Cover Page

Project Title:	Brazil-USA Collaborative Research: Modifications by Anthropogenic Pollution of the Natural Atmospheric Chemistry and Particle Microphysics of the Tropical Rain Forest During the GoAmazon Intensive Operating Periods (IOPs)
Applicant/Institution:	Harvard University
Street Address/City/State/Zip:	1350 Massachusetts Ave., Cambridge, MA 02138-3826
Postal Address:	as above
Lead Principal Investigator:	Scot T. Martin, (617) 495-7620, scot_martin@harvard.edu
Administrative Contact:	Marrybell Ramos, (617) 495 0460, marrybell_ramos@harvard.edu
Funding Opportunity Announcement Number:	DE-FOA-0000919
DOE/Office of Science Program Office:	Office of Biological and Environmental Research
DOE/Office of Science Program Office Technical Contact for Research Area:	Dr. Ashley D. Williamson
PAMS LOI tracking number:	LOI-0000003731

Cover Page Supplement

Collaborating Institutions

Harvard University, Scot Martin, Lead Principal Investigator (PI)

University of Colorado, Boulder, Jose Jimenez

University of California, Irvine, Saewung Kim, with subcontract to James Smith and Alex Guenther, University Center for Atmospheric Research (UCAR)

University of São Paulo (Universidade de São Paulo; USP), Henrique Barbosa (PI)

Subproject to Federal University of São Paulo (Universidade Federal de São Paulo; UNIFESP), Luciana Rizzo, Theotonio Pauliquevis

University of the State of Amazonas (Universidade do Estado do Amazonas; UEA), Rodrigo Souza (PI), including Julio Tota

Budgets

Partner	Year 1	Year 2	Year 3	Total
DOE				
Harvard	US$150,141	US$149,182	US$150,679	**US$450,001**
Colorado	US$150,000	US$150,000	US$150,000	**US$450,000**
Irvine	US$150,000	US$150,000	US$150,000	**US$450,000**
FAPESP				
USP	R$300,764.80 + US$83,828.66**	R$300,764.80 + US$83,828.66	R$150,382.40 + US$41,941.33	**R$751,912.00 + US$209,571.65**
FAPEAM				
UEA	R$600,000	R$400,000	R$223,764	**R$1,223,764**
Total	**US$533,969.70 + R$900,764.80**	**US$533,010.70 + R$700,764.80**	**US$492,620.30 + R$377,146.40**	**US$1,559,601 + R$1,978,676**

*1 January 2014 through 31 December 2016, **FAPESP accepts values in US dollars.

Table of Contents

Project Narrative

1. Introduction

The effects of aerosol particles on cloud microphysics, cloud cover, precipitation, and regional climate are significant. The Amazon region is particularly susceptible to changes in number-diameter distributions $n(d)$ of the atmospheric particle population because of the low background concentrations and high water vapor levels, indicating a regime of cloud properties that is highly sensitive to aerosol microphysics (Fig. 1). Present and future anthropogenic activities can significantly alter the number-diameter distribution that prevails under natural conditions. At present time, the prevailing distribution $n(d)$ undergoes rapid transient changes between wet season and dry season as well as when affected by biomass burning. There are also possible secular trends in $n(d)$ related to economic development. The climatic implications are profound,[2-5] ranging from modulation of local precipitation intensity to modifying large-scale circulations and energy transport associated with deep convective regimes.[6] Any changes in tropical precipitation can have significant, potentially global consequences because of non-linear multiscale interactions of tropical waves with precipitation in the Amazon, leading also to possible changes in the Atlantic intertropical convergence zone (ITCZ).[7]

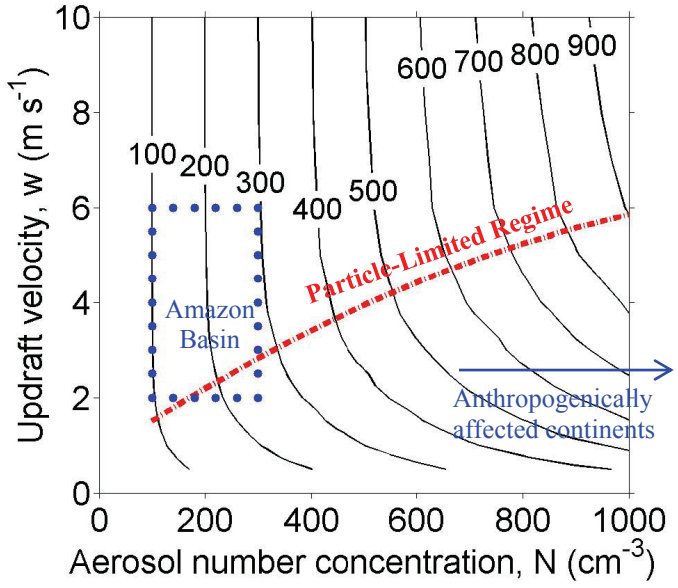

Figure 1. Regimes of cloud activation. Under clean conditions, the Amazon basin is in a particle limited regime with respect to $n(d)$, i.e., closer to a marine environment than a typical continental regime. Because of background pollution, 'clean' regions of the Northern Hemisphere are in a different regime than the Amazon basin. Pollution in a plume like Manaus shifts the regime of cloud activation. Contour lines show simulated cloud droplet number concentration. Adapted from ref 1.

As a Brazil-USA collaboration, the goals of this proposal are (i) to measure and mechanistically understand the factors affecting $n(d)$ over a tropical rain forest, especially the effects of anthropogenic pollution as a perturbation to natural state, and (ii) to develop and implement an upscaling analysis from this new data set and knowledge of $n(d)$ to prognosticate possible climatic impacts of present-day urban pollution and possibly greater pollution in the future. The proposal is to conduct measurements downwind of Manaus and carry out related data analysis and interpretation for the Intensive Operating Periods (IOPs), one in the wet season (Feb 1 – Mar 30) and one in the dry season (Aug 15 – Oct 15), of the Green Ocean Amazon experiment (GoAmazon2014/5).[*] The planned IOPs, one in the wet season and one in the dry season, coincide with the timing of the operation of the DOE AAF G1 aircraft in the Manaus region.

[*] http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/, accessed 7 June 2013
http://campaign.arm.gov/goamazon2014/, accessed 7 June 2013

Manaus, a city of two million people and growing rapidly, is an isolated, highly polluted urban area located in the central Amazon basin with clean conditions in the surrounding 2000 km (Fig. 2). The city has been a free trade zone since the 1960's, and this status was recently renewed for another 50 years by the Brazilian government. As a result, it is an industrial manufacturing city with one of the highest per capita incomes in Brazil. Most of the manufactured products are shipped approximately 3000 km by barge to the consumer market in the state of São Paulo. As a consequence of this industrial and other economic activities (e.g., the city's electricity is produced in large part by burning high-sulfur fuel oil, there is a large fleet of diesel trucks, etc.), there are high levels of air pollution in the city's outflow. The width of the urban plume is about 20-25 km, resembling the dimension of the city itself, with little downwind spreading, i.e., there is distinct clean air on both sides of the pollution plume (Figs. 3 and 4). The atypically small edge mixing along the plume is a consequence of the persistent easterly winds throughout the year. Also in consequence to these persistent winds, the urban plume of Manaus passes reliably westward toward the main proposed research site T3 north of the city of Manacapuru (Fig. 2). The plume from Manaus has high concentrations of SO_2, NO_x, and soot, among other pollutants (Fig. 4). Measurements in the plume show very strong formation of photochemical pollution, e.g., a threefold increase in ozone mixing ratios within the atmospheric boundary layer occur within 100 km downwind of Manaus while peak NO concentrations of >10 ppb near Manaus drop precipitously with travel distance. Particle number and mass concentrations are 10 to 100 times greater in the pollution plume compared to the times when pristine conditions prevail.

As a combined consequence of the meteorology, emissions, and chemistry, **the fetch of the main research site T3 in Figure 2 oscillates between the extremes of (a) a pristine atmosphere when the Manaus pollution plume meanders somewhat north or south and (b) heavy pollution and the interactions of that pollution with the natural environment when the plume conforms to its mean flow**. The distinct Manaus plume provides an opportunistic setting for a mechanistic evaluation of anthropogenic perturbations to the properties of the atmospheric particle population, including $n(d)$ (Fig. 5). Direct comparisons will be carried out between periods with pollution influence and those under clean conditions.

