DOE/SC-ARM-16-004

GoAmazon 2014/15: SRI-PTR-ToFMS Field Campaign Report

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March 2016

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

Executive Summary

Our science team, including Dr. Alex Guenther (previously at Pacific Northwest National Laboratory (PNNL) and now at the University of California, Irvine) Dr. Saewung Kim and Dr. Roger Seco, and Dr. Jim Smith (previously at NCAR and now at UC Irvine), deployed a selected reagent ion – proton transfer reaction – time-of-flight mass spectrometer (SRI-PTR-TOFMS) to the T3 site during the GoAmazon study. One of the major uncertainties in climate model simulations is the effects of aerosols on radiative forcing, and a better understanding of the factors controlling aerosol distributions and life cycle is urgently needed. Aerosols contribute directly to the Earth's radiation balance by scattering or absorbing light as a function of their physical properties and indirectly through particle-cloud interactions that lead to cloud formation and the modification of cloud properties. On a global scale, the dominant source of organic aerosol is biogenic volatile organic compounds (BVOC) emitted from terrestrial ecosystems. These organic aerosols are a major part of the total mass of all airborne particles and are currently not sufficiently represented in climate models. To incorporate quantitatively the effects of BVOCs and their oxidation products on biogenic organic aerosol (BOA) requires parameterization of their production in terrestrial ecosystems and their atmospheric transformations. This project was designed to reduce the gaps in our understanding of how these processes control BVOCs and BOAs, and their impact on climate. This was accomplished by wet and dry season measurements at the U.S. Department of Energy (DOE)'s Atmospheric Radiation Measurement (ARM) Climate Research Facility T3 site along with a comprehensive suite of complementary measurements. The specific goals were to 1) measure and mechanistically understand the factors affecting aerosol distributions over a tropical rain forest, especially the effects of anthropogenic pollution as a perturbation to the natural state, and 2) develop and implement an upscaling analysis from this new data set and knowledge of aerosol distributions to prognosticate possible climatic impacts of present-day urban pollution and possibly greater pollution in the future.

The SRI-PTR-TOFMS measured BVOC and oxidation products in support of the testing of the following hypotheses:

1. 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 SRI-PTR-TOFMS) leading to altered rates of particle growth (to be tested by number-diameter distribution measurement of MAOS and AAF).
2. 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) 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. These significant changes in the atmospheric particle population can be monitored regionally by satellite.

These hypotheses were 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 planned field observations during intensive operational period (IOP) I and II, post-field campaign calibrations, and preliminary data reports have been completed. We presented preliminary data analysis results in the 2014 and 2015 American Geophysical Union (AGU) Fall meetings and the GoAmazon

Science Meeting in Boston (May of 2015). We are in the process of preparing a couple of manuscripts to be submitted to the GoAmazon special issue in *Atmospheric Chemistry and Physics*.

Acronyms and Abbreviations

AGU	American Geophysical Union
ARM	Atmospheric Radiation Measurement Climate Research Facility
BOA	biogenic organic aerosol
BVOC	biogenic volatile organic compounds
CCN	cloud condensation nuclei
LIF	laser-induced fluorescence
NCAR	National Center for Atmospheric Research
OFR	Oxidation Flow Reactor
PNNL	Pacific Northwest National Laboratory
PTR-tof-MS	Proton Transfer Reaction Time-of-Flight Mass Spectrometer
SRI-PTR-TOFMS	Selected Reagent Ion–Proton Transfer Reaction–Time-of-Flight Mass Spectrometer
VOC	volatile organic compounds

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1.0 Background

GoAmazon 2014/2015 is a large-scale research initiative integrating field observation, process-level modeling, and regional climate modeling efforts to gain better understanding of how changes in natural and anthropogenic environmental factors will affect the regional climate (http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/WhitePaperonIrandubaManacapuruIOPGoAmazon2014.pdf) as shown in Figure 1.

