or baseflow, runoff response via a nonlinear deep soil drainage parameterization.

For our application, it is important not only that river discharge be reproduced accurately, but also that the processes that can effect carbon exchange (e.g., pathways by which moisture moves through the subsurface, and channel travel times including tributaries of all stream orders) be represented properly. In the spirit of the VIC macroscale structure, these processes will be parameterized, but some attention will need to be given to verification and/or development of new parameterizations that describe the

pathways by which moisture reaches river outlets, as well as the bulk fluxes. To do so, we propose to utilize our high-resolution hydrologic model, the Distributed Hydrology Soil Vegetation Model (DHSVM, see Wigmosta et al, 1994 for details). Unlike VIC, DHSVM is intended for application to small to moderate (typically less than about 1000 km²) drainage areas, over which digital topographic data allows explicit representation of the mechanisms by which water travels over the surface and through the subsurface. Like VIC, it represents runoff generation via the saturation excess mechanism. Unlike VIC, it explicitly represents topographic effects, including the formation of perched water tables, runoff generation, incident solar radiation (hence net radiation), and explicitly represents the vegetation and its properties (like root depth), as well as soil properties, on a pixel-by-pixel basis.

The model grid resolution typically is 30-150 m, several orders of magnitude higher than VIC. However, because of the large computational burden, DHSVM is restricted to relatively small catchments. We have conducted some limited experiments comparing DHSVM sensitivity, for instance, to vegetation and vegetation change (Van Shaar et al, 2002). Although the macroscale performance of the two models is similar in gross features (e.g., ability to reproduce seasonal fluctuations in runoff), there are important differences in predicted runoff and other surface fluxes, especially at shorter time scales. In this respect, DHSVM provides a useful "laboratory" for evaluation of VIC parameterizations such as contact times of subsurface moisture with various elements of the soil horizon, and movement through the stream channel system (which, unlike VIC, DHSVM represents directly from digital topographic information, down to first order streams as identified using a support area concept, which is field-verifiable). We will focus on the Ji-Parana, where our evolving geospatial model and access to data can support this work, then apply what is leaned to VIC at broader regional scales.

Task 4.2. Evaluation of Areal Extent of Flooded Areas. In our original analysis, we divided hydrographic environments into areas 100 > m in width (because of pixel limitations of the data from the Japanese Earth Resources Satellite-1 (JERS-1) L-band synthetic aperture radar) and < 100 m in width. For our work here, we will continue to collaborate with the Melack/Novo team on the >100 m coverages. They will be producing the large-scale inundation patterns required here (letter attached).

Accounting for river corridors <100 m in width, however, is a different matter. We originally computed an area density function by extending a geometric series relating stream length and width to stream order from the river network for the whole basin, and applied it to the study area. This analysis suggested that the streams were comparable in magnitude to the mainstem floodplain, but considerably smaller than the larger tributaries and their floodplains. The relationship of stream width to upstream drainage area can be referred to as a unit stream power (downstream width increases with the square root of basin area). We intend to extend general landscape evolution models (Ahnert 1970; Summerfield and Hulton 1994; Pinet and Souriau 1988) to fine spatial scales by confirming, with direct field observations, the unit stream power at spatial scales finer then the grid cell size of digital elevation models and multispectral remote sensing. The focus of the work will be the Ji-Parana, then we will explore extrapolating to other regions.

Task 5. Synthesis of Measured Distributions, Exchange Rates, Flow Paths, and Areal Extent to Spatial and Temporal Finally, we are ready to synthesize the overall information from chemical distributions, processes and exchange rates, areal extent, and water movement into computations of the seasonally and temporally varying CO2 outgassing in the Amazon. We propose to use the ROMBUS construct (above) coupled to

the hydrologic modeling (Fig. 6). This model provides 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 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 spatial compartment, each including concentrations of dissolved and particulate size fractions of OM, concentrations of DIC and CO₂, the age (via Δ^{14} C) of each carbon pool, its δ^{13} C and C/N, and O₂. 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 O₂ concentrations.

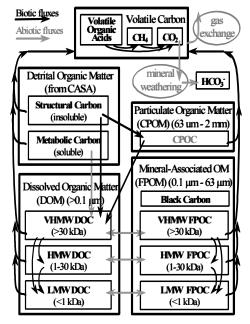


Fig 6. Schematic of the ROMBUS model; calculates biogeochemical reactions at each location and timestep within a spatially-distributed, integrated model framework.