The wet and dry seasons (i.e., the two periods of the planned IOPs) offer an additional important scientific contrast. In the wet season, in regions outside of the Manaus plume, the Amazonia is one of the cleanest continental locations on Earth.[8,9] The particle population is in dynamic balance with the ecosystem (which produces them directly and indirectly) and the hydrologic cycle (which removes them). In the dry season, there can be extensive biomass burning in Amazonia, often ranging from a dominating perturbation at the southern edge of the Amazon basin to a diffuse elevation of background pollution in the central part of the basin where Manaus is located. There is also less removal by precipitation in the dry season. These spatial and temporal differences can dramatically affect the cloud-aerosol-precipitation interactions in the different seasons.[3,10]

An important factor affecting the steady-state number-diameter distribution of the atmospheric particle population is the rate of new particle production.[†] New particle formation is observed around the world in many forested environments. A mystery for Amazonia, however, is that in over one year of measurements there was an absence of new particle formation (NPF) events, at least right above the canopy.[12] NPF events are also scarce in pasture areas in Amazonia.[13]

[†] http://asr.science.energy.gov/science/working-groups/fg/docs/npf_fg_whitepaper.pdf, accessed 7 June 2013

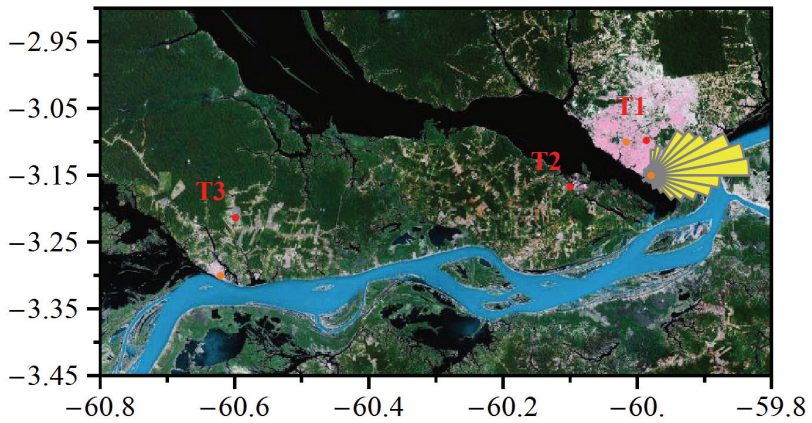

Figure 2. Map showing Manaus (pink) and the location of research sites. The **main research site T3** is downwind of Manaus and along the prevailing trajectory of pollution outflow. One year of 1-km winds is represented by the yellow inset. The westward orange dot shows the location of Manacapuru.

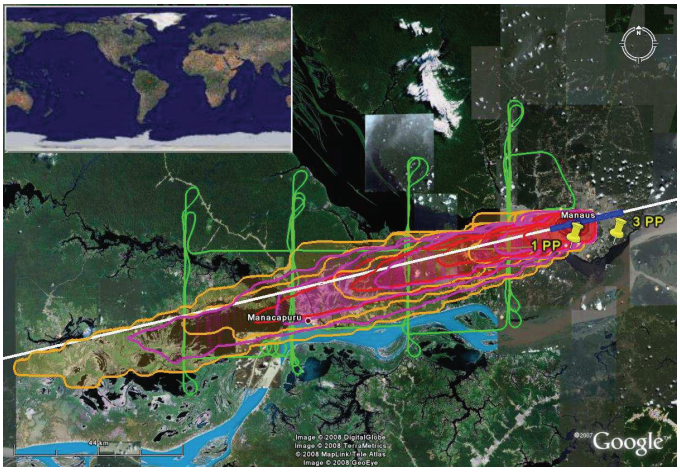

Figure 3. Land cover image with an overlay of a flight pattern on 19 July 2001 that samples the Manaus plume. Flight track data are shown in green line. The output of a HYSPLIT dispersion model run from the Manaus plume is indicated by the red/orange contour lines. The two yellow pins indicate the locations of power plants. The research site T3 is slightly north of Manacapuru. Figure is adapted from Kuhn et al.[11]

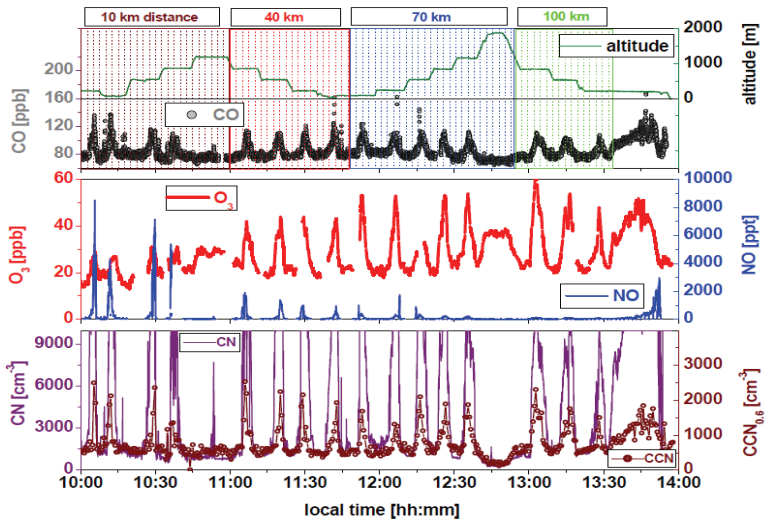

Figure 4. Time series of trace constituent measurements on plume transects on 19 July 2001, 10:00–14:00 LT. Vertical profiles of crosswind transects in the urban outflow are shown for successive distances (10, 40, 70 and 100 km) downwind of Manaus. Figure is adapted from Kuhn et al.[11]

Nevertheless, new particles must form somewhere in the Amazon basin in order to sustain the particle population, e.g., either by homogeneous nucleation or alternatively as primary emissions or a mix of the two depending on conditions. The prominent Aitken mode, especially in wet season, is consistent with NPF events. But what are the mechanisms of new particle formation in Amazonia, and why are they different from other forested environments?

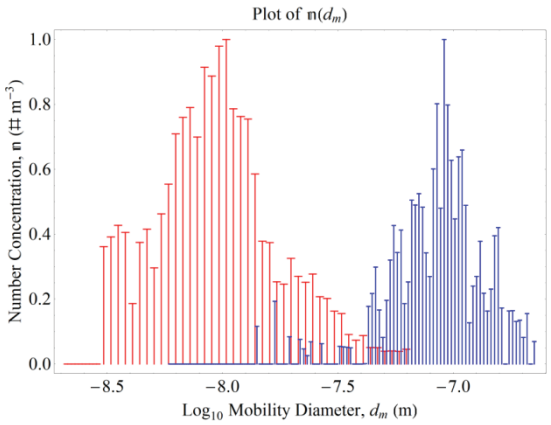

Figure 5. Examples of particle number-diameter distributions observed on 23 July 2012 inside Manaus (red) and 27 July 2012 at a clean site north of Manaus (blue). The x-axis represents particles of 3 nm to 250 nm (i.e., $10^{-8.5}$ to $10^{-6.6}$ nm). The y-scaling of the size distributions is normalized because the actual particle number concentrations in Manaus are more than 50× those of the clean site. The results show the presence of a large nano-mode in the Manaus urban environment that is entirely absent in the naturally functioning ecosystem of Amazonia. Source: S. Martin, J. Wang, R. Souza, P. Artaxo, Y. Ishida, J. Jimenez, private communication.

Compared to other parts of the world, large isoprene emissions from the Amazon forest might help to suppress NPF.[14,15] Global chemical transport models suggest another potential explanation for the absence of NPF in the Amazon basin: modeled H_2SO_4 concentrations are below the threshold of homogeneous nucleation. Alternatively, emissions of primary biological particles may be sufficient enough to scavenge gas-phase precursors and inhibit nucleation. In particular, a study by Poehlker et al.[16] suggests that aqueous particles formed as part of fungal spore emission evaporate to leave behind 10 to 20 nm dry cores that can serve as condensation nuclei for deposition of secondary organic material (i.e., diameter growth). According to Poehlker et al., these condensation nanoparticles can be distinguished by a highly enriched potassium content, in view of their ultimate origin from the aqueous detritus of fungal spore emission. As part of the proposed research, these different possibilities of the mechanisms of new particle formation in the tropical rain forest will be tested with the collected data sets.

Subsequent to NPF, the particles grow during their time in the atmosphere. The steady-state number-diameter distribution depends on the growth rate compared to the residence time of individual particles.[17] In Amazonia, particle growth is governed by production rates of secondary organic material, at least for natural conditions.[1,18] Data to this effect were a main result of the Amazonian Aerosol Characterization Experiment in 2008 (AMAZE-08) to the north of Manaus.[19] Secondary organic material results from the atmospheric oxidation of volatile organic compounds (VOCs) in the gas phase and in hydrometeors (i.e., cloud droplets). In natural conditions in Amazonia, biogenic VOCs (BVOCs) are emitted in great quantities and undergo oxidation principally with OH and to a lesser extent O_3. The oxidation pathways that transform BVOCs into particle-phase secondary organic material are not fully understood, especially for regimes like the tropical forest that are dominated by HO_2 pathways for the organic peroxy radical intermediates. Accurate implementation of particle growth rates and hence of $n(d)$ in a modeling framework necessitate an increased understanding of BVOC oxidation chemistry under natural conditions. Furthermore, the pathways can be greatly altered when affected by pollution, both because of anthropogenic VOCs as well as possible shifts in the dominant chemical mechanism from HO_2-dominant pathways that favor production of organic peroxides to NO-dominant pathways that recycle peroxy radicals into alkoxy radicals. As part of the proposed

research, these shifts due to anthropogenic perturbations will be investigated and better defined by the collected data sets, toward the final aim of predicting particle growth rates and thus differences in $n(d)$ under polluted compared to natural conditions of the tropical rain forest.

