U.S. DEPARTMENT OF ENERGY | Office of Science

DOE/SC-ARM-13-011

Green Ocean Amazon Terrestrial Ecosystem Collaborative Project Science Plan

J Chambers

May 2013

ARM CLIMATE RESEARCH FACILITY

DISCLAIMER

DOE/SC-ARM-13-011

Green Ocean Amazon Terrestrial Ecosystem Collaborative Project Science Plan

J Chambers

May 2013

Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Abstract

The overall goal of Green Ocean Amazon (GOAMAZON) is to advance a mechanistic understanding of how land-atmosphere processes affect tropical hydrology and climate. One critical terrestrial component of these interactions is the emission of biogenic volatile organic compounds (BVOCs) from Amazon forests, which serve as cloud condensation nuclei (CCN) precursors that influence precipitation dynamics, and modify the quality of incoming light for photosynthesis. However, our ability to represent these coupled biosphere-atmosphere processes in earth system models (ESMs) is constrained by an extremely poor understanding of the identities, quantities, and seasonal patterns of BVOC emissions from tropical forests. Moreover, we are further limited by our incomplete mechanistic understanding of leaf-level and understory-to-canopy emissions of BVOCs and canopy responses to changes in light quality. Thus, this Green Ocean Amazon terrestrial ecosystem project (Geco) is designed to evaluate the strengths and weaknesses of leaf-level BVOC emission algorithms for forests near Manaus and conduct targeted field studies designed to fill knowledge gaps toward improving the models and testing a few key hypotheses. We are currently exercising the Model of Emissions of Gases and Aerosols from Nature (MEGAN), which comprises the BVOC submodel of the Community Earth System Model (CESM), to explore sensitivities with respect to plant-BVOC-aerosol-cloud relationships and how these vary with factors associated with a warming climate. Based on that analysis, a combination of observations and experiments will be carried out to test existing parameterizations and algorithm structures, and the models will be modified as needed to improve BVOC emission simulations. Changes in the atmospheric light environment brought about by varying aerosol loading and cloud properties, and related responses of forest tree ecophysiology and BVOC production processes, will also be explored. Overall, Geco studies will address key questions on mechanistic controls over landscape-scale tropical forest BVOC emissions, and driving factors that are expected to change with a warming climate. Geco will work closely with other projects associated with GOAMAZON and will assemble and motivate a collaborative team of scientists and students in Brazil, the U.S., and with other international partners, toward addressing complex BVOC-related questions employing interdisciplinary approaches.

Acronyms and Abbreviations

AMF	ARM Mobile Facility
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BEACHON	Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen
BVOC	biogenic volatile organic compounds
CAM	Community Atmosphere Model
CCN	cloud condensation nuclei
CESM	Community Earth System Model
CLM	Community Land Model
DBH	diameter at breast height
DOE	Department of Energy
EC	eddy covariance
ESMs	earth system models
FID	flame ionization detector
GC	gas chromatography
Geco	Green Ocean Amazon terrestrial ecosystem project
GPP	canopy photosynthesis
IARA	Intensive Airborne Research in Amazonia
INPA	National Institute for Research in the Amazon
LAI	leaf area index
LBA	Large Scale Biosphere Atmosphere Experiment
LBNL	Lawrence Berkley National Laboratory
MEGAN	Model of Emissions of Gases and Aerosols from Nature
MS	mass spectrometry
NEP	noise equivalent power
PFT	plant functional types
PI	principal investigator
PID	photoionization detector
RAINFOR	Amazon Forest Inventory Network
REA	relaxed eddy accumulation
RH	relative humidity
TACAPE	Tree Assimilation and Carbon Allocate Physiology Experiment

Contents

Figures

Tables

1.0 Introduction

How land-atmosphere processes affect tropical hydrology, deep convection, and climate are poorly understood (Ervens et al. 2008; Pacifico et al. 2009), and there are insufficient observational data sets to constrain these processes in ESMs (Oleson et al. 2008). To advance scientific knowledge in this area, the Department of Energy's (DOE) Office of Biological and Environmental Research's Climate and Environmental Sciences Division will conduct an integrated project to study coupled atmosphere-cloud-terrestrial interactions in the Amazon basin near Manaus. This GOAMAZON project will include deployment of the Atmospheric Radiation Measurement (ARM) Climate Research Facility's Mobile Facility (AMF) for the calendar years 2014 and 2015, research activities from DOE's Regional and Global Climate Modeling, Earth System Modeling (ESM), Atmospheric System Research (ASR), and Terrestrial Ecosystem Science programs, and observational resources from the Environmental Molecular Sciences Laboratory. A critical goal of GOAMAZON and associated research activities is to evaluate and improve the representation of coupled tropical systems in ESMs.

GOAMAZON is designed to enable the study of cloud life cycles, cloud-aerosol-precipitation interactions, and the surface fluxes of aerosols, moisture, and energy under both clean atmospheric conditions and under the influence of pollutant outflow from the tropical megacity of Manaus. Observations associated with studying these processes will provide critical data sets to constrain tropical forest model parameterizations for aerosols, cloud convection schemes, and terrestrial ecosystems, and how these processes are perturbed by pollution. A critical missing piece of the plant-ecosystem-atmosphere-cloud system is leaf-level emissions of BVOCs and how these emissions are controlled by both physiological processes and environmental constraints (Goldstein and Galball 2009). Thus, Geco will focus on leaf-level BVOCs comprising the bulk of total forest emissions and additional BVOCs that play critical roles in atmospheric reactions (Table 1). Additional studies will investigate within-canopy and canopy-to-atmosphere BVOC emission and reaction processes and the effects of aerosol-mediated changes in the light environment on canopy photosynthesis (GPP) and evapotranspiration. Field studies carried out by Geco will be informed by a critical analysis of an existing BVOC emission model, MEGAN (Guenther et al. 2012), which comprises the BVOC submodel of the CESM. A key Geco goal is to thoroughly test and evaluate MEGAN prognoses for the tropics under changing climate conditions and carry out necessary improvements to provide leaf-level BVOC emission algorithms for the coupled plant-ecosystem-atmosphere-cloud system. Overall, Geco will provide the mechanistic biological basis for the production of BVOCs and the forest exchange of mass and energy, under a varying atmospheric aerosol environment, that will be utilized by ARM, ASR, and other GOAMAZON programs and projects in the context improved ESM development.