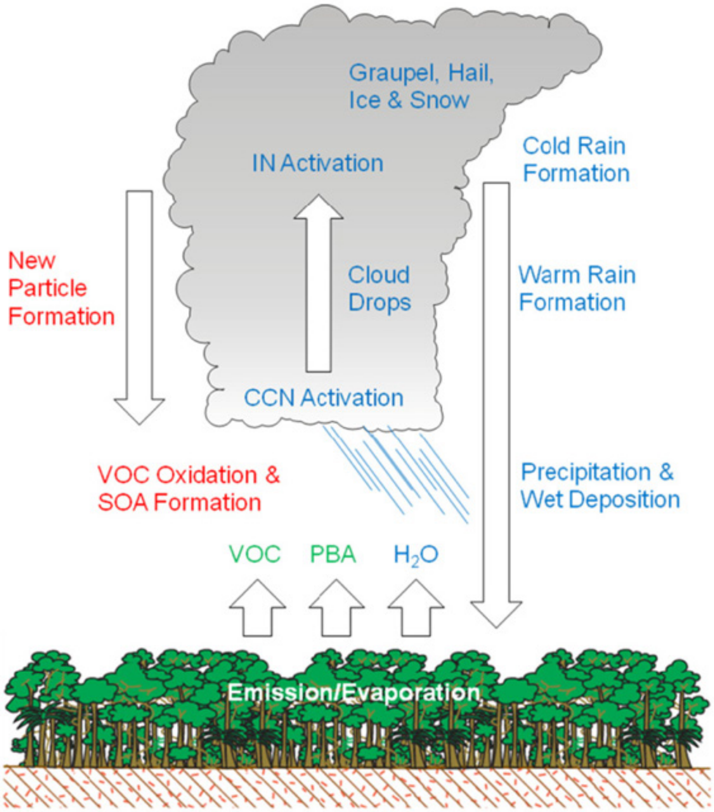

Figure 1. A schematic diagram showing interactions between chemistry-aerosol-precipitation over the tropical rain forest environment (Poschl et al. 2010).

The goal of our research team was to deploy a SRI-PTR-TOFMS and a CIMS system for hydroxyl radical (OH) quantification to experimentally constrain biogenic VOC chemistry in Amazonia. The photo-oxidation of VOCs especially biogenic origin is considered significantly contributing to cloud condensation nuclei (CCN) formation (Figure 1). However, recent field OH observations in pristine rain forest regions have consistently reported higher than expected OH (Lelieveld et al. 2008; Whalley et al. 2011). The very reactive nature of OH requires significant recycling sources to maintain enhanced levels (e.g., 3-10 x 10^6 molecules cm^{-3}) and it has been accepted that the NO mediated recycling process is the only recycling process (Levy 1971; Logan et al. 1981). Therefore, the enhanced OH concentrations in pristine rain forest environments with very low NO concentrations (<50 ppt) have caused us to explore unidentified OH recycling processes related to isoprene photo-oxidation processes because isoprene is the most dominant reactive trace gas in that environment (Archibald et al. 2010 and references therein). At the same time, investigations on potential positive artifacts on the laser-induced fluorescence (LIF) instrumentation has been conducted because the enhanced OH was all quantified by the technique (Mao et al. 2012). In addition, new particle formation events have not been observed in the Amazon rainforest environment. The most plausible speculative explanation has been below-threshold gas-phase sulfuric acid (H_2SO_4) levels, which are critical for the formation of gas molecule clusters (Spracklen et al. 2006).

Therefore, we deployed a proton transfer reaction time-of-flight-mass spectrometry (PTR-ToF-MS manufactured by IONICON Analytik, GmbH) to quantify and identify isoprene, isoprene oxidation products, other biogenic VOCs (BVOCs), and anthropogenic VOCs. In addition, we deployed OH CIMS instrumentation that can quantify both atmospheric OH and H_2SO_4 (Tanner et al. 1997). This was deployed to address the current uncertainty in photochemical processes over the Amazon rain forest region. The instrumentation was integrated in the DOE T3 site in Manacapuru, Amazonas, Brazil. This site is located in the east (~ 80 km) of Manaus, which is the most populated city in the Amazon. Therefore, we expected to sample various anthropogenic influences in the pristine rainforest background. We participated in wet- and dry-season intensives, IOP I (February-March, 2014) and IOP II (late August-early October, 2014), respectively. The preliminary data has been processed for IOP I; IOP II data processing has just finished and analysis has begun.

Team members are listed below:

Saewung Kim, PI, UC, Irvine; Roger Seco, Co-I, UC, Irvine; Jim Smith, Co-I, National Center for Atmospheric Research (NCAR), now at UC, Irvine; and Alex Guenther, Co-I, (PNNL), now at UC, Irvine).

