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GoAmazon 2014/15 Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) Field Campaign Report

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Executive Summary

The Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) deployment to the U.S. Department of Energy (DOE)'s Atmospheric Radiation Measurement (ARM) Climate Research Facility T3 site in Manacapuru, Brazil, was motivated by two main scientific objectives of the Green Ocean Amazon (GoAmazon) 2014/15 field campaign. 1) Study the interactions between anthropogenic and biogenic emissions by determining important molecular species in ambient nanoparticles. To address this, TDCIMS data will be combined with coincident measurements such as gas-phase sulfuric acid to determine the contribution of sulfuric acid condensation to nucleation and growth. We can then compare that result to TDCIMS-derived nanoparticle composition to determine the fraction of growth that can be attributed to the uptake of organic compounds. The molecular composition of sampled particles will also be used to attribute specific chemical species and mechanisms to growth, such as the condensation of low-volatility species or the oligomerization of α -dicarbonyl compounds. 2) Determine the source of new ambient nanoparticles in the Amazon. The hypothesis prior to measurements was that potassium salts formed from the evaporation of primary particles emitted by fungal spores can provide a unique and important pathway for new particle production in the Amazon basin. To explore this hypothesis, the TDCIMS recorded the mass spectra of sampled ambient particles using a protonated water cluster Chemical Ionization Mass Spectrometer (CIMS). Laboratory tests performed using potassium salts show that the TDCIMS can detect potassium with high sensitivity with this technique.

We have completed processing of TDCIMS data and are participating in collaborative publication efforts as well as preparing a manuscript that will focus on TDCIMS observations. The latter will provide unique information on the molecular composition of ultrafine (sub-100 nm diameter) particles in the Amazon basin. The main findings are:

- Peaks in most detected compounds in ultrafine aerosol particles occur in “plumes” in early morning under stagnant wind conditions.
- Ultrafine aerosol particles are primarily composed of oxidized and nitrogen-containing organics, the latter includes cyanate (from isocyanic acid), which is likely linked to biomass burning.
- Particulate “potassium episodes” are observed occasionally. The source of these is still unknown.

Acronyms and Abbreviations

AC	alternating current
ARM	Atmospheric Radiation Measurement Climate Research Facility
CIMS	Chemical Ionization Mass Spectrometer
CNPq	Brazilian National Council for Scientific and Technological Development
DOE	U.S. Department of Energy
GoAmazon2014/15	Observations and Modeling of the Green Ocean Amazon2014/15
INPA	Instituto Nacional de Pesquisas da Amazonia, Brazil
IOP	intensive operational period
LBA	Large-Scale Biosphere Atmosphere Experiment in Amazonia
NCAR	National Center for Atmospheric Research
NPF	new particle formation
PAH	polycyclic aromatic hydrocarbon
TDCIMS	Thermal Desorption Chemical Ionization Mass Spectrometer
UEA	Universidade do Estado do Amazonia, Brazil
UFOPA	Federal University of Western Pará, Brazil
UPS	uninterruptible power supply

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1.0 Background

The Amazon rainforest is a unique and important place for studying aerosol formation and its impacts on atmospheric chemistry and climate. In remote areas, the atmosphere is characterized by low particle number concentrations and high humidity; perturbations in the particle number concentrations and climate-relevant physical and chemical properties could have a great impact on cloud formation and thus on regional climate and precipitation. While it was previously believed that new particle formation occurs rarely in the Amazon, observations in the Amazon of a sustained steady-state particle number concentration, along with an abundance of dry and wet surfaces upon which particles may deposit, imply that sources of new particles must exist in this region.

As part of the two Green Ocean Amazon (GoAmazon) 2014/15 Intensive Operational Periods (IOPs), the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) performed measurements of the molecular composition of 10-100 nm diameter particles. TDCIMS observations address two objectives of GoAmazon2014/15. For studying the interactions between anthropogenic and biogenic emissions, the TDCIMS quantifies the composition of nanoparticles that nucleate from anthropogenic emissions in neighboring urban areas such as Manaus, and the role of biogenic precursors in the growth of these particles. Coincident measurements of gas-phase sulfuric acid allow us to determine the contribution of sulfuric acid condensation to growth, which we can compare to TDCIMS-derived nanoparticle composition to determine the fraction of growth that can be attributed to the uptake of organic compounds. The molecular composition of sampled particles will be used to attribute specific chemical species and mechanisms to growth, such as the condensation of low-volatility species or the oligomerization of α -dicarbonyl compounds. The second objective of TDCIMS observations is to determine the source of new ambient nanoparticles in the Amazon. These measurements are used to test the hypothesis that potassium salts formed from the evaporation of primary particles emitted by fungal spores provides a unique and important pathway for new particle formation (NPF) in the Amazon. To explore this hypothesis, we obtained positive ion mass spectra of sampled ambient aerosol. Our tests performed using potassium salts show that the TDCIMS can detect potassium with high sensitivity; the fact that potassium has two stable isotopes aids in the identification of this ion.