Terrestrial ecosystems produce an array of BVOCs that can act as critical CCN, influence planetary albedo and the direct and diffuse components of incoming solar radiation, and play important roles in atmospheric chemical reactions. Tropical trees alone are estimated to account for ~50% of total global BVOC emissions, yet the mechanistic basis for predicting leaf-level controls over BVOC emissions is based primarily on temperate forest studies (Guenther et al. 2012). To develop improved prognoses of BVOC response to variables associated with a changing climate, additional leaf-level studies on controls over emissions are needed from tropical forest ecosystems. Important tropical forest BVOC questions that will be addressed in Geco with respect to developing improved ESMs include:

1. What are the identities, amounts, and seasonal patterns of BVOC emissions?
2. What are the functional biological roles of BVOC emissions with respect to climate change variables?
3. What controls how much assimilated carbon is allocated to the production and emission of BVOCs?

An overarching approach for Geco includes carrying out baseline evaluations of MEGAN, followed by focused field studies in forests near Manaus to improve MEGAN performance for tropical forests. Research questions and hypotheses are outlined below, followed by a Methods section with descriptions of the detailed methodologies that will be employed.

Table 1. Leaf-level BVOCs comprising the bulk of total forest emissions and additional BVOCs that play critical roles in atmospheric reactions.

Class	Volatile Organic Compounds	Leaf Scale	Ecosystem Scale	Laboratory
light alkanes	ethane, propane, i-butane, n-butane, i-pentane, n-pentane	Branch chamber/ flasks	REA/ Teflon bags	GC-FID
isoprene	isoprene	Li-Cor 6400/ handheld PID	REA/ cartridge/ Teflon bags	GC-MS/FID
other light alkenes	ethene, propene, 1-butene, 2-methyl propene, 2-butene,	Branch chamber/ flasks	REA/ Teflon bags	GC-FID
alkynes	acetylene	Branch chamber/ flasks	REA/ Teflon bags	GC-FID
isoprene oxidation products	methacrolein, methyl vinyl ketone, 3-methyl furan, 2-methyl-3-buten-2-ol	Branch chamber/ flasks	REA/ cartidges	GC-FID
monoterpenes	α-pinene, β-pinene, β-ocimene, limonene, sabinene, 3-carine, myrcene	Li-Cor 6400/ cartridges	REA/ cartridges	GC-MS
sesquiterpenes	β-caryophyllene, α-farnascene, β-farnascene, α-humalene, α-bergamotene	Li-Cor 6400/ cartridges	REA/ cartridges	GC-MS
green leaf volatiles	3-hexenal, 3-hexen-1-ol, 3-hexen-1-yl acetate	Li-Cor 6400/ cartridges	REA/ cartridges	GC-MS
C1-3 oxygenated VOCs	methanol, acetaldehyde, acetic acid, acetone, methyl acetate	Branch chamber/ flasks	REA/ Teflon bags	GC-MS/FID
aromatics	e.g. benzene, toluene, xylene, benzaldehyde, methyl salicylate	Branch chamber/ flasks	REA/ Teflon bags	GC-MS
sulfides	dimethyl sulfide, hydrogen sulfide, carbon disulfide	Branch chamber/ flasks	REA/ Teflon bags	GC-MS

2.0 Key Geco Research Questions for Manaus Forests

2.1 Geco BVOC Modeling Study

What are the strengths and weaknesses of current leaf-level BVOC emmission models in ESMs, and how can they be improved?

A number of ESMs are currently being developed to improve prognoses of future climate change under a variety of scenarios. There are some large uncertainties associated with the terrestrial components of these models, particularly for tropical forests which differ markedly from the temperate ecosystems where these models were originally developed and parameterized. For this study, we will focus on BVOC emission algorithms for tropical forests as encoded in MEGAN, which is currently linked with the Community Land Model (CLM) and Community Atmosphere Model (CAM) in the CESM (Guenther et al. 2006) and represents the only existing community BVOC emission model. Global runs of the current version of MEGAN-CLM-CAM estimate that (1) isoprene accounts for ~50% of total 1 Pg BVOC emissions, (2) 10 additional compounds (methanol, ethanol, acetaldehyde, acetone, α-pinene, β-pinene, t-β-ocimene, limonene, ethene, and propene) comprise another 30% of the total, and (3) 20 more compounds (mostly terpenoids) comprise 17%, with the remaining 3% distributed among 125 compounds. Tropical trees alone accounted for 60% of terpenoid emissions and 48% of total global BVOC emissions in these runs (Guenther et al. 2012). Overall, these emission estimates are based on algorithms that represent a set of testable hypotheses for tropical forests. Thus Geco will first focus first on running MEGAN for our Amazon forest sites to generate a set of testable predictions and then carry out extensive field measurements to evaluate these predictions. Next, for those emission fluxes that are poorly represented by MEGAN, additional field studies will be carried out to improve model structures.

There are a number of unresolved questions concerning the complex relationships among the ecophysiological functioning of trees, changes in environmental conditions, phylogenetic associations, and corresponding BVOC emissions. Addressing these questions will aid in the development of improved BVOC emission models. For example, BVOC emissions for tropical forests may vary more with species identities and phylogenetic associations than with physiological responses to a changing environment, representing testable hypotheses that have not been rigorously evaluated in field studies. Also, although studies on canopy photosynthesis and light quality with changing atmospheric aerosol loading have been carried out in Amazon forests (Doughty et al. 2010), no studies have explored changes in BVOC emissions with the direct and diffuse components of incoming solar radiation and atmospheric aerosol loading. Overall, the measurement studies proposed below will improve our mechanistic understanding of Amazon forest BVOC emissions, and these studies will be designed to inform improved algorithm development for MEGAN-CLM-CAM.

Regional emissions of BVOCs in MEGAN are modeled by first defining emission factors for individual plants and then simulating processes that control landscape-scale emissions. Processes that control emission variations in MEGAN include light, temperature, leaf age, soil moisture, leaf area index (LAI), and CO_2 inhibition (Guenther et al. 2012), with each of these algorithms representing testable hypotheses. However, a large number of tropical forest processes that control BVOC emissions are poorly simulated with the current generation terrestrial ecosystem models, although progress is being made (Verbeeck et al. 2011), and a large number of comprehensive data sets have been developed for tropical forests ecosystems over the past few decades which can aid in the development of improved models. These data sets include those associated with Large Scale Biosphere Atmosphere Experiment (LBA) (Davidson et al. 2012; Keller et al. 2004), Amazon Forest Inventory Network (RAINFOR) (Malhi et al. 2002), the Center for Tropical Forest Science/Smithsonian Institution Global Earth Observatory Global Forest Carbon Research Initiative e.g., (Chave et al. 2008), and other comprehensive tropical forest studies (Chambers et al. 2004; Malhi et al. 2009). For this project, these data sets will be thoroughly exploited to evaluate structural and parameter uncertainty in CLM with respect to processes controlling emissions in MEGAN. Overall, these analyses will generate an optimum CLM parameter scheme for Amazon forests and indicate areas where structural changes to the models are required.