2.0 Notable Events or Highlights

During both IOP1 and IOP2, the SRI-PTR-TOFMS was used to measure concentrations of the following VOCs: acetonitrile (often used as a biomass burning tracer), benzene (primarily from fossil fuel combustion and biomass burning), toluene (often thought to be primarily from fossil fuel combustion and biomass burning, but now recognized to have an important biogenic component), total monoterpenes (primarily biogenic), isoprene (primarily biogenic), MVK and methacrolein (primarily from isoprene oxidation in the atmosphere), acetaldehyde (various sources), acetone (various sources), and methanol (primarily biogenic). The SRI-PTR-TOFMS sampled from three locations and typically cycled sequentially among the three locations, which include the inlet and the outlet of University of Colorado Oxidation Flow Reactor (OFR) chamber and ambient air. The OFR inlet and outlet measurements were used along with aerosol chemical composition measurement to investigate the aerosol formation potential of known observed VOC with the aerosol formation observed in the OFR chamber. The results generally show that the known observed VOC cannot account for all of the measured secondary organic aerosol.

During IOP2, the SRI-PTR-TOFMS was used to separately measure two of the main isoprene oxidation products: MVK and methacrolein. The average diurnal profile of isoprene, MVK, and methacrolein are shown in Figure 2 and the ratios are shown in Figure 3. The ratios were used to estimate the photochemical lifetime of isoprene as shown in Figure 4. These results indicate that the average isoprene photochemical age follows a diurnal pattern with an age of about 5 hours in morning and evening and a peak of over 6 hours in midday.

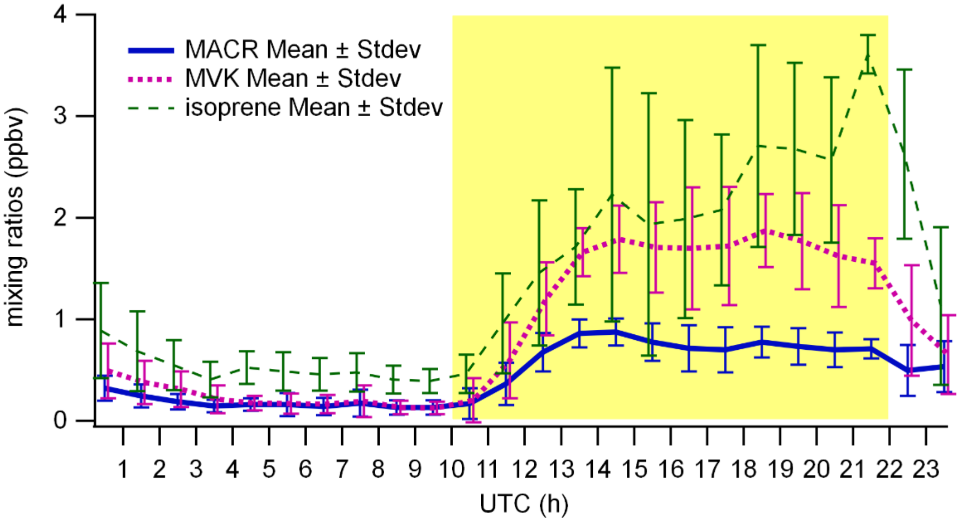

Figure 2. Average diurnal profile of isoprene, MVK, and methacrolein measured during GoAmazon 2014 IOP2. Yellow shading denotes daytime.

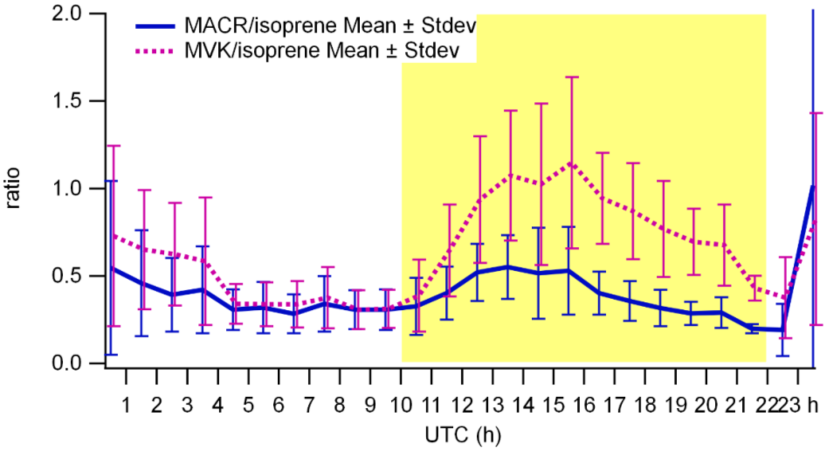

Figure 3. Average diurnal profile of the ratio of MVK and methacrolein to isoprene measured during GoAmazon 2014 IOP2. Yellow shading denotes daytime.