Biogenic-anthropogenic interactions have been a topic of intense investigation in temperate regions. Evidence from the northeastern USA,[20] southern USA,[21,22] and northern mid-latitudes,[23] and two global modeling studies,[24-26] have converged on the conclusion that interactions between urban anthropogenic emissions and a geographically dispersed pool of biogenic emissions can lead to a large enhancement of SOA production. Direct evidence of anthropogenic-biogenic interactions comes from ^{14}C observations that indicate that there is a large fraction of contemporary carbon in rural and remote areas when affected by episodic regional pollution (e.g., ref 23). Satellite retrieval of aerosol optical thickness has also been informative. Goldstein et al.[22] showed that the southeastern USA, which should be heavily affected by anthropogenic sulfate and to a lesser extent organic aerosol, instead has an aerosol optical thickness which follows the spatial, temporal, and temperature patterns of biogenic emissions. Although current models predict an enhancement of biogenic SOA in polluted regions via several mechanisms,[27] there are indications that in the real world the enhancement is much larger (e.g., ref 24). This topic will be thoroughly investigated by the comparison in the proposed project of data collected when the research site lies within the Manaus plume compared to when it is outside of it.

The proposed work, as its third component, has a focus on the upscaling of the data sets and findings concerning new particle formation and secondary organic aerosol production to the climatic effects. Principally, the additional organic material of biogenic-anthropogenic interactions can shift the mode diameter of the number-diameter distribution of the atmospheric particle population to larger diameters. In this way, it has the potential to influence downstream cloud microphysics.[28-31] The altered organic material can also shift the intrinsic CCN activity (i.e., solubility) of the particle components.[32-38] Quantifying and understanding these potential shifts in CCN activity because of anthropogenic modification of the natural atmospheric aerosol is a priority research focus of the proposed work.

An increase in the mode diameter, because of enhanced SOA production rates, to larger diameters implies a more CCN-active particle population because of the physics of particle activation.[39-44] The equation describing the relationship between the critical saturation ratio s_c of particle activation[‡] and the mass-equivalent diameter d_{me} of the dry particle for a water-soluble species can be expressed to first approximation for some idealized assumptions (not described herein), as follows:[45] $\ln s_c = C\, d_{me}^{-3/2}$, where C includes terms that describe the physical and chemical properties of the particle. Although the given relationship for s_c is defined for a purely water soluble material and for some idealized assumptions, the important point of the basic feature of a strong dependence on the dry particle diameter remains an overall true statement for more complex cases of partially water insoluble materials, uptake of gas-phase materials during growth, and refinement of idealized assumptions.[41,42,46] Therefore, anthropogenic influences that increase the growth rates of particles has the general effect of increasing the number of particles that activate for fixed s_c because of the shifts in the diameter distribution. A part of the proposed research project is to quantify how the increases in the rates of diameter growth that are produced by anthropogenic-biogenic SOA production (associated with the pollution plume) affect climatically relevant cloud properties. The topic is complex because of the intertwined effects of

[‡] The definition of s_c is that $s_c = 1$ at 100% RH, $s_c = 1.001$ at 100.1% RH, and so forth.

increase diameter growth, altered particle chemistry, and increased particle number concentration in the pollution plume.

Comparison among modeling results shows that GCM simulations are highly sensitive to changes in cloud properties such as droplet concentration, droplet effective radius, the shape of the distribution, and liquid water content.[47-49] Cloud microphysical regimes are most sensitive to shifts of increasing CCN concentration from a few hundred up to 1000 cm^{-3}, above which cloud droplet activation is insensitive to increasing particle concentration. For clean conditions in the wet season, total particle concentrations average around 300 cm^{-3} in Amazonia, which can be compared to contemporary background continental concentrations in the Northern Hemisphere of 2,000 to 3,000 cm^{-3}. Economic development in Amazonia can therefore be anticipated to shift background particle concentrations to values much higher than 300 cm^{-3}. Within the basin, both numerical simulations[50] and empirical studies[51] show that the sensitivity of precipitation to cloud microphysical properties is complex. Depending on environmental conditions, higher CCN concentrations can increase or decrease total precipitation, as well as affecting the timing of precipitation. The project presents a unique opportunity for exploration of cloud-aerosol-precipitation interactions over a tropical rain forest for which contrasting conditions of clean compared to polluted conditions are clearly and regularly delineated depending on the day-to-day variability in the position of the research site relative to the Manaus plume.

In respect to a broader context of scientific impact, the proposed studies, focusing on a clean tropical forest punctuated by episodic infusions of fresh pollution plumes, follow two related studies in temperate continental regions: a highly polluted environment of minimal BVOC emissions (CalNex 2010 in Los Angeles[§]) and a regionally polluted environment of high BVOC emissions (SOAS 2013 in Alabama[**]). The studies have in common a design to comprehensively examine how BVOC emissions and their interactions with anthropogenic pollution alter the atmosphere's oxidative capacity, influence secondary aerosol formation, atmospheric composition and, ultimately, affect the earth's radiation balance and climate. Although the three studies address many of the same key scientific questions, they do so in vastly different environments (i.e., GoAmazon2014: (case a) clean, high BVOCs and (case b) fresh pollution; CalNex: minimal BVOCs; SOAS: regional pollution, high BVOCs). The scientific concept is that data sets from contrasting environments lead to the potential for substantial and novel progress in addressing the common set of key science questions. As with previous campaigns, the resulting very rich data sets will become a community resource, and data analysis will involve collaboration with various experimental and modeling teams to advance understanding of the atmospheric particle population and its role in climate processes in these contrasting environments, especially for anthropogenically perturbed compared to natural conditions.

2. Project Objectives

The GoAmazon campaign seeks to quantify and understand how aerosol and cloud life cycles in a particularly clean background in the tropics are influenced by pollutant outflow from a large tropical city, all in the context of addressing the susceptibility of cloud-aerosol-precipitation interactions to present-day and future pollution in the tropics. Within this context of GoAmazon, the overall goals of the proposed research are (i) to measure and mechanistically understand the factors affecting the number-diameter distribution $n(d)$ of the atmospheric particle population

[§] http://www.arb.ca.gov/research/calnex2010/calnex2010.htm
[**] http://climate.envsci.rutgers.edu/SOAS/

over a tropical rain forest (especially the effects of anthropogenic pollution as a perturbation to natural state) and (ii) to develop and implement an upscaling analysis from this new data set and knowledge of $n(d)$ to prognosticate possible climatic impacts of present-day urban pollution and possibly greater pollution in the future. In relation to these goals, the proposed project has three objectives, as follows:

The **first objective** is to understand and quantify the interactions of biogenic and anthropogenic emissions with respect to the production of secondary organic aerosol. Hypotheses to be tested are that (i) a shift takes place under anthropogenic conditions in the fate of organic peroxy radicals from HO_2 to NO pathways (to be tested by gas-phase analysis by CIMS and PTR-MS; §3.1.3 and §3.1.4) leading to altered rates of particle growth (to be tested by number-diameter distribution measurement of MAOS and AAF; §3.1.1 and §3.1.2), (ii) a significant increase occurs under anthropogenic conditions in the total potential material that can ultimately condense after atmospheric aging to the particle phase (to be tested by the data set of the oxidation flow reactor; §3.1.6) as well as in chemical composition that can influence optical properties and CCN activity (to be tested by the data sets of MAOS and AAF; §3.1.1 and §3.1.2), and (iii) these significant changes in the atmospheric particle population can be monitored regionally by satellite (§3.2.2).

The **second objective** is to understand and quantify the mechanisms of new particle production over the tropical rain forest, both for natural and anthropogenically influenced conditions. Hypotheses to be tested are that (i) new particle formation occurs above the boundary layer (to be tested by aircraft observations of number-diameter distributions; §3.1.2), (ii) new particles are produced from the evaporation of the jet droplets from fungal spore emission (to be tested by nanoparticle analysis for potassium by the TDCIMS; §3.1.5), and (iii) an absence of sufficient H_2SO_4 concentration in the gas phase explains the differences for Amazonia compared to other observational sites worldwide (to be tested by gas phase analysis for H_2SO_4 by CIMS; §3.1.5). These hypotheses will be separately evaluated for conditions when the research site T3 is under influence or not of the plume from Manaus (i.e., natural compared to anthropogenically influenced conditions).

The **third objective** is to translate the new microphysical knowledge (i.e., as resulting from objectives #1 and #2) into a refined quantitative understanding of the links to climate. Hypotheses to guide the proposed upscaling analyses are that (i) microphysical modeling coupled with aircraft and ground site observations can prognosticate and validate the anthropogenic influence on cloud-aerosol-precipitation interactions associated with the Manaus plume (§3.2.1) and (ii) satellite-based products can be validated by in situ observations and subsequently used to provide a quantitative assessment of the regional effects of Manaus pollution (e.g., such as on direct and indirect radiative forcing, air quality, and human health, with a focus of the funded study on the first of these three; §3.2.2).