2.2 Geco BVOC Leaf Emissions Study

How do leaf-level BVOC emissions mechanistically relate to climate change variables?

Tropical trees cover ~18% of land surface but account for an estimated 60% of terpenoid emissions and 48% of all other BVOC emissions (Guenther et al. 2006). However, due to the high tree species diversity and difficulties scaling from individual trees to ecosystems, tropical forest BVOC emission factors are primarily based on above canopy measurements, and there are few mechanistic studies of leaf-level

BVOC emissions in the tropics (Harley et al. 2004; Kesselmeier and Staudt 1999; Niinemets et al. 2011). Thus, improved models of tropical forest BVOC emissions require a better understanding of environmental controls over leaf-level emissions and how these vary with plant functional types (PFTs) and phylogenetic associations.

A number of complex biochemical, physiological, and ecological processes control many aspects of leaf-level BVOC emissions, and a mechanistic basis for the production and emission for many BVOCs is not well understood (Guenther et al. 2006; Niinemets et al. 2010). For example, the functional role of isoprene in plants, which accounts for ~50% of global BVOC emissions, is not clear. Recently, Jardine et al. (2012) found that isoprene (i) is oxidized (i_{ox}) in leaves in a tropical environment, and that the i_{ox}/i emission ratio increased with temperature. They hypothesized that this increase in the i_{ox} fraction was due to chemical deactivation of reactive oxygen species, which are damaging to plant tissues under high temperature stress. Overall, additional mechanistic studies are needed to develop improved prognostic models of BVOC emission response to variables associated with a changing climate.

This Geco BVOC leaf study will focus on how emissions relate to factors that are expected to vary with a changing climate, including: (1) leaf temperature (T_{leaf}), (2) internal leaf CO_2 concentration (C_i) and stomatal conductance (g_s), (3) leaf water potential (Ψ_w) and ecosystem moisture status, (4) species identity and PFT characteristics, and (5) ecological factors such as stand age and phenology. Our overall goal for this leaf-level study is to develop an improved process-level understanding of how BVOC emission are related to these factors and to codify this knowledge in MEGAN for an improved representation of BVOC processes in CESM. We will focus on studying those BVOCs comprising the bulk of total emissions and additional BVOCs that have the potential for high atmospheric aerosol yield.

2.3 Geco BVOC Forest Canopy Study

How do BVOC species and concentrations vary from the soil surface to the top of the canopy?

Canopy-to-atmosphere BVOC emissions can vary significantly from leaf-level emissions due to a number of within-canopy processes (Helmig et al. 1998; Holzinger et al. 2005). This Geco BVOC canopy study will quantify within-canopy and canopy-to-atmosphere (“canopy”) gradients of key BVOCs to improve our understanding of these complex canopy processes. Canopy fluxes of BVOCs to the atmosphere are often carried out employing an eddy covariance (EC) system (Karl et al. 2002; Spirig et al. 2005). However, fast sensors appropriate for EC flux measurements of BVOCs (e.g., PTR-MS) are costly, and there will be a number of other groups at the ZF2 Reserve who will be employing PTR-MS systems for EC flux measurements of BVOCs. Thus, Geco will employ a complementary approach called relaxed eddy accumulation (REA) (Lee et al. 2005; Rinne et al. 2002), which will enable studies of important BVOCs not amenable to measurement using PTR-MS-EC. For example, PTR-MS-EC gives total monoterpenes, while REA enables quantification of the contribution of individual compounds, which is critical for understanding mechanistic controls over emissions for ESM algorithm development (Table 1). Overall, this REA approach will involve storing samples during updraft and downdraft periods (as determined using a sonic anemometer) and then analyzing those samples at our National Institute for Research in the Amazon (INPA) laboratory. The ability to deploy multiple REAs, ease of transport to new sites, and low power requirements, also enables sampling spatial variability in BVOC emissions along important environmental gradients. Thus, Geco will focus on understory-to-canopy BVOC compound speciation, and landscape-scale spatial variability in BVOC emissions.

In addition to the above-canopy REA system for exploring canopy-atmosphere BVOC exchange, we will also deploy vertical profiling systems to quantify how BVOC concentrations vary from the soil surface to the top of the canopy. These profiles will provide important information on concentration gradients of key BVOCs and how the emissions of particular BVOC compounds vary with height, which enables distinguishing belowground and aboveground emission sources. These data will also provide information on chemical transformation of BVOCs, including BVOC oxidation products, which will enable characterization of bi-directional exchange processes. To enable characterization of spatial gradients in BVOC emissions (e.g., plateau versus valley forests "baixios", which are strongly influenced by spatially heterogeneous factors such as tree species composition, soil properties, and other ecosystem processes), multiple REA and profiling systems will be deployed. These will be supplemented with a series of surface flux chamber measurements to quantify soil emission and uptake rates.

2.4 Geco Light Quality Study

How does varying light quality driven by changes in atmospheric aerosol loading affect GPP and noise equivalent power (NEP)?

Changes in light quality, including shifts in the direct and diffuse components of incoming solar radiation, can effect GPP and the net ecosystem exchange of CO_2. For example, forest studies outside of the tropics found an increase in whole-canopy and shade-leaf photosynthesis under cloud or aerosol conditions that enhanced the diffuse fraction of irradiance (Gu et al. 2003; Still et al. 2009). Recent work in Amazon forests near Santarem, Brazil, found that photosynthesis in old-growth tropical forests exhibited complex relationships with the quality of solar radiation (Doughty et al. 2010; Doughty and Goulden 2008). Doughty and Goulden (2008) found that GPP initially increased with sunny periods following cloudy conditions, but then decreased with extended sunny periods as leaf temperature rose, evaporative demand increased, and canopy conductance decreased. However, Doughty et al. (2010) also found that net carbon uptake in an Amazon forest increased significantly during smoky periods, with 80% of that increase due to diffuse light penetration into lower canopy levels and 20% due to decreased temperature stress under smoky conditions. Thus, changes in the atmospheric aerosol environment can have complex effects on the physiological functioning of tropical trees, which can in turn effect BVOC emissions. These interactions among atmospheric aerosol loading, light quality, tree ecophysiology, and forest-atmosphere interactions have not been explored in detail for Amazon forests.