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 $\sim 100 \text{ km}^2$ 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. 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 CO₂ from *Terra Firme* to the river system and total CO₂ evasion from open waters.

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Plan for Integrative Science

The research proposed here intends extensive collaborations with other LBA project. For us the core thematic areas of cooperation include:

- (1) Seasonality of Inundation. Our primary collaboration on this is with the Melack/Novo team. The immediate focus of this collaboration will be on the seasonality of inundation regimes of water bodies >100 m in width. This work is key to our ability to make regional calculations of flux. Further, they will be making measurements of pCO2 at sites within the Rio Negro basin which will be of significant utility. Their work on macrophyte production will enable us to make much better estimates of the effects of macrophytes on CO_2 than we could otherwise. We have had a long and productive collaboration with this group, with the most recent product being the Richey et al (in press) *Nature* paper. A letter from Melack is attached.
- (2) Regional-scale CO₂ fluxes. Through multiple discussions, the groups listed below have "stated their intention to work cooperatively on the overall issue of deconvolving regional/mesoscale signals of CO₂ in the atmosphere into forest, grassland, mixed wetlands, and open water signals, with the overarching goal of placing strong constraints on the carbon balance of the Amazon region.. We expect that these efforts, combined with and open to other LBA activities, will promote an unprecedented degree of synthesis leading to new insight. We will exchange data, plan joint campaigns (in so far as possible), and actively participate in synthesis workshops." Briefly, the research groups include: the respective Brazilian co-investigators and S. Denning (mesoscale modeling with SiB and RAMS), J. Ehleringer/J. Berry (measurements of ¹³C and ¹⁸O in CO₂ from forests, pastures, and rivers; carbon models from leaf to canopy), S. Wofsy (towers, aircraft), P. Bakwin (light aircraft measurements), J. Melack (above), and J. Richey (this proposal).
- (3) Water chemistry and nutrient dynamics. This includes the L. Deegans/C. Neil team in Rondonia, who also work with the CENA group. Samples are analyzed in common. E. Davidson (Paragominas) also works with the CENA group.
- (4) Regional to basin scale modeling. Among the groups focusing on basin-scale modeling, the teams of Foley/Costa and Potter have interests, which are very complementary to our own. We anticipate that our synthesis efforts, building on the modeling and fieldwork, would provide them with very useful information. Certainly their products will help constrain our activities.

For all groups, the central endeavor is to communicate as rapidly as possible, to plan joint field activities where feasible, and to exchange data and ideas as rapidly as possible. We feel that the understanding of the regional scale distributions, some of which is represented in this proposal, has advanced rapidly in a short period of time, through exactly this open communication. With this basis, the prospectus for more rapid advances in the next Phase is very exciting.

Training and Education Plan

We have 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 webenabled 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.

In this next phase of work, we will:

- (1) Continue to support current students and seek new students at regional institutions. The "extensive" sites work proposed here is predicated on being able to work with students at these institutions
- (2) Conduct short courses on analytical environmental chemistry. A network of liquid chromatographs is being installed in eh Amazon (INPA, Paragominas, possibly Belém, as well as Ji-Paraná). We will setup a course on analytical techniques for water sampling, storage and analysis, which could also meet the requirements of other LBA projects (e.g. Davidson', Deegans).
- (3) Similarly, we will investigate short courses on watershed analysis.
- (4) We will sponsor an annual workshop for the project, with the particular theme of regional-scale integration of CO₂ fluxes.
- (5) We will continue to work with local media. Our recent *Nature* paper is already attracting attention from the *Folha de Sao Paulo* newspaper, as well as the Science Museum of London.

<u>Data Plan</u>

The goal of our project's Data Management Plan is to facilitate the connectivity between our researcher teams at CENA, the UW, other regional institutions, on-site field investigators, and the ultimately the LBA-DIS. Our objectives are:

(1) To provide data of specific chemical measurements of gas emissions and soil and water chemistry within the riparian corridor in spatially and temporally explicit terms to our research teams and LBA participants as a web based node of the Beija-flor data sharing component of LBA-DIS.

(2) To comparing this spatially explicit data to the tower measurements and available remotely sensed data products as quickly as possible, as a participant subscriber through LBA-DIS.

(3) To extend the LBA Metadata editor (LME) application of the Mercury XML webbase solution to specifically integrate our biogeochemical metadata collections and physical chemical transport measurements as a locally based web node.