The TDCIMS is conceptually simple: nanoparticles are charged and size-selected, and then collected on a metal filament. This sampling technique involves low-resolution mobility classification followed by electrostatic precipitation (Smith et al. 2004). The low-resolution mobility classification allows a sufficient mass of nanoparticles (10-100 pg) to be collected in sampling times of about 15-30 minutes, while ensuring that sampled particles fall within a well-determined size interval with no possibility of sample contamination by larger particles, which account for the vast majority of the mass. After the sample is collected, the filament is moved into an atmospheric pressure, chemical ionization source region. The filament is resistively heated by passing a constant or time-varying alternating current (AC) through it, thus heating and desorbing aerosol constituents. Desorbed molecules and decomposition products were ionized and ultimately detected using a quadrupole mass spectrometer (Extrel Corp.). Instrument backgrounds were assessed for each collection by performing the identical analysis without applying a collection high voltage. The TDCIMS is capable of detecting both positive and negative ions, but only one polarity can be monitored for each sample collected. Chemical ionization reagent ions are generated by an Am source kept in a clean flow of zero air. Impurity H_2O and O_2 in the N_2 gas result in $(\text{H}_2\text{O})_n\text{H}^+$ reagent ions for positive mode, and $(\text{H}_2\text{O})_n\text{O}_2^-$ reagent ions in negative mode.

Measurements took place at the T3 site, located near Manacapuru, Brazil. The instrument operated during the wet season (1 February-31 March 2014) and dry season (15 August-15 October 2014). Difficulties with intermittent and poor-quality power provided to the site (see Section 3) were significant during the wet season IOP, thereby reducing the number of days with high-quality data to 20 (10-30 March 2014). IOP2 was characterized by high levels of accumulation mode particles with diameter of 100-200 nm, most likely emitted by local and regional biomass burning activities. Because of the much higher particulate surface area present in the atmosphere-scavenged small particles, ultrafine particle concentrations were quite low during the dry season and presented major difficulties for collecting sufficient sample sizes for analysis. The number of days in which we obtained high-quality data during IOP2 was 14 (17-31 August 2014). In spite of these difficulties, we performed the first direct measurements of ultrafine aerosol particle chemical composition in the Amazon. A number of interesting observations emerged from these measurements, which we will highlight below.

We acknowledge the support from the Central Office of the Large-Scale Biosphere Atmosphere Experiment in Amazonia (LBA), the Instituto Nacional de Pesquisas da Amazonia (INPA), and the Universidade do Estado do Amazonia (UEA). The work was conducted under 001030/2012-4 of the Brazilian National Council for Scientific and technological Development (CNPq).

2.0 Notable Events or Highlights

The following observational highlights can be made from these TDCIMS measurements:

- Low levels of sulfate observed in nanoparticles confirms that sulfur-containing compounds, such as sulfuric acid, are not important contributors to ultrafine particle growth in this region.
- High levels of m/z 42, which can be attributed to cyanate, during the wet season (IOP1) suggest that compounds arising from biomass burning could play a major role in the formation of ultrafine particles in this region. This compound, which can be linked to health impacts such as cataracts and inflammation that can trigger cardiovascular disease and rheumatoid arthritis, has been observed previously in the gas phase (Roberts et al. 2011)
- Low levels of potassium measured by the TDCIMS suggest that the mechanism for ultrafine particle formation proposed by Poehlker et al. (2012), could be unique to certain environments in the Amazon Basin. Additional measurements in a greater variety of sites are needed to confirm this hypothesis.

3.0 Lessons Learned

While overall the campaign was successful, we can nonetheless provide feedback as to what we feel went well and what went wrong, which we hope will prove helpful to the ARM Facility in future campaigns. The following went well:

- The T3 IOP trailers provided an excellent base of operations. Although our instruments require a great deal of power, cooling was largely sufficient given the large number of heat-generating instruments in the building (this was partly due to the fact that our instrument was situated next to the

wall-mounted air conditioner). Space was also sufficient and the infrastructure provided by the ARM Mobile Facility was a huge benefit.

- Shipping our instrument to Brazil was very easy due to the work that the ARM Facility undertook to handle all shipping and customs clearance from the United States to Brazil.
- ARM staff were very pleasant and supportive.

The following went wrong:

- Research-grade instruments occasionally fail during every intensive campaign. GoAmazon2014/15 was no exception. Much of our effort focused on instrument repair of the TDCIMS.
- From the perspective of the TDCIMS, the performance of the backup generator during IOP1 was a real problem. Our special issue was that the TDCIMS required quite a bit of protected power, and the higher power Smart-uninterruptible power supply (UPS) was not an option for us because it would not switch back to the wall-socket power once the generator kicked on. In the end we found a work-around using several “dumb” smaller UPSs and other parts, but the AC voltage coming out of the wall sockets when the generator was running was really distorted (varied a lot in amplitude) and our UPSs did nothing to change that. So, when I was running on the generator power, I could see the panels of my instruments flickering at the same frequency as our room lights, which may have contributed to instrumentation problems later on during IOP2. The problem could have been solved with the purchase of a very expensive UPS, but this is not in our GoAmazon2014/15 budget and no additional sources of funding existed (such UPS units were extremely expensive in Brazil).