3.0 Detailed Materials and Methods

3.1 Geco BVOC Modeling Study

The modeling study will carry out a detailed process-level evaluation of MEGAN-CLM-CAM for those tropical forest processes important in controlling BVOC emissions. Linkages among algorithms in this current framework will be determined, and interactions among these key processes will be evaluated against a large number of empirical data sets. For example, as part of an INPA PhD thesis, comprehensive data sets on upper-canopy leaf temperature and related leaf-level photosynthetic responses are available (Tribuzy 2005), which are critical in controlling BVOC emissions. A large number of Amazon forest data sets are available from the LBA project (http://lba.cptec.inpe.br/lba/site/), which will be mined for our modeling study. In addition, the LBA Model Intercomparison Project has organized a large number of data sets for model parameterization and evaluation (http://www.climatemodeling.org/lba-mip/). This comprehensive evaluation of MEGAN will take place during the first few months of Geco and will generate a series of testable hypotheses that will be evaluated during field measurement campaigns.

Results from the model evaluation and uncertainly analysis will be used to develop a detailed plan for recommended parameter and structural changes to MEGAN-CLM to improve simulation of tropical forest BVOC emissions. Processes that will be evaluated that exert strong controls over BVOC emissions in MEGAN include: (1) T_{leaf} and relationships among soil and leaf water potential, solar radiation, and seasonal changes in precipitation, (2) leaf-level photosynthetic rates and related physiological parameters (e.g., C_i, $V_{c,max}$, J_{max}, g_s), seasonality in LAI, and changes in light-dependent BVOC emissions, and (3) relationships among PFTs and stand development (e.g., pioneer, late successional species) that can inform future versions of the CLM Ecosystem Demography model (Moorcroft et al. 2001). This will be an interactive process, with changes in model structure generating a new set of hypotheses to be tested in the field.

To explore how BVOC emissions for the Amazon are currently predicted by CESM, CLM4.0 (which includes MEGAN) was run (by C Coven) for a box bounding 10°S, 5°N: 70°W, 55°W, which roughly comprises the Amazon basin, and compared the output with remote observations of the BVOC oxidation product formaldehyde (Barkley et al. 2009) (Figure 1). Overall, data and results from Geco will allow us to better understand and implement these types of seasonal cycle controls on BVOC production and better constrain how climate changes may affect emissions.

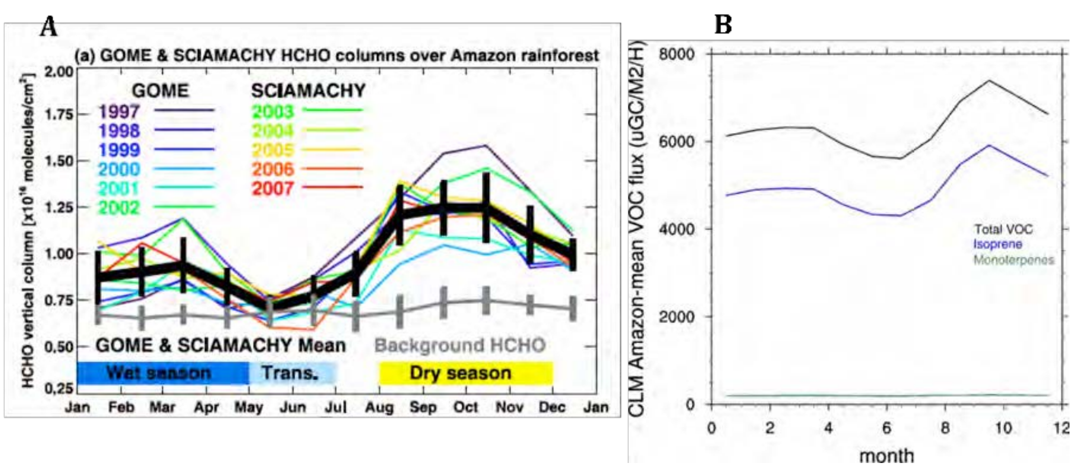

Figure 1. (A) Data from Barkley et al. (2009) show a distinct seasonal cycle with a decline in BVOC emissions during the transition from wet to dry season. (B) The MEGAN emissions algorithm as implemented in CLM4 predicts the basic features of this seasonal cycle, but with reduced amplitude.

3.2 Geco BVOC Leaf Emissions Study

Developing an improved mechanistic understanding of leaf-level BVOC emissions for tropical forests presents a number of challenges. Thus, this study will focus on developing projects outside the Manaus pollution plume to limit the number of potentially confounding factors and also to utilize the excellent infrastructure provide at INPA's ZF2 Reserve. First, we will take advantage of a number of canopy towers at the ZF2 Reserve to access the crowns of trees for carrying out leaf-level measurements (Figure 2). These include three fixed walk-up towers > 50m (~ 20m above the mean canopy height) in height (k14, k34 plateau [k34p], and k34 valley [k34v]) where a number of forest-atmosphere studies are being conducted. In addition, there are three portable 30-m scaffold towers that were designed by the principal investigator (PI) and collaborators at INPA to carry out an upper-canopy photosynthesis project (Tribuzy 2005). These portable towers will be set up in an area near the ZF2 road that was impacted by a large squall line in 2005 (Negrón-Juárez et al. 2010), which will provide canopy access to young stands with a large number of early successional species. From past experience, each tower will provide access to 5–7 canopy trees, and canopy profiles (including sun and shade leaves) of diurnal leaf emissions can be carried out on one tower per day. To access additional crowns, our Max Planck collaborator (Dr. Trumbore) has purchased a towable 30-m canopy lift (Denka DL30, expected to arrive in Manaus late 2012) for use with the Tree Assimilation and Carbon Allocate Physiology Experiment (TACAPE), which will enable crown access to trees on plateau forests within a few kilometers of the ZF2 road. We are currently developing a light trail system for the DL30 on one large plateau along the ZF2 road where the TACAPE project is being established. For trees of interest in the permanent plots that cannot be sampled directly from towers or the DL30 lift, branches will be cut while immersed in water by tree climbers to maintain xylem and phloem functionality prior to measurement (Harley et al. 2004).