Our approach to data management divides the tasks into four areas of responsibility:

1. Project management; responsible for the overall direction, technical feasibility, and coordination and compliance with FGDC standards, LME compatibility, and the needs of the individual investigator,

2. Data management; responsible for coordinate, unit, and/or datum consistency, and resolving discrepancy of definitions between investigators and LBA-DIS metadata standards,

3. System management; responsible for both software and hardware administration in support of data connectivity between project team members, local collections, and LBA-DIS, and

4. Product Management; responsible for tracking the completeness of data collections from initial requests to final archive status and responding to data delivery by web-downloads, ftp, CD, and/or tape.

Data Tracking, Verification, and duplication. The "keystone" of a successful data information management program is a useable Data Tracking system which provides the research team with the current status of any data request or completeness of any dataset. We will use a compliment (or extension) of the XML metadata approach adopted by LBA-DIS to coordinate a dataset synchronization with the University of Washington and CENA research labs. This extension of LME to include biogeochemical tags and version tracking is intended to facilitate both internal consistency between collaborative research sites as well as contributions to the LBA-DIS. The basis of this application is a proposed web-based data tracking form maintained at the UW and is first generated when an investigator outlines data collection methods at the sampling sites, or when obtaining data from secondary (outside) sources. This services as a mechanisms to assure that researcher's data meet the highest data quality standards and timely contributions to the shared database. Within two months following reception of field data the quality and/or appropriateness of the dataset is to be verified. Within one year of the initial collection the data should be made available to all LBA participants through Beija-flor.

Hierarchical Data Archiving Program. To insure continuous support to researchers and the various proposed activities of the LBA program our teams work will be archived using a standard hierarchical backup format. Each month full system backups will be made to 8mm tape and stored off-site. Weekly incremental backups to tape will remain on-site. Daily incremental backups will be written to an on-line disk. Finally, off-line microfiche services are available through U.W. Academic Computing Center for the long-term archiving of ASCII files and tabular data.

Data Retrieval and Delivery. We propose to use the World Wide Web as the primary tool for the distribution of general information concerning our research as well as facilitating communication and collaboration between ourselves, other investigators, and the public. We envision extending the current Internet activity to participate fully in metadata searches, a distributed bibliography database, and services for teachers and students. The Web-site as well as the CD-ROM products will be used as forms of data delivery and/or outreach to community organization, schools, and investigators that require specific information with a minimum of software overhead.

<u>Management Plan</u>

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. The co-Principal Investigators will be J. Richey (UW) and R. Victoria (Director, CENA, letter attached). Co-Investigators include A. Devol (UW, chemistry and gas evasion, field work), D. Lettenmaier (UW, hydrologic modeling), A. Krusche (CENA, chemistry and field expeditions), V. Ballester (CENA, geospatial modeling), and M. Bernandes (CENA, chemistry, fieldwork). They will be responsible for overall project supervision and communication. Richey will also be responsible for over-seeing the modeling.

We have requested three years of funding. Because we are already well-set up in Ji-Parana, we anticipate being able to start the work proposed here as soon as funding arrives. We anticipate that the work at the extensive sites will lag by about 6 months. We will sue the July 2002 LBA Science Meeting in Manaus as the opportunity to have (1) A meeting of the team, and (2) a chance to work out the details of collaboration with other teams and sites.

We have proposed a three-year project. 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 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).

Letter of Commitment



UNIVERSIDADE DE SÃO PAULO

CAMPUS "LUIZ DE QUEIROZ"

Centro de Energia Nuclear na Agricultura



Piracicaba, February 28, 2002.

To: NASA

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 carbon and 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 NASA):

(1) Commitment of the time of myself and the CENA co-Is, Krusche, Ballester, 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 NASA 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,

Viotona

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

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Facilities and Equipment.

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

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 (CO₂, N₂O and CH₄) 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.

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 ${}^{17}\text{O}/{}^{16}\text{O}$ and ${}^{18}\text{O}/{}^{16}\text{O}$. 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 ¹³C/¹²C and ¹⁵N/¹⁴N 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 O_2 , CO and CH₄, dissolved inorganic carbon (DIC) in seawater and particulate organic material, the D/H of atmospheric H₂ and CH₄ and particulate organic material, and the ¹⁵N/¹⁴N of NO₃ 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 "¹⁴C-free building. No enriched ¹⁴C 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 \sim 300 Gb of storage, including three Sun workstations and multiple PCs.

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.

(ii) The primary equipment that we intend to seek out within our institutions or across LBA is the setup for the eddy co-variance studies of evasion. We have requested this in the budget, but if a suitable system could be made available from elsewhere, we would not need to buy one.