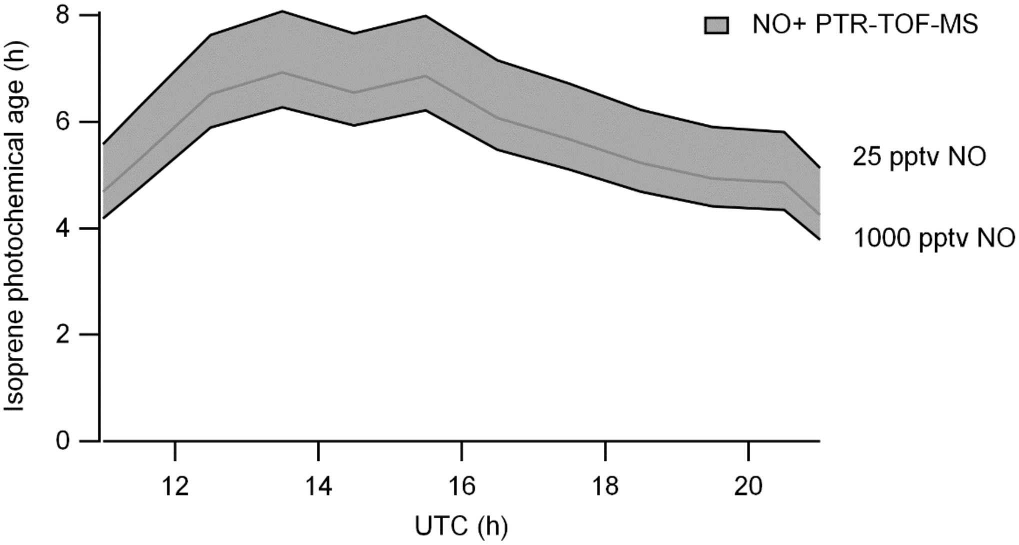

Figure 4. Average diurnal profile of isoprene photochemical age.

3.0 Lessons Learned

The ARM shipment for the hazardous material arrived at Manaus without any problems. However, other commercial gas shipments that vendors promised for timely deliveries did not pass through customs on time. We heard anecdotal stories that some investigators delivered their hazmat shipments from the U.S. In summary, it appeared that a group of knowledgeable shippers are capable of getting things through Brazilian customs. If ARM is committed/interested in future field observations in the Brazilian Amazon, compiling each investigator's successful or failed attempts at shipping would be highly beneficial to future missions.

4.0 Results

Brief scientific findings are provided in Section 2.0. We are developing several collaborative research journal manuscripts. We expect that our observational results could constrain uncertainty in our understanding of isoprene chemistry and SOA formation in Amazonia.

5.0 Public Outreach

Our research group participated in the open house event organized by ARM. In addition, we participated the National Geographic crew site visit in the beginning of IOP II.

6.0 GoAmazon Publications

6.1 Journal Articles/Manuscripts

Kim, S, et al. "Measurements of OH in the Amazon rain forest environment with various anthropogenic influences*,"* in preparation.

Seco, R, et al. "Measurement of isoprene and its oxidation product using NO^+ reagent ion – exploring potential artifacts in the application of H_3O^+ ion chemistry," in preparation.

6.2 Meeting Abstracts/Presentations/Posters

AGU Fall Meeting December 2014, San Francisco, CA

Seco, R, S Kim, et al. "Isoprene and its oxidation products in the rural atmosphere of the Amazon during the GOAmazon 2014/5 campaign," poster presentation.

Kim, S, R Seco, et al. "A comprehensive evaluation of H2SO4 formation from OH and sCI pathways in high BVOC environment," oral presentation.

GoAmazon Data Meeting, May 2015, Cambridge, MS

Seco, R, S Kim, et al. "Isoprene and its oxidation products in the rural atmosphere of Amazon during the GOAmazon 2014/5," oral presentation.

Kim, S, R Seco, et al. "Hydroxyl and sulfuric acid observations," oral presentation.

AGU Fall Meeting December 2015, San Francisco, CA

Kim, S, R Seco, et al. "OH observations in a tropical rain forest environment using a chemical ionization mass spectrometry technique during GOAmazon intensive."

Seco, R, S Kim, et al. "Volatile organic compound and oxidation capacity of the atmosphere in the Brazilian Amazon during the GoAmazon campaign."

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