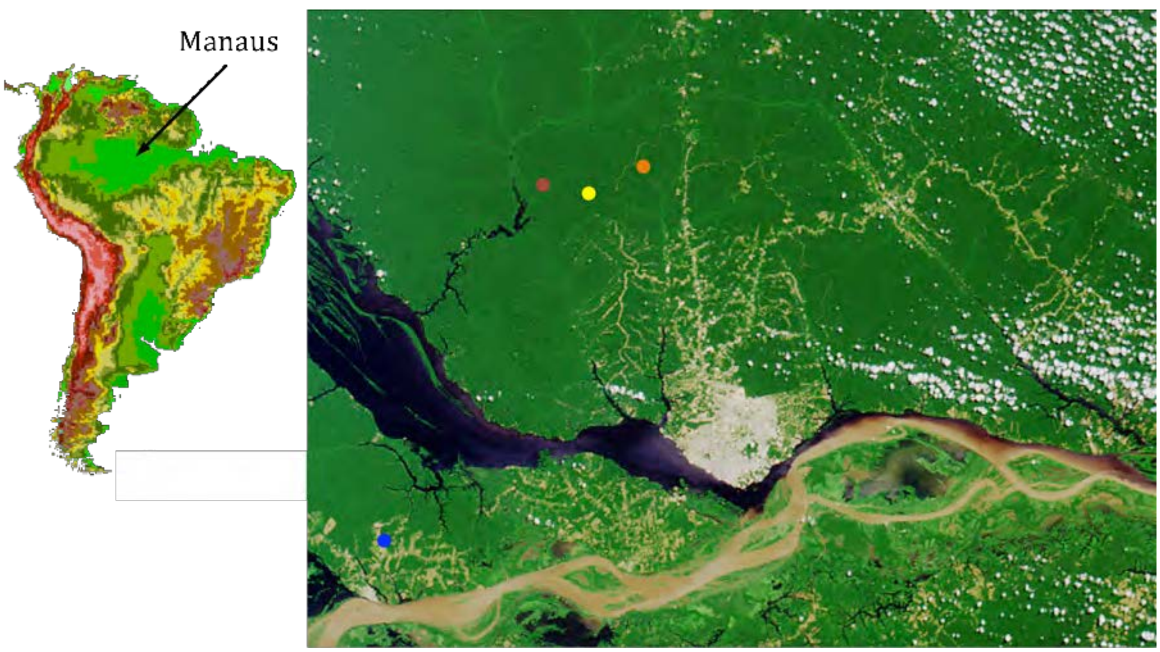

Figure 2. Location of the ZF2 Reserve and the k14 tower (orange circle), k34 towers (yellow), and the 2005 blowdown sites (red) approximately 50 km north of the ARM Mobile Facility in Amazônia (blue) deployment location.

To ensure sampling across a broad range of stand ages, PFTs (e.g., successional guilds, habitat preferences) and phylogenetic associations, we will take advantage of a large network of forest permanent sample plots in the ZF2 Reserve. Detailed measurements of tree species IDs, growth, recruitment, and mortality in these permanent plots have been carried out for decades, providing a solid foundation for carrying out ecophysiological BVOC studies. For example, previous studies at the ZF2 Reserve have explored plant carbon allocation strategies and how these vary with tree growth rates and stand development (Chambers et al. 2004; Teixeira 2003; Teixeira 2010), and these studies will enable exploration of relationships among carbon allocation and BVOC emissions. Permanent plots where all trees > 10 cm diameter at breast height (DBH) have been tracked over time include: (1) those associated with the Biomass and Nutrient Experiment, which includes control plots (3 ha) and replicated logging treatments (and hence stand age variability) (9 ha), which have been monitored almost every year since the mid-1980s; (2) the "transect" plots comprising two 20 x 2,500 m (5 ha each) permanent plots that sample the local undulating topography and related shifts in tree species community composition, which have been inventoried every two years since 1998, (3) the "quadradão," a 300 x 300 m (9ha) that has been re-inventoried twice and includes detailed species composition down to 5 cm DBH; and (4) permanent plots totaling 5 ha distributed across tree mortality gradients and large blowdown clusters associated with the 2005 Amazon squall line event (Negrón-Juárez et al. 2010). Overall, these 36 ha of permanent plots provide long-term data for over 18,000 trees, which will provide an excellent foundation for sampling across a broach range of PFT and phylogenetic variation and for scaling BVOC estimates from individual trees to the ecosystem. For Geco, we proposed to sample about 15 trees from these plots monthly, comprising ~180 trees per year. These trees will be randomly sampled from our 36 ha database stratified by size (i.e., DBH), growth rate, wood density (a surrogate for PFT variation), and across phylogenetic associations known to emit key classes of BVOC compounds.

A variety of methods will be employed to develop a better understanding of how leaf-level BVOC emissions respond to factors associated with a changing climate. First, considering isoprene accounts for ~50% of total tropical BVOC emissions, we will utilize a modified LiCor Portable Photosynthesis System (LI6400) (Harley et al. 2004) to study how isoprene emissions vary with T_{leaf}, C_i, g_s, Ψ_w, phylogenetic relationships, and PFT characteristics (e.g., wood density). Isoprene emissions will be quantified first by passing air through an activated charcoal filter to remove hydrocarbons and then through the 6400 leaf chamber at a known flow rate. Air exiting the LI6400 leaf cuvette will be analyzed in the field using a fast-response, handheld photoionization detector (PID) (Thermo Environmental Instruments, Inc., Woburn, MA, USA, Model 580B) and also collected onto sorbent cartridges for subsequent analysis in the laboratory by gas chromatography (GC) with mass spectrometry (MS) (to identify) and flame ionization detectors (FID) (to quantify).

The handheld PID will detect all terpenoid compounds and many other BVOCs. However, the response differs considerably for various BVOCs, and the PID can only be used to quantitatively assess BVOC if emissions are dominated by a single compound, as is often the case for isoprene-emitting trees. An initial survey using cartridges will indicate which tree species can be investigated using the handheld PID. Other compounds, including monoterpenes, sesquiterpenes (which are important for controlling atmospheric aerosols and CCN production), and "stress" compounds, will be investigated by using cartridges. Many of the these larger BVOCs exhibit differing degrees of "stickiness" and thus can adhere to surfaces associated with the 6400. For these "sticky" BVOCs, we will employ branch enclosures (Teflon or glass), which will be sampled by extracting a known volume of air at a set flow rate using a mass flow controller. These enclosures will also be outfitted with photosynthetically active radiation sensors and thermocouples to monitor changes in light and leaf temperature. Cartridges will be transported to the laboratory at INPA; the absorbed compounds will be thermally desorbed and collected on a cryotrap. Other smaller molecular weight compounds including alkanes, alkenes, and some sulfur compounds will be sampled using air canisters (SilicoCan) or gas-tight syringes. Samples will then be injected onto a GC-FID or GC-MS outfitted with the appropriate detectors at our INPA laboratory. Because different cartridges and different

GC setups are required to measure different classes of compounds, we will limit leaf-level emissions work to a reasonable number of important BVOC compounds comprising the bulk of emissions or that play critical roles in atmospheric chemical reactions (Table 1). Leaves associated with emission samples will be collected in the field, dried for 24 hours at 70°C, and weighed, and emission rates will be expressed as µg X g^{-1} h^{-1}, where X is the BVOC of interest.