The proposed activities and associated three objectives, when taken together as a whole, respond to the **Thematic Area** of Atmospheric System Research (ASR) of DOE DE-FOA-0000919, FAPESP Chamada FAPESP 21/2013, and FAPEAM EDITAL N. 013/2013. With respect to **Science Areas** of those calls, the proposal will "improve understanding of the life cycle of aerosols… including the interaction of pristine and polluted air masses" (80% of proposed effort) as well as "improve understanding of the interaction of aerosols and clouds over the Amazon basin, including aerosol impacts on precipitation… as well as cloud impacts on aerosol transport, chemistry, and removal" (20% of proposed effort).

3. Approach (Methods)

The assembled team of Brazil and USA investigators has the wide range of expertise and experience to successfully and collaboratively achieve the objectives of the proposal.

- **Martin** (lead PI) has expertise in gas and aerosol chemistry and physics, specifically related to secondary organic aerosol production. He previously led the Amazonian Aerosol Characterization Experiment in 2008 (AMAZE-08) at a site north of Manaus. In conjunction with strong support from USA and Brazil collaborators, he wrote the proposal that led to GoAmazon2014/5, and he is Lead Scientist for it. He has published widely in the past five years with Brazil co-authors, including those of this proposal.
- **Souza** (PI, FAPEAM) has recently developed air quality and meteorological networks in and around Manaus. He has additional expertise in satellite-based observations of gases and aerosols, both of which are essential to providing regional context and upscaling to the data sets.
- **Barbosa** (PI, FAPESP) has expertise in atmospheric modeling, specifically related to radiation and cloud processes. He contributes leadership to the team in the observation and modeling expertise in cloud-precipitation-aerosol interactions. This contribution is essential for the upscaling analysis of the proposed work.
- **Guenther** has been a leader in measurements of biogenic chemical emissions and atmospheric transformation in tropical forest, including Amazonia, for nearly two decades. The gas-phase transformations are an integral aspect of the growth of particle diameter (i.e., influencing $n(d)$) by secondary organic aerosol production.
- **Jimenez** contributes deep expertise in aerosol analysis, chemistry, and transformations and previously participated in AMAZE-08, specifically related to SOA production.
- **Kim** is an expert in the gas-phase radical chemistry and brings to the team measurements capability in that regard so that the transformations from biogenic emissions from plants to atmospheric particles can be studied.
- **Pauliquevis** has expertise in modeling of CCN activity. He brings to the team research capability concerning the upscaling connections regulated by microphysics between aerosol size/ chemistry and cloud properties.
- **Rizzo**'s knowledge about number-diameter distribution dynamics of Amazonian particles will be essential for generalization of the measurements of the proposed study to broader spatial and temporal scales. She also has expertise on particle optical properties and will contribute to the assessment of direct impacts of natural/anthropogenic aerosols on climate.
- **Smith** is a leader in the analytical chemistry of freshly nucleated particles, and his contribution is key for elucidation of the pathways of new particle formation, i.e., a fundamental aspect of the number-diameter distribution of atmospheric particle population.
- **Tota** is an essential partner for measurement and knowledge of atmospheric species that participate in SOA production. He has worked in a wide range of tropical forests, and his contributions will be essential in upscaling and generalization of the proposed study's results.

3.1 *Datasets*

3.1.1 ARM Mobile Aerosol Observing System (MAOS)

Aerosol Properties

MAOS-A, MAOS-C, and AMF1 will be used for ground-site characterization of aerosols, clouds, radiation, and meteorology. A scanning mobility particle sizer (SMPS) and an ultra-high

sensitivity aerosol spectrometer (UHSAS) provide size distributions, ranging from 15 nm to 1 μm. A nanoSMPS (from Ciencia sem Fronteiras grant) measures particles from 3 to 150 nm. Size-resolved aerosol mixing state and hygroscopicity are measured using a humidified tandem differential mobility analyzer (HTDMA). A particle-into-liquid sampler (PILS) coupled to chromatographic analysis and an aerosol chemical speciation monitor (ACSM) provides particle chemical composition in real time. A cloud condensation nuclei counter (CCNC), coupled to a differential mobility analyzer (DMA), measures the size-resolved CCN activation of aerosols. A suite of instruments, including nephelometer, aethelometer, humidgraph, and multi-filter rotating shadowband radiometer (MFRSR), characterize aerosol optical properties. Scattering and absorption coefficients, single scattering albedo, hygroscopic response (i.e., "*f*(RH")), and AOD are measured. The micro-pulse lidar (MPL) maps the vertical distribution of aerosol and, under non-cloudy sky conditions, these data when combined with surface radiation data permit direct calculations of radiative heating; under cloudy sky conditions, the MPL data provide estimates of particle number being entrained into cloud base. Gases including carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), sulfur dioxide (SO_2), ozone (O_3), oxides of nitrogen (NO_x), and volatile organic compounds (VOCs) are measured by trace gas analyzers (including a LANL PICARRO cavity-ring down spectrophotometer) and a high-resolution proton-transfer mass spectrometer (PTR-MS). Accurate CO measurements are essential for distinguishing natural air masses (60 to 90 ppb CO in the Amazon basin) from those influenced by anthropogenic activities. Likewise, capability for NO_x measurement to 20 ppt is required. For ozone, values as low as 5 ppb must be accurately measured. These requirements are within the performance capabilities of the ARM instruments. A solar-tracking Fourier Transform Spectrometer (FTS) measures columnar concentrations of CO_2, CH_4, N_2O, CO, NO_2, and H_2O, as well as AOD. Of particular interest is the measurement of pollutant concentrations such as NO_2 and CO that are present in the Manaus pollution plume as well as of several organic species that are possible precursors to aerosol formation. This suite of measurements allows examination of the controlling processes for the production and aging of aerosols and identification of air masses.

Cloud properties

AMF1 includes a suite of active and passive remote-sensing instrumentation for the observation of clouds. The dual-wavelength Ka/W-band scanning cloud radar (Ka-SACR/W-SACR) with Doppler and polarimetric capability provides simultaneous observations of clouds and light precipitation over a 15-20 km range. The three-channel microwave radiometer (MWR3C; 20, 30, and 89 GHz) is a vertically pointing system that provides improved retrievals of integrated water vapor content and cloud liquid water path. The flexible, adaptive capabilities of these radars allow for dynamic operational scanning strategies to approach the cloud-scanning challenges in the Amazon basin. Measurements will include base radar and polarimetric moments (e.g., radar reflectivity at an estimated sensitivity of -30 dBZ at 10 km as well as radial velocity) and detailed Doppler spectra. AMF1 also includes a vertically pointing W-band cloud radar (WACR) that provides base radar moments and Doppler spectra, an MPL providing information on clouds in the vertical column, a ceilometer providing measurements of cloud base height (below approx. 7.5 km), and a Doppler lidar providing sub-cloud vertical velocities. The ARM Surface Meteorological Instrumentation provides 1-min statistics of surface wind speed, wind direction, air temperature, relative humidity, barometric pressure, and rain-rate. These data are employed to understand the basic atmospheric conditions near the surface and are crucial for modeling studies. Four times per day, radiosondes acquire profiles of temperature, humidity, and horizontal winds providing the basic data to understand atmospheric conditions. As a package,

this set of measurements provides a data set for testing the proposed microphysical modeling to connect measurements of aerosol properties with those of cloud properties under clean and polluted conditions.

3.1.2 ARM Aerial Facility (AAF)

During both IOPs, coordinated flights by the DOE G1 aircraft are planned. The aircraft payload[††] includes a range of instruments that further support the science goals of the proposed study, including basic tracers of air quality (CO, CO_2, SO_2, NO, NO_2, NO_y, and O_3). CO, SO_2, and the ratio CH_3CN/CO are tracers of urban, power plant, and biomass burning pollution, respectively. Measurements from a quadrupole PTR-MS will be used for identification and quantification of VOCs (biogenic + anthropogenic). Ratios of compounds that react at different rates such as NO_x/NO_y and benzene/toluene serve as photochemical clocks providing the exposure of emissions to OH radical. Information on atmospheric processing of isoprene is obtained by the product/parent ratio (methyl vinyl ketone + methacrolein)/isoprene. An HR-ToF-AMS will be used for mass spectral characterization of atmospheric particles, both to use signature to distinguish anthropogenic and biogenic SOA as well as elemental analysis of O:C and H:C ratios to characterize the extent of average extent of atmospheric aging of the particle population. Measurements will also be made of the number-diameter distributions of the particle population by fast integrated mobility spectrometer (FIMS) and optical properties by nephelometry and PSAP. CCN activity will be measured at multiple supersaturations.