To better understand how leaf-level BVOC emissions vary with changes in leaf temperature (T_{leaf}), evapotranspiration (ET), and water potential (Ψ_w), we will rotate deployment among the towers of an automated "biophysical" system for quantifying continuous changes in these parameters. The T_{leaf} system will deploy 25 chromel-constantan thermocouples on leaves of 5–7 canopy trees near the deployment tower, following a system we deployed for an INPA PhD thesis project using a Campbell Scientific CR10X and an AMT-25 (Tribuzy 2005). To quantify ET, thermal dissipation (sap flow), sensors will be installed on all trees where the T_{leaf} system is deployed to estimate flux density (J_s – e.g., kg H2O dm^{-2} h^{-1}) as a function of tree biophysical parameters (Granier et al. 2000; Wullschleger and King 2000) in conjunction with leaf-level measurements of ET with the LiCor 6400 system. Pressure bomb measurements will also be carried out on leaves of the tower trees on a weekly basis to determine Ψ_w throughout the day, and an automated time domain reflectrometry system will be deployed to relate Ψ_w to changes in soil water potential with precipitation. Ultimately, these measurements will enable exploration of the complex relationships among J_s, Ψ_w, T_{leaf}, precipitation, and BVOC emissions, which will inform algorithm development and parameterization in MEGAN. We will also deploy an existing micrometeorological station on one of the portable 30-m canopy towers in conjunction with deployment of the automated biophysical system to measure air temperature and relative humidity (RH), windspeed, solar insolation, and precipitation.

3.3 Geco BVOC Forest Canopy Study

The within-canopy-to-atmosphere study will focus on quantifying spatial variability in BVOC emissions for forests on plateaus and forests associated with perennial streams in small valleys ("baxios"). Overall, plateau and valley forests represent the largest fraction of central Amazon forest, yet there have been no studies comparing BVOC emissions from these forest types, which vary in a number of ecosystem processes and tree species composition (Chambers et al. 2004; da Silva et al. 2002). Our overall approach will utilize REA systems that will be established at two existing walkup towers sampling plateau (k34p) and valley (k34v) forests to collect above-canopy BVOC samples and a profiling system to measure BVOC concentration gradients from the soil surface to the top of the canopy. All compounds amenable to measurement with the leaf-level studies will be quantifiable using this REA and profiling system. In addition to measuring canopy emissions with the REA system, quantification of BVOC oxidation products with this system will also enable estimates of canopy bi-directional exchange processes. Overall, our REA system will quantify canopy fluxes for a number of atmospherically important BVOCs that cannot be measured directly using PTR-MS-EC systems, including some important compounds that have not been quantified at the ecosystem scale for Amazon forests.

For the REA systems, vertical wind speed will be measured with a sonic anemometer at the sample inlet location, and air will then be drawn into Teflon tubing, either an up tube or a down tube depending on whether an updraft or downdraft is observed. Over 30-minute periods, air sub-samples will be run through separate traps for the updrafts and downdrafts when vertical wind velocities exceed the threshold or deadband velocity (Guenther et al. 1996; Schade and Goldstein 2001). Sample segregation based on the vertical wind measurements will occur using fast-response Teflon solenoid valves, controlled by a datalogger. The profiling system will function similar to the REA system without the need to track updrafts and downdrafts. Samples collected on these systems will be stored in appropriate canisters or cartridges, transported to Manaus, and analyzed on GC-FID and GC-MS systems we will establish in our laboratory at INPA.

3.4 Geco BVOC Light Quality Study

To study the effects of changing atmospheric aerosol load on light quality and forest ecophysiology, we will take advantage of the existing ZF2 k34p tower, and provide additional instrumentation required to study these processes. The k34p tower is a 1.5m x 2.5m-section 54 m aluminum tower located on a medium-sized plateau with a footprint of ~2-3 km^2 (Araújo et al. 2002), and has been in operation since 1999. The tower includes a CO_2 vertical profiling system to measure the storage flux (F_{bc}), an EC system at 53m to measure the above-canopy flux (F_{ac}), and ancillary meteorological instrumentation. A number of published studies have utilized this tower (Araújo et al. 2010; Araújo et al. 2002; Chambers et al. 2004), including BVOC studies (Rizzo et al. 2010), and Geco studies will be designed to build from this previous work.

To quantify changes in light quality, we will add a multifilter shadowband radiometer (MFR7, Yankee Environmental Systems) to the k34p tower. The MFR7 will enable the separation of light into direct and diffuse components and determine light intensity as a function of wavelength. In addition, a profiling system for photosynthetically active radiation will be added to the k34p tower to quantify the light environment from the top of the canopy to the understory. As described in the leaf-level study above, this tower will also be instrumented with a biophysical system to quantify T_{leaf}, ET, and Ψ_w, and canopy photosynthesis profiles will be carried out when quantifying leaf-level BVOC emissions with the 6400 system. This will enable us to explore relationships among GPP, NEP, T_{leaf}, soil-to-leaf moisture potential, and light quality to develop a better understanding of the effects of atmospheric aerosol loading on tree ecophysiology and BVOC emissions. Also, the ARM Mobile Facility in Amazônia, which will be deployed ~50 km south of the ZF-2 site in the Manaus pollution plume (Figure 1), will be collecting large data sets on relationships among atmospheric aerosol conditions, cloud properties, and the light environment. Although the Manaus plume will potentially confound direct relationships between the AMF and ZF2 sites, there will be enough overlap in conditions to provide critical links among clouds, aerosols, and the light environment for a broad set of environmental conditions. Overall, this light quality study will leverage many of the measurements carried out for other studies in this project and other ongoing projects at the ZF2 Reserve, representing a high potential return for a minimum additional investment.

4.0 Interactions with Related Projects

The GOAMAZON AMF deployment (PI Scot Martin) to the Manacaparu site within the Manaus pollution plume is slated for 2014–2015 and will include large number of interacting collaborative projects, including:

1. a cloud life cycle project (GPM- CHUVA; Luiz Machado, PI)

2. aerosol-cloud-precipitation interactions (Aeroclima; Paulo Artaxo, PI)
3. the Intensive Airborne Research in Amazonia (IARA; Scot Martin, PI)
4. cloud life cycle project (NSF EOL/S-POL Facilities; Courtney Schumacher, PI)
5. aerosol life cycle project (Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen [BEACHON]; Alex Guenther, PI)
6. other related activities.

This larger community has been engaged, and a number of researchers carrying out BVOC-related activities have agreed to collaborate with Geco (e.g., Artaxo, Manzi, Gonçalves, and Guenther). We are also communicating with Juergen Kesselmeier (Max Planck) and Oscar Vega (Instituto de Pesquisas Energéticas e Nucleares – INPE), and will work closely with these and other groups to help maximize our collective effort. The PI (Dr. Chambers) also has a faculty appointment at INPA and has advised and co-advised a large number of INPA students over the past ~15 years. Other INPA collaborators on this project (Drs. Manzi, Higuchi, and Gonçalves) have also agreed to involve INPA students in Geco activities. To help facilitate these interactions, the PI will establish monthly conference calls to help coordinate activities. In addition, the PI will work with these other groups to coordinate travel plans to Manaus to interact once a year in BVOC mini-workshops, with the intent of coordinating project activities, developing collaborative goals, and maximizing synergistic interactions.

In addition to a number of collaborative BVOC studies in the Manaus region, the PI is also working closely with Susan Trumbore at the Max Planck Institute for Biogeochemistry (Jena, Germany) in developing and implementing the TACAPE project. TACAPE will include the experimental creation of replicated canopy gaps of varying size and study how tree species community composition and tree ecophysiological processes respond to this large increase in resource supply. The use of the 30-m canopy lift (DL30) will enable sampling of the crowns of a large number of canopy trees at the TACAPE site. The experimental manipulation of gap size and the resulting response of the tree community will provide excellent opportunities for developing a better understanding of mechanistic controls over BVOC emissions, including feedbacks and forcings associated with gap-phase succession. TACAPE has a strong focus on elucidating carbon allocation patterns in response to changing environmental conditions and will thus serve as an excellent foundation for exploring the role of BVOCs in these varying allocation schemes.

5.0 References

Araújo, AC, AJ Dolman, MJ Waterloo, JHC Gash, B Kruijt, FB Zanchi, JME de Lange, R Stoevelaar, AO Manzi, AD Nobre, RN Lootens, and J Backer. 2010. “The spatial variability of CO(2) storage and the interpretation of eddy covariance fluxes in central Amazonia.” *Agricultural and Forest Meteorology* 150: 226–237.

Araújo, AC, AD Nobre, B Kruijt, JA Elbers, R Dallarosa, P Stefani, C Randow, AO Manzi, AD Culf, JHC Gash, R Valentini, and P Kabat. 2002. “Comparative measurements of carbon dioxide fluxes from two nearby towers in a Central Amazonian rainforest: The Manaus LBA site.” *Journal of Geophysical Research-Atmospheres* 107 (D20): 8061.

Chambers, JQ, ES Tribuzy, LC Toledo, BF Crispim, N Higuchi, J dos Santos, AC Araújo, B Kruijt, AD Nobre, and SE Trumbore. 2004. "Respiration from a tropical forest ecosystem: Partitioning of sources and low carbon use efficiency." *Ecological Applications* 14: S72–S88.

Chave, J, R Condit, HC Muller-Landau, SC Thomas, PS Ashton, S Bunyavejchewin, LL Co, HS Dattaraja, SJ Davies, S Esufali, CEN Ewango, KJ Feeley, RB Foster, N Gunatilleke, S Gunatilleke, P Hall, TB Hart, C Hernandez, SP Hubbell, A Itoh, S Kiratiprayoon, JV LaFrankie, SL de Lao, JR Makana, NMS Noor, AR Kassim, C Samper, R Sukumar, HS Suresh, S Tan, J Thompson, MDC Tongco, R Valencia, M Vallejo, G Villa, T Yamakura, JK Zimmerman, and EC Losos. 2008. "Assessing evidence for a pervasive alteration in tropical tree communities." *Plos Biology* 6: 455–462.

da Silva, RP, J Santos, ES Tribuzy, JQ Chambers, S Nakamura, and N Higuchi. 2002. "Diameter increment and growth patterns for individual tree in Central Amazon, Brazil." *Forest Ecology and Management* 116: 295–301.

Davidson, EA, AC de Araujo, P Artaxo, JK Balch, IF Brown, MMC Bustamante, MT Coe, RS DeFries, M Keller, M Longo, JW Munger, W Schroeder, BS Soares, CM Souza, and SC Wofsy. 2012. "The Amazon basin in transition." *Nature* 481: 321–328.

Doughty, CE, MG Flanner, and ML Goulden. 2010. "Effect of smoke on subcanopy shaded light, canopy temperature, and carbon dioxide uptake in an Amazon rainforest." *Global Biogeochemical Cycles* 24.

Doughty, CE and ML Goulden. 2008. "Are tropical forests near a high temperature threshold?" *Journal of Geophysical Research-Biogeosciences* 113.

Ervens, B, AG Carlton, BJ Turpin, KE Altieri, SM Kreidenweis, and G Feingold. 2008. "Secondary organic aerosol yields from cloud-processing of isoprene oxidation products." *Geophysical Research Letters* 35.

Goldstein, AH, and IE Galbally. 2009. "Known and unexplored organic constituents in the Earth's atmosphere." *Geochimica et Cosmochimica Acta* 73: A449.

Granier, A, P Biron, and D Lemoine. 2000. "Water balance, transpiration and canopy conductance in two beech stands." *Agricultural and Forest Meteorology* 100: 291–308.

Gu, L, DD Baldocchi, SC Wofsy, JW Munger, JJ Michalsky, SP Urbanski, and TA Boden. 2003. "Response of a deciduous forest to the Mount Pinatubo eruption: enhanced photosynthesis." *Science* 299: 2035–2038.

Guenther, A, W Baugh, K Davis, G Hampton, P Harley, L Klinger, L Vierling, P Zimmerman, E Allwine, S Dilts, B Lamb, H Westberg, D Baldocchi, C Geron, and T Pierce. 1996. "Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques." *Journal of Geophysical Research-Atmospheres* 101: 18,555–18,567.

Guenther, A, T Karl, P Harley, C Wiedinmyer, PI Palmer, and C Geron. 2006. "Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature)." *Atmospheric Chemistry and Physics* 6: 3181–3210.

Guenther, AB, X Jiang, CL Heald, T Sakulyanontvittaya, T Duhl, L Emmons, and X Wang. 2012. "The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions." *Geoscientific Model Development Discussions* 5: 1–58.