Three sets of flight plans are in place for characterizing the plume: transverse cuts along the outflow from Manaus, longitudinal transects along the plume, and vertical profile through and above the boundary layer to characterize upward mixing. The plume will be crisscrossed at multiple downwind distances so that evolution of properties along the plume can be determined. The Manaus plume is well defined because of persistent easterly winds. An upwind transect as well as continuations of transects beyond plume boundaries will yield a direct comparison between pristine and polluted air masses. The aircraft will also fly along a gradient downwind of Manaus to capture the spatial extent of the plume. The aircraft data, by characterizing the position, extent, and properties of the plume (including chemical characterization with distance), will provide regional and vertical complementarity to the ground site measurements.

3.1.3 Chemical Ionization Mass Spectrometer (CIMS)

Deployment of a CIMS instrument is proposed for the quantification of the ambient concentrations of a suite of trace gases that, though of central importance for the processes controlling secondary aerosol production, are rarely measured, especially in a tropical forest environment. These species include H_2SO_4 (sulfuric acid), OH (hydroxyl radical), and HO_2+RO_2 (peroxy radicals). CIMS for H_2SO_4 quantification is based on an atmospheric pressure ionization method using NO_3^- to generate HSO_4^-. The ion detection system consists of a cluster-dissociation-chamber/octopole-ion-guide/quadrupole unit.[52] OH is measured by this instrument by adding excess isotope labeled $^{34}SO_2$ upstream of the sampling port and measuring the isotope-labeled $H_2{}^{34}SO_4$ produced in proportion to the OH concentration. The approach is highly sensitive and has been successfully used and evaluated during the past two decades.[53] The sum of HO_2 and RO_2 concentrations is measured by adding excess NO to convert these radicals to OH and then quantifying the amount of OH.[54] The CIMS approach is suitable for quantifying the

[††] Payload: http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/AircraftPayload.pdf, accessed 7 June 2013.

expected H_2SO_4, OH, and HO_2+RO_2 ambient concentrations in both the pristine Amazon and in highly polluted conditions. It has been successfully deployed in harsh and humid environments and in both extremely clean and highly polluted environments.[55] Calibration employs carbon-monoxide-scrubbed nitrogen as a matrix with humidity control for multi-point calibration.[56]

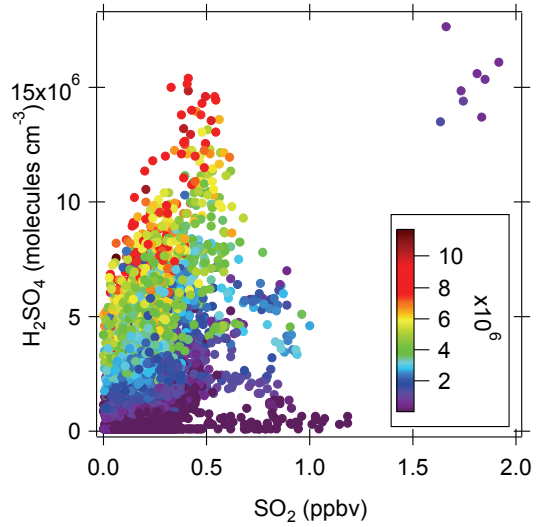

Figure 6. A correlation plot between ambient concentration of H_2SO_4 and SO_2. Color-coding denotes OH concentrations. The plot shows that ambient H_2SO_4 concentrations are limited both by SO_2 and OH concentrations (credit for SO_2 concentrations, Barry Lefer at University of Houston). Source: The Eagle Lake Air Quality Monitoring Site in Ft. Worth, Texas, in June 2011.

Achieving **objective 1** of the proposed project requires comprehensive observations of the key biogenic and anthropogenic precursors and atmospheric oxidants that interact to produce secondary aerosol. Observations of OH and HO_2+RO_2 provide key observational constraints for studies that form the basis for our understanding of the atmospheric oxidation processes of VOCs and subsequent secondary aerosol formation and growth.[57] The OH and HO_2+RO_2 observations will provide critical constraints on the atmospheric oxidation rates of the organic gases that are the precursors of the oxidized species that can condense and form aerosol matter.

Achieving **objective 2** of the proposed project requires key baseline information on the ambient concentration of H_2SO_4 in the tropical rain forest. This quantity has not been measured before for Amazonia. Although SO_2 is easier to measure and its measurement is also part of the suite of instrument in MAOS, Fig. 6 shows that SO_2 concentration measurements alone are not adequate for characterizing ambient levels of H_2SO_4, which can be limited by both SO_2 and OH under different conditions. Modeling studies suggest ambient H_2SO_4 concentrations under clean conditions in Amazonia are an order of magnitude lower than other continental regions because of an absence of sources and that these low concentrations are insufficient for new particle production by typical mechanisms.[58] However, this hypothesis, derived from modeling, remains to be tested. The proposed CIMS quantification of H_2SO_4 serves as a direct test of the hypothesis. Moreover, the perturbation by the anthropogenic influence of H_2SO_4 in the Manaus outflow can be assessed. This information is fundamental for delineating in any accurate chemical transport model the dominant mechanisms of new particle production, as perhaps by potassium salts formed from the evaporation of primary biological particles under clean conditions compared perhaps to pathways involving sulfuric acid under polluted conditions and as more prevalent in other parts of the world.

The H_2SO_4 measurements related to new particle production will be complemented by deployment of a Neutral and Air Ion Spectrometer (NAIS) at no cost to the proposal (Dr. Tuukka Petäjä; see letter of collaboration). The NAIS is an instrument that measures the number concentration of ambient neutral and charged particles in the diameter range from 1 to 40 nm. This capability is applied to measure the number concentration of freshly nucleated molecular clusters, which have physical diameters in the diameter range of 1 to 2 nm and thus cannot be

detected by conventional ultrafine condensation particle counters. This data set will be analyzed for time correlation with H_2SO_4 concentrations under polluted and clean conditions.

3.1.4 Temperature Profiler in front of Proton-Transfer Mass Spectrometer (PTR-TOF-MS)

Deployment of a temperature profiler[59] in front of a PTR-TOF-MS[60] is proposed for separation and differential classification of BVOC oxidation products. The aim is to elucidate the major products that occur under clean compared to anthropogenic conditions and how each chemical regime affects SOA production and possibly new particle formation. Keeping in mind that additional aspects may emerge during the course of project, at the outset the proposed project has a specific focus on isoprene photooxidation for two reasons. First, the reactive chemistry of isoprene represents an important source of SOA formation, particularly over tropical rainforest regions characterized by high isoprene emission.[61,62] Second, motivated in part by this observation, a laboratory study on temperature profiling from the Harvard Environmental Chamber (HEC) was recently undertaken.[59] This study can guide the data interpretation from Amazonia (Fig. 7). The temperature profiler is presently being deployed in SOAS (Tennessee site) as a dry run for Amazonia. A letter of collaboration from Tom Watson, mentor to the MAOS PTR-MS, is included in the appendix of this proposal.

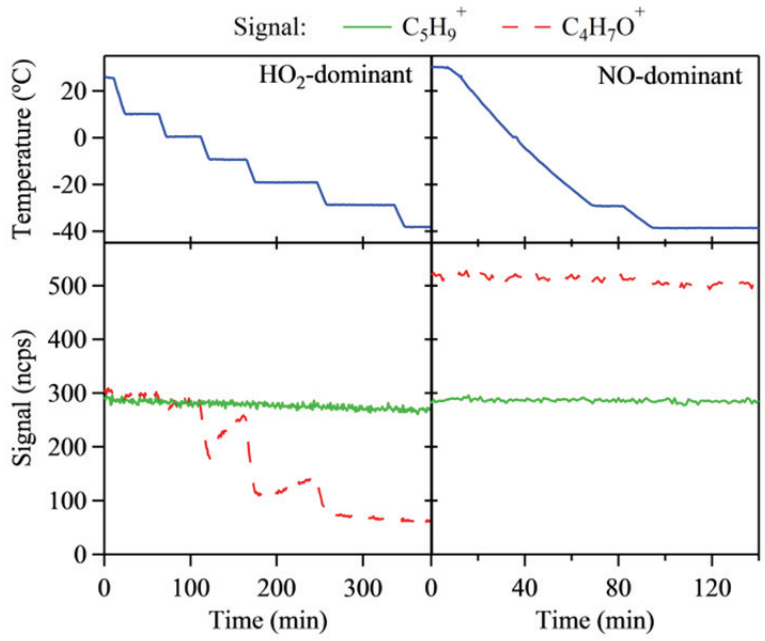

Figure 7. Time series of (top) trap temperature and (bottom) signal intensities of $C_5H_9^+$ and $C_4H_7O^+$ ions in PTR-MS for isoprene photooxidation experiments conducted in the Harvard Environmental Chamber. These ions nominally represent isoprene and the sum of MACR and MVK, respectively, and have been interpreted in this way in several field studies. Results are shown for HO_2- and NO-dominant conditions. The change in signals with temperature for HO_2-dominant conditions shows that for -20 °C and warmer the nominal signals have interferences, presumably from organic hydroperoxides produced by isoprene photooxidation. Adapted from ref 59.

The processes governing SOA formation from isoprene oxidation are only beginning to be understood.[63,64] The photochemistry of isoprene produces chemically different oxidation products depending on the fate of isoprene-derived peroxyl radicals. Under clean conditions characterized by sufficiently low NO_x concentrations, the reaction with HO_2 dominates the isoprene peroxyl chemistry, mainly forming hydroperoxides.[59,63] Further reaction of hydroperoxides produces epoxides, identified as important reactive intermediates of SOA formation.[64,65] In the presence of anthropogenic pollution, however, the reaction with NO dominates and hydroperoxides are not produced at high yield.[66]

The proposed deployment of the temperature profiler in front of the PTR-TOF-MS responds to **objective 1** to understand and quantify the interactions of biogenic and anthropogenic emissions

with respect to the production of secondary organic aerosol. Figure 7 shows the result of temperature profiling in the HEC under HO_2-dominant and NO-dominant conditions, representing extremely clean and polluted environments, respectively. Prior to the study, the $C_4H_7O^+$ ions in PTR-MS spectra had been exclusively attributed to and used to quantify isomeric MVK and MACR in field studies.[67] Figure 7 shows that this approach is not correct under clean conditions; the temperature profiling reveals that isoprene hydroperoxides fragment upon reaction with H_3O^+ to also produce $C_4H_7O^+$.[59] MVK and MACR are isolated by preconditioning the flow stream to -40 °C to selectively remove hydroperoxides. The abundance of hydroperoxides is semi-quantified by the difference in $C_4H_7O^+$ ion signals at low and high temperatures.

By providing the ratio of hydroperoxides signal to that of MVK and MACR, the data set from the temperature profiler during the GoAmazon IOPs will serve as an indicator of the relative importance of the HO_2 and NO reaction pathways of isoprene chemistry, i.e., as a measure of the extent to which an air parcel is anthropogenically influenced in regard to its BVOC chemistry. This metric is essential for understanding conditions relevant to SOA production. The data set, including a coupling of the temperature profiler to changes in full mass spectra, will also be interpreted with respect to the presence of organic hydroperoxides and epoxides, species both understood academically as integral to SOA production yet difficult to measure analytically under field conditions due to their low volatilities. The strategy is to analyze the difference spectra at different temperatures to inferentially study these semivolatile species.

3.1.5 Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)

Deployment of a TDCIMS instrument is proposed for online measurements of the chemical composition of nanoparticles as small as 10 nm and up to 50 nm at a time resolution of 20 min.[68,69] The TDCIMS instrument uses low-resolution electrostatic classification to select a mobility fraction of the atmospheric particle population, electrostatic precipitation to collect this fraction on a metal filament, resistive heating to desorb the chemical constituents of this fraction to the gas phase, and chemical ionization mass spectrometry to identify and quantify those constituents. Given its focus on nanoparticles, the instrument has been deployed in many locations to study the chemical processes that affect atmospheric new particle production.[70-73]

The proposed TDCIMS deployment responds to **objective 1** concerning the effects of anthropogenic and biogenic interactions on SOA production by analyzing the composition of nanoparticles under clean conditions and quantifying perturbations under times of anthropogenic influence.[71,74-76] One possibility that could be determined is that the anthropogenic component directly contributes to SOA, in which case the detected organic compounds differ from those of natural conditions. An alternate possibility is that the anthropogenic component indirectly contributes to SOA by more rapid conversion of biogenic gases into particle-phase material; in this case, the TDCIMS measurements could show only minor changes in chemical composition whereas concurrent SMPS measurement could show much more rapid diameter growth. Another possibility that could be determined is that H_2SO_4 condensation contributes strongly to particle growth; high sulfur diesel is an important source of electricity in Manaus. In short, the proposal is to use the molecular composition of sampled particles under different conditions of clean and polluted conditions to understand variability and dominance of different mechanisms of growth.

In relation to **objective 2**, the proposal is to use the TDCIMS to test specific hypotheses regarding new particle production in Amazonia and possible differences for clean and polluted

conditions. Poehlker et al.[16] put forth the idea that potassium salts formed from the evaporation of primary particles emitted by fungal spores provides a unique and important pathway for new particle production in the tropical rain forest of Amazonia. The data set of Poehlker et al., however, required extrapolation of measurements of particles of several hundred nanometers to implications for nanosize particle (i.e., new particles). The proposed deployment of TDCIMS is to directly test the idea of Poehlker et al. without the need for extrapolation across one to two orders of magnitudes in diameter. The proposal is to sample the positive-ion mass spectra of nanoparticles to analyze with high sensitivity for the presence and (according to Poehlker et al.) signature enrichment of potassium. The two stable isotopes of potassium aid in its quantification, and the proposed instrument is configured with a quadrupole mass spectrometer to maximize reliability and sensitivity for focus on a specific species (i.e., potassium). Conversely, under polluted conditions, the results of the analysis can contribute to the question of the relative roles of sulfuric acid compared to organic carboxylic acids in the perturbation of mechanisms of new particle production, e.g., to what extent is one enriched compared to the other.[70,72]

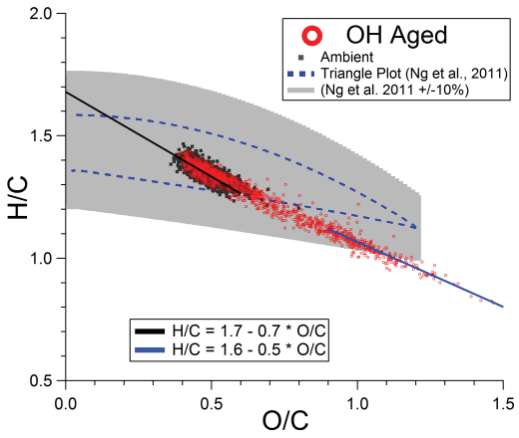

Figure 8. OFR-AMS results from BEACHON experiment conducted in a mountain pine forest.[84] A van Krevelen diagram of O:C vs. H:C atomic ratios of organic particles is shown for increasing OH concentrations produced by the OFR.

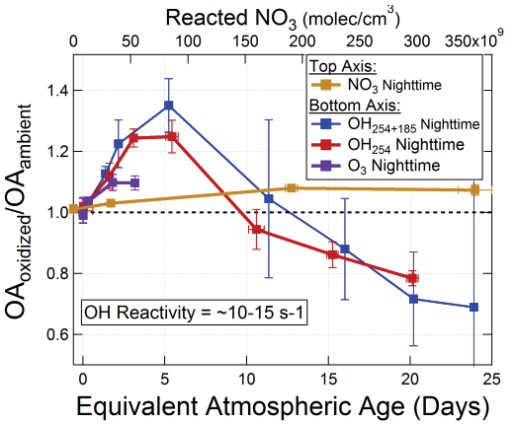

Figure 9. Ratio of mass concentrations of organic aerosol particles when oxidized in the OFR compared to ambient conditions. Data are from the BEACHON experiment during nighttime for different oxidants:[84] OH produced with and without 185 nm light, O_3, and NO_3. OH exposure led to the highest ratios and was the only oxidant that led to new particle formation. The x-axis represents equivalent atmospheric aging based on OH exposure.

3.1.6 Oxidation Flow Reactor (OFR) in front of Aerosol Mass Spectrometer (HR-TOF-AMS)

Deployment of an OFR in front an AMS and SMPS is proposed for characterization of SOA production and chemical evolution across atmospheric-equivalent ages of a few hours to a few weeks. The OFR is used to expose ambient air to varying degrees of oxidation by oxidants OH, O_3, and NO_3.[77-79] The OH radical dominates atmospheric oxidation in Amazonia under clean conditions, but O_3 and NO_3 can become important under polluted conditions. The flow reactor is employed using a valve switching schedule so that simulated atmospheric aging multiplexes among sampling (i) ambient, (ii) OH-processed, (iii) ambient, (iv) O_3-processed, (v) ambient, and (vi) thermal denuder-processed air. High OH concentrations are produced in the OFR by in situ photolysis of O_2 and H_2O. Externally produced ozone is introduced by direct injection into the OFR for investigating O_3-initiated oxidation. In conjunction with downstream AMS and SMPS measurements, changes associated with (i) to (vi) in particle mass concentration, particle number concentration, number-diameter distribution of the particle population, chemical composition, and oxidation state are characterized in real time. The approach has been

demonstrated for biomass burning smoke,[80,81] crude oil,[82] urban pollution,[83] and temperate forest environments.[84] Figures 8 and 9 show example results obtained using OFR-AMS in a pine forest. Exposure to additional oxidation in the OFR alters the oxidation state (Fig. 8) and total mass concentration (Fig. 9) of the aerosol particles because of additional BVOC oxidation. Sometimes oxidation can alternatively cause net loss in mass concentration at the highest exposures because of molecular fragmentation and subsequent evaporation. A new unique data set is anticipated for deployment in a tropical forest for contrasting conditions of polluted and clean conditions as part of GoAmazon.