Harley, P, P Vasconcellos, L Vierling, CCD Pinheiro, J Greenberg, A Guenther, L Klinger, SS De Almeida, D Neill, T Baker, O Phillips, and Y Malhi. 2004. "Variation in potential for isoprene emissions among Neotropical forest sites." *Global Change Biology* 10: 630–650.

Helmig, D, J Greenberg, A Guenther, P Zimmerman, and C Geron. 1998. "Volatile organic compounds and isoprene oxidation products at a temperate deciduous forest site." *Journal of Geophysical Research-Atmospheres* 103: 22,397–22,414.

Holzinger, R, A Lee, KT Paw, and AH Goldstein. 2005. "Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds." *Atmospheric Chemistry and Physics* 5: 67–75.

Jardine, KJ, RK Monson, L Abrell, SR Saleska, A Arneth, A Jardine, FY Ishida, AMY Serrano, P Artaxo, T Karl, S Fares, A Goldstein, F Loreto, and T Huxman. 2012. "Within- plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein." *Global Change Biology* 18: 973–984.

Karl, TG, C Spirig, J Rinne, C Stroud, P Prevost, J Greenberg, R Fall, and A Guenther. 2002. "Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry." *Atmospheric Chemistry and Physics* 2: 279–291.

Keller, M, A Alencar, GP Asner, BH Braswell, M Bustamante, EA Davidson, E Feldpausch, ML Goulden, P Kabat, B Kruijt, F Luizao, SD Miller, D Markewitz, AD Nobre, CA Nobre, NP Filho, HRd Rocha, PLS Dias, C Randow, and GL Vourlitis. 2004. "Ecological research in the Large Scale Biosphere Atmosphere Experiment in Amazonia (LBA): early results." *Global Change Biology,* in press.

Kesselmeier, J and M Staudt. 1999. "Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology." *Journal of Atmospheric Chemistry* 33: 23–88.

Lee, A, GW Schade, R Holzinger, and AH Goldstein. 2005. "A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpene flux." *Atmospheric Chemistry and Physics* 5: 505–513.

Malhi, Y, LEOC Aragao, DB Metcalfe, R Paiva, CA Quesada, S Almeida, L Anderson, P Brando, JQ Chambers, ACL da Costa, LR Hutyra, P Oliveira, S Patino, EH Pyle, AL Robertson, and LM Teixeira. 2009. "Comprehensive assessment of carbon productivity, allocation and storage in three Amazonian forests." *Global Change Biology* 15: 1255–1274.

Malhi, Y, OL Phillips, J Lloyd, et al. 2002. "An international network to understand the biomass and dynamics of Amazonian forests (RAINFOR)." *Journal of Vegetation Science* 13:439–450.

Moorcroft, PR, GC Hurtt, and SW Pacala. 2001. "A method for scaling vegetation dynamics: The ecosystem demography model (ED)." *Ecological Monographs* 71: 557–585.

Negrón-Juárez, RI, JQ Chambers, G Guimaraes, H Zeng, CFM Raupp, DM Marra, GH Ribeiro, SS Saatchi, BW Nelson, and N Higuchi. 2010. "Widespread Amazon forest tree mortality from a single cross-basin squall line event." *Geophysical Research Letters* 37: L16701.

Niinemets, U, U Kuhn, PC Harley, M Staudt, A Arneth, A Cescatti, P Ciccioli, L Copolovici, C Geron, A Guenther, J Kesselmeier, MT Lerdau, RK Monson, and J Penuelas. 2011. "Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols." *Biogeosciences* 8: 2209–2246.

Niinemets, U, RK Monson, A Arneth, P Ciccioli, J Kesselmeier, U Kuhn, SM Noe, J Penuelas, and M Staudt. 2010. "The leaf-level emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling." *Biogeosciences* 7: 1809–1832.

Oleson, KW, GY Niu, ZL Yang, DM Lawrence, PE Thornton, PJ Lawrence, R Stockli, RE Dickinson, GB Bonan, S Levis, A Dai, and T Qian. 2008. "Improvements to the Community Land Model and their impact on the hydrological cycle." *Journal of Geophysical Research-Biogeosciences* 113.

Pacifico, F, SP Harrison, CD Jones, and S Sitch. 2009. "Isoprene emissions and climate." *Atmospheric Environment* 43: 6121–6135.

Rinne, HJI, AB Guenther, JP Greenberg, and PC Harley. 2002. "Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature." *Atmospheric Environment* 36: 2421–2426.

Rizzo, LV, P Artaxo, T Karl, AB Guenther, and J Greenberg. 2010. "Aerosol properties, in-canopy gradients, turbulent fluxes and VOC concentrations at a pristine forest site in Amazonia." *Atmospheric Environment* 44: 503–511.

Schade, GW and AH Goldstein. 2001. "Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation." *Journal of Geophysical Research-Atmospheres* 106: 3111–3123.

Spirig, C, A Neftel, C Ammann, J Dommen, W Grabmer, A Thielmann, A Schaub, J Beauchamp, A Wisthaler, and A Hansel. 2005. "Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry." *Atmospheric Chemistry and Physics* 5: 465–481.

Still, CJ, WJ Riley, SC Biraud, DC Noone, NH Buenning, JT Randerson, MS Torn, J Welker, JWC White, R Vachon, GD Farquhar, and JA Berry. 2009. "Influence of clouds and diffuse radiation on ecosystem-atmosphere CO2 and (COO)-O-18 exchanges." *Journal of Geophysical Research-Biogeosciences* 114.

Teixeira, LM. 2003. Influencia da intensidade de exploração selectiva da madeira no crescimento e respiração das árvores em uma floresta tropical de terra-firme na região de Manaus [Masters thesis]: Manaus, INPA.

Teixeira, LM. 2010. Variáveis ecofisiológicas do tronco como indicadores de sustentabilidade da floresta tropical manejada seletivamente [Ph.D. thesis]: Manaus, Brazil, INPA.

Tribuzy ES. 2005. Variaçoes da temperatura foliar do dossel e o seu efeito na taxa assimilatória de CO2 na Amazonia Central [Ph.D. thesis]: Piracicaba, Universidade de São Paulo/ESALQ.

Verbeeck, H, P Peylin, C Bacour, D Bonal, K Steppe, and P Ciais. 2011. "Seasonal patterns of CO(2) fluxes in Amazon forests: Fusion of eddy covariance data and the ORCHIDEE model." *Journal of Geophysical Research-Biogeosciences* 116.

Wullschleger, SD and AW King. 2000. "Radial variation in sap velocity as a function of stem diameter and sapwood thickness in yellow-poplar trees." *Tree Physiology* 20: 511–518.