Depending on prevailing wind speeds, the T3 research site is 2 to 6 hours downwind of Manaus. The OFR-AMS data set serves the purpose of considering longer range impacts of the Manaus pollution plume. The primary questions to be addressed with the data set are as follows: (1) How does the degree or type of anthropogenic influence affect the production of new particle mass on CCN-relevant aerosol particles compared to natural conditions? (2) Can the flow reactor be used as a predictive indicator of new particle formation potential? (3) Can these in situ and perturbation measurements be used to create parameterizations useful to climate models?

The OFR data set is important for achieving **objective 1**, i.e., quantifying and understanding how anthropogenic emissions influence SOA production in a biogenically rich environment. Understanding the shifts in particle mass concentration, chemical composition, and oxidation state upon oxidation and how these changes vary with air mass (i.e., extent of anthropogenic influence such as by SO_2 or NO_x concentrations) will provide time-resolved views of SOA production and properties as the intercepted airmass varies. Coincident characterization of unprocessed particle oxidation (O:C) and CCN activity, combined with the oxidant-processed data set, can be used to help predict chemical effects on CCN properties downwind of the site. The data set can also be correlated with observations of new particle production (**objective 2**). Taken together, the OFR-AMS and OFR-SMPS measurements add an additional time/space coordinate to the ground site by probing how SOA in different airmass changes under further oxidation. This wider-scale information represents an important data set for the upscaling integration and analysis of the proposed work (§3.2.1).

3.2 *Upscaling Integration and Analysis*

3.2.1 Microphysical modeling

The physical and chemical characteristics of the aerosol particles are crucial in their role as cloud condensation nuclei (CCN) and hence cloud formation. Despite their importance, these parameters are yet hard to measure and hence not very well known. This lack of knowledge explains in part why IPCC classified cloud-climate-interactions as the largest source of uncertainty in future climate projections[85] and general circulation models (GCM) do not simulate many cloud processes and feedbacks,[86,87] including the most recent simulations of the Coupled Model Intercomparison Project (CMIP5).[88] The aerosol effects on clouds may be due to changes on the thermodynamic profile[10,89] or changes on cloud microphysics.[90-93]

Differently from temperate latitudes, in the tropics rotational constraints are weak and perturbations from diabatic heating are rapidly redistributed over large distances. Therefore, models in the tropics depend on the parameterization of subgrid scale processes. These unresolved scales are those at which aerosol-cloud interactions take place, influencing the whole cloud life cycle. The proposed project focuses on understanding the interaction of aerosols and clouds over the Amazon basin, specifically how variability in the $n(d)$ of the particle population

for natural and polluted conditions as well as variability in the intrinsic effective hygroscopicity κ of the particles affects cloud properties.

The first impact of variability of aerosol properties on cloud properties is the effect on cloud base. In the case of clean Amazonia, cloud formation occurs in an aerosol-particle-limited regime (cf. Fig. 1). An aerosol-particle-limited regime means that for modest to vigorous updrafts the cloud droplet number concentration (CDNC) is dominated by CCN number instead of updraft velocity. This regime is different from most other continental areas worldwide, e.g., in Northern Hemisphere, where background aerosol particle number concentration is much higher than over Amazonia. However, even modest increases in aerosol particle number concentration in Amazonia could shift the activation mechanism to an updraft-limited regime, similar to other continental sites.[1,43] Thus, the first scientific question of the proposal upscaling analysis from the data sets under clean and polluted conditions (i.e., **objective 3**) is, "How much must the aerosol particle number concentration increase to shift cloud regimes in Amazonia?"

To answer this question, during IOPs a data set of the number-diameter distribution $n(d)$ of the aerosol particle population under variable natural and polluted conditions will be obtained. An additional data set will be obtained from a cloud condensation nuclei counter coupled to a differential mobility analyzer. From this data set, the size-resolved effective hygroscopicity parameter κ will be obtained. Based on the data sets of $n(d)$ and κ, microphysical modeling will be conducted for different case studies. The cloud droplet number concentration (CDNC) will be calculated using the parcel model *COGr-Model* ("CONdensational Growth Model"). *COGr-Model*, a particle tracer model, simulates the time evolution of cloud droplet number-diameter distribution by condensational growth. The trajectory history of each particle or group of particles is followed from the beginning to the end of the simulation. For each initial particle size class, a bin size is defined. The model solves numerically for each time step the diffusion equation for a supersaturated environment.[45] The droplet growth is driven by the difference between ambient supersaturation and particle/droplet critical supersaturation. The equation is similar to that used in Seinfeld and Pandis[45] but uses the κ-model parameterization for the determination of the critical supersaturation,[94] thus including chemical composition and curvature effects. Latent heat release effects are also taken into account.

The second scientific question to be addressed in further support of **objective 3** is, "For the shifts in cloud regime in variable natural and polluted conditions (i.e., the first scientific question), what is the follow-on effect on the cloud life cycle?" Changes in CDNC induce important changes in the time and height of rain in a convective cloud by several effects. In the warm rain phase, warm rain can be delayed and subsequently shift to mixed phase. In respect to the liquid water content (LWC), the postponing of precipitation induces higher LWC and consequently higher cloud albedo. These changes are especially critical for shallow convection in Amazonia formed by fair weather cumulus during the morning.[96] To address this question, the proposal is to employ a bin-microphysics scheme in a 2D model. Shallow clouds will be the focus of the study. The microphysics scheme is the TAU Cloud Microphysical Code.[97,98] It uses the method of moments to solve the stochastic equation for collection and breakup, thus explicitly conserving both mass and number of hydrometeors. Size distribution is divided into 34 bins with radius starting at 1.56 μm and doubling in mass for each next bin. Sedimentation is considered as a first-order upwind scheme. The standard version treats aerosol particles as ammonium sulfate with a log-normal distribution.[99] In the proposed work, this scheme will be modified to use the size-resolved and chemically resolved data sets to represent cases from the experimental site.

The dynamic framework of the model is the Kinematic Driver Model (KiD), developed by the Hadley Center-UK to facilitate a consistent intercomparison of the microphysics parameterizations in the context of GEWEX Cloud System Study.[100] The simulations domain will be aligned along the path of Manaus plume and driven by winds simulated by the Weather Research and Forecast (WRF) model. This approach is especially important in the case of GoAmazon due to the strong local effect of river breeze throughout daytime.

As a complementary effort to assess the effects of urban emissions not only on aerosol particle and cloud properties but also on precipitation chemistry, the proposed project will also examine the wet deposition of key species. Wet deposition is an important removal mechanism for pollutants in Amazonia, and the project will examine changes in precipitation chemistry before and after exposure to the Manaus plume. Deposition patterns will be separated for convective clouds compared to shallow clouds to examine the expected different effects of these regimes on chemistry. In this way, feedbacks will be examine of cloud-aerosol-precipitation interactions on aerosol particle chemistry (i.e., in the case that hydrometeors evaporate instead of raining out).

3.2.2 Satellite observations

Atmospheric particles can affect the climate system indirectly by changing cloud properties, such as cloud particle sizes, and therefore affect condensation and evaporation rates, latent heat release, collision coalescence efficiency, cloud reflectance, lifetime, and precipitation.[101,102] The accurate quantification of these aerosol effects, however, is still largely uncertain. One reason for the uncertainty in the so-called aerosol indirect effect is that it is extremely difficult to observe aerosol particles in the presence of clouds.[103] One way to infer the presence of aerosol particles inside or near clouds is to use an observable pollutant as a proxy for the particles. Anthropogenic fine-mode particles are formed directly and indirectly by combustion processes, and these are the same processes that lead to the emission of carbon monoxide (CO) into the atmosphere. Carbon monoxide is successfully monitored from space.[104,105]

The strategy of the proposed project is to use observations of carbon monoxide to expand the regional representativeness of the ground and aircraft measurements, including the associated implications of anthropogenic particles in the Manaus plume on climate-relevant quantities. Related to this strategy and in support of **objective 3**, the proposed project seeks to: (1) to validate the quality of CO retrievals from AQUA satellite over Manaus and surrounding grid points by use of in situ data, including profiles, especially from the AAF (§3.2.2) as well as column-concentrations from the FTS measurements (§3.2.1), (2) to establish the local sensitivity factor between CO and particle number and mass concentrations in the Manaus region, and (3) to use the CO satellite data in conjunction with the derived local sensitivity factor to project aerosol particle concentrations and their climatic effects over space and time downwind of Manaus.

To validate the quality of CO concentrations retrieved from AQUA satellite over Manaus and surroundings (activity #1), an intercomparison will be made of the CO concentrations observed by aircraft and those retrieved by AQUA. The atmospheric infrared sounder on the Aqua satellite retrieves CO profiles at a horizontal resolution of 45 km and a vertical resolution of up to 1 km from the surface through the atmosphere (Figure 10). The measurements for the aircraft campaigns will cover different flight altitudes (1500', 4000', 10000', and 18000'). One important approved flight plan for this activity will take place across metropolitan Manaus, downwind of Manaus over the main research site (T3) and beyond, and upwind of Manaus (cf. Figure 11). The satellite data will be matched to the flight track by averaging the AQUA profiles on the same

time and calendar day along the flight track. Likewise, aircraft observations from AAF will be averaged over the AQUA foot print for comparison. In addition, an averaged satellite profile in different levels will be interpolated to aircraft altitude. In a parallel activity, the data set of column-concentrations from the FTS measurements will be used for comparison to MODIS retrievals of the same.

With respect to activity #2, the proposed project will make use of the knowledge base and techniques that have been successfully applied previously with respect to the correlations between enhanced particle loadings and high CO concentrations.[106,107] Each region, however, needs a local sensitivity factor (i.e., empirical correlation) given that the mix of combustion sources varies (implying different amounts of CO and aerosol particles) and given that aerosol particles are subject to regionally variable removal processes, such as wet and dry deposition, whereas CO is not subject to these processes but instead to chemical sinks by reaction with OH. Hence, when and where CO can be used as a proxy for aerosol particle concentrations requires careful analysis. This activity (#2) will be executed toward the beginning of the proposed project, with analyses focusing on correlations among the different data sets, primarily those of the aircraft platform, complemented by MODIS and the different regional models that are part of GoAmazon.

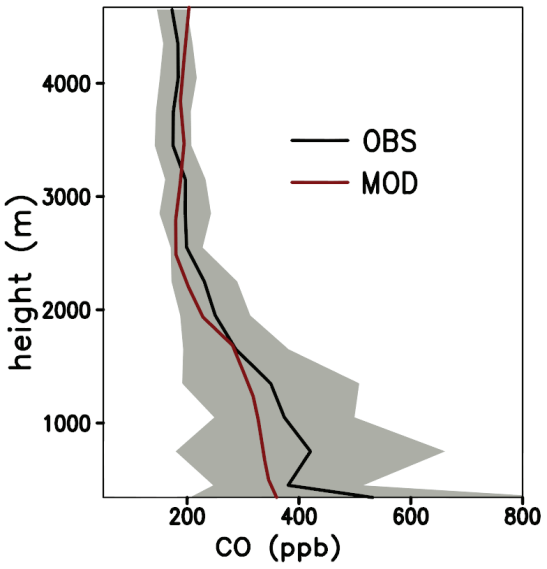

Figure 10. Comparison between the mean CO (ppb) observed during sixteen flights of the LBA-SMOCC/RaCCI field campaign (black solid line represents the mean while the grey zone shows the standard deviation range) and the mean of model results (red).[95]

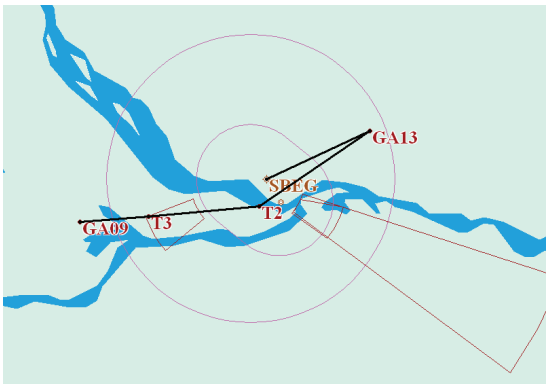

Figure 11. One of the approved flight plans for the AAF. Manaus is at location SBEG. The main research site is at T3. The flight plan represents vertical profiling along the dominant direction of the Manaus plume (see windrose in Fig. 2). Flight altitudes are 1500', 4000', 10000', and 18000'. Relevant data sets for §3.2.2 that will be collected along these profiles include (i) CO, NO, NO_2, SO_2, and O_3 concentrations for gases and (ii) number concentrations and size distributions $n(d)$ for particles.

With the local sensitivity factor in place, the next activity (#3) will be to project particle concentrations and their climatic effects over space and time downwind of Manaus, including comparisons with the particle effective size and AOD retrieved from MODIS as well as GoAmazon regional models. As a representation of the proposed approach, Jiang et al.[103] used the close correlation of CO with aerosol optical thickness to establish that polluted clouds (defined by high CO) have smaller cloud effective radii than the clean clouds (defined by low CO). The polluted clouds also had weaker precipitation than the clean clouds. The reduction of cloud particle size has important radiative and microphysical effects on climate that will be projected in the proposed project.

4. Timetable of Activities

Activity	YR1		YR2		YR3	
Record Data Sets						
• ARM Mobile Aerosol Observing System (MAOS)	×	×				
• ARM Aerial Facility (AAF)	×	×				
• Chemical Ionization Mass Spectrometer (CIMS)	×	×				
• Temperature Profiler in front of Proton-Transfer Mass Spectrometer (TP-PTR-MS)	×	×				
• Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)	×	×				
• Oxidation Flow Reactor in front of Aerosol Mass Spectrometer (OFR-AMS)	×	×				
• Satellite Observations	×	×				
Analysis and Publications						
• Objective 1 (MAOS, AAF, CIMS, TP-PTR-MS, TDCIMS, OFR-AMS) *Outcomes: process-level understanding and quantification of the interactions of biogenic and anthropogenic emissions with respect to the production of secondary organic aerosol and the climate-relevant number-diameter distribution n(d) of the atmospheric particle population for variable extents of anthropogenic compared to natural influence in the Manaus region.*			×	×	×	×
• Objective 2 (MAOS, AAF, CIMS, TDCIMS, OFR-AMS) *Outcomes: process-level understanding and quantification of the mechanisms of new particle production over the tropical rain forest and associated effects on the climate-relevant number-diameter distribution n(d) of the atmospheric particle population for variable extents of anthropogenic compared to natural influence in the Manaus region.*			×	×	×	×
• Objective 3 (microphysical modeling; satellite observations) *Outcomes: upscaling integration and analysis; microphysical predictions of shifts in cloud-formation regimes and droplet concentrations (i.e., cloud properties) for variable extents of anthropogenic compared to natural influence in the Manaus region; local sensitivity factor between CO and particle concentrations; projected aerosol particle concentrations and their climatic effects over space and time downwind of Manaus.*		×	×	×	×	×

5. Human Resources Development

Brazil-side partners, especially those in Amazonia, have emphasized that one of the greatest legacies of the GoAmazon experiment for the Amazonian and Brazilian community should be the expertise (both knowledge and training/education) that will be transferred through the joint work between Brazilian and foreign scientists and students. The present proposal therefore includes a comprehensive plan to this purpose. The overall project is strongly oriented to the training and teaching of students. The development of analytical methods and measurement capabilities, operation of a wide range of instruments over extended periods, and analysis of the large associated data sets will prepare students for a wide range of future technical careers.

Under the leadership of Prof. R. Souza (UEA, FAPEAM PI of present proposal), students and personnel of local major Universities and Research Centers are envisaged for inclusion in this project, including UEA, INPA, UFAM, SIPAM, EMBRAPA, and other organizations traditionally involved in the Amazon studies within LBA/INPA Program will be contacted. These organizations will be contacted, involved in the process, and requested to provide personnel (scientists and students). This aspect of outreach and inclusion is very important in the context of the long-term positive impact of GoAmazon in the state of Amazonas because the techniques and analysis for the physical/chemical characterization of the atmosphere are not well known by the Amazonas scientific community. Scientists and students will be involved in data collection, followed by post-processing of data after training by international counterparts.

This outreach effort, led by Souza in Amazonas, will be strongly supported by Barbosa (FAPESP, PI) from São Paulo. Barbosa and colleagues at the University of São Paulo (USP) already collaborate with all Amazonas institutions involved in this proposal. These colleagues from USP are registered as advisors at the graduate program (Climate and Environment Program - CLIAMB) from UEA-INPA. Five of these mentored students are currently involved in topics directly related to this proposal and will strongly profit from the project.

In addition to the research work, this proposal envisions a field course (open to a mix of USA, Amazonas, and São Paulo students) of one full week of both theoretical and practical, hands-on training. Scientists will give a complete description of the instruments of both the surface ARM and aerial AAF components. This course will be organized by the local participants (INPA and UEA) and is projected to have 20-25 students (MSc and PhD levels). It will be taken as a special course in CLIAMB at INPA/UEA in Manaus.

For the data analysis phase, an interchange of students (mainly PhD students) among the senior participants from Brazil and foreign counterparts will be established, identifying mutual interests and potential collaborations. From the Brazilian side, the "sandwich scheme" (usually promoted by CAPES and CNPq) can be used. Recently, the Federal Government of Brazil, through the Science and Technology Minister (MCT) has launched a program (*Ciência Sem Fronteiras - Science without Borders*; http://www.cienciasemfronteiras.gov.br/web/csf-eng/) that can distribute and sponsor scholarships for short duration courses (up to 1 academic year) outside of Brazil. Martin (PI, Harvard), for example, has thus far received three Brazilian students into his group for visits of 3 to 9 months. The USA-based PI's and collaborators of this proposal intend to serve as further hosts for additional students during the course of the proposed project. All costs are paid by the Brazilian government, and the Brazilian students act as bridge between USA-based and Brazilian-based scientists. In this way, the USA-Brazil network of partnerships will be enhanced by the proposed project.