4.0 Results

Figure 1 shows an overview of the wet season particle size distribution together with pertinent meteorological parameters. Two major observations can be made that are relevant to particle formation processes: 1) the highest number concentrations of ultrafine particles, defined as those with diameters in the range of 10 to 100 nm, correspond to winds from the east, which is in the direction of Manaus; 2) wind speeds are very low at night, creating a stagnant air mass results in an increased influence of local emissions and atmospheric processes at the site. Figure 2 shows the diurnal pattern of ultrafine particles and ions observed in these particles by the TDCIMS in the negative ion mode, using $(\text{H}_2\text{O})_n\text{O}_2^-$ as the reagent ion. Ultrafine particle number concentration (upper left) shows a small diurnal trend that peaks in the evening hours and has a minimum in the morning (8:00-10:00 local time). In contrast to this, the peak concentration of many chemical species such as nitrogen-containing organic molecules (represented by the fragment ion cyanate, OCN^-) and oxygenated organic molecules (represented by hydrogen oxalate, HC_2O_2^- , and acetate, $\text{C}_2\text{H}_3\text{O}_2^-$) occur in the early morning hours between 2:00 and 6:00 local time. Sulfate (represented by bisulfate, HSO_4^-) is a relatively minor constituent during the period of these observations, and does not appear to exhibit any diurnal patterns. An interesting aspect shown in Figure 2 is that the clear diel pattern of acetate, cyanate, and oxalate does not appear similar to the ultrafine particle concentration. One interpretation is that the constituents that cause the peak in the number concentration in the evening, between 16:00 and 24:00, are not detected by the TDCIMS. This could include certain products of combustion such as long-chain alkanes or polycyclic aromatic hydrocarbons (PAHs) that are not detectable by our chemical ionization reagents. A peak of the detected compounds in the early

morning hours could be due to very calm wind conditions during that time, and could be aided by a lower boundary layer that traps locally produced ultrafine particles close to the ground.

Figure 3 shows the diurnal pattern of ions observed in particles by the TDCIMS in positive ion mode, using $(\text{H}_2\text{O})_n\text{H}^+$ as the reagent ion. While particulate “potassium episodes” were observed occasionally, they did not appear to have a diurnal pattern. The source of these is still not known. The ion identified as protonated 3-methylfuran (m/z 83) could be any C4-5 oxidized organic or a fragment of isoprene epoxydiols (Nguyen et al. 2014).

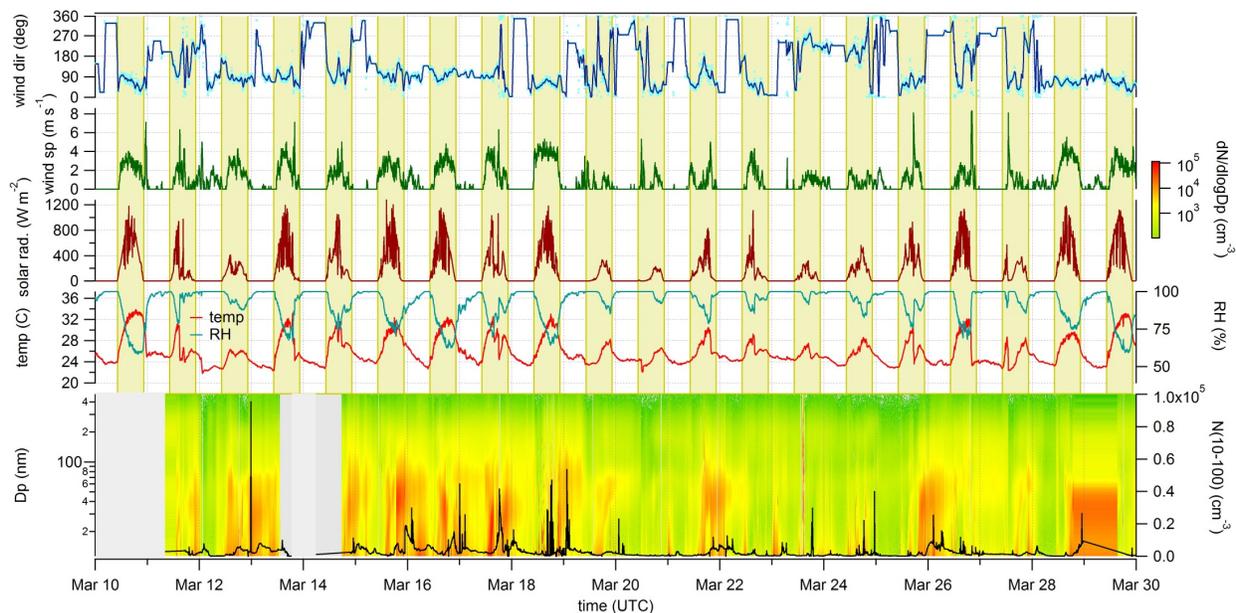


Figure 1. Meteorology (top panels) and particle size distribution with number concentration of 10-100-nm-diameter particles (bottom panel) during the IOP1 (10-30 March 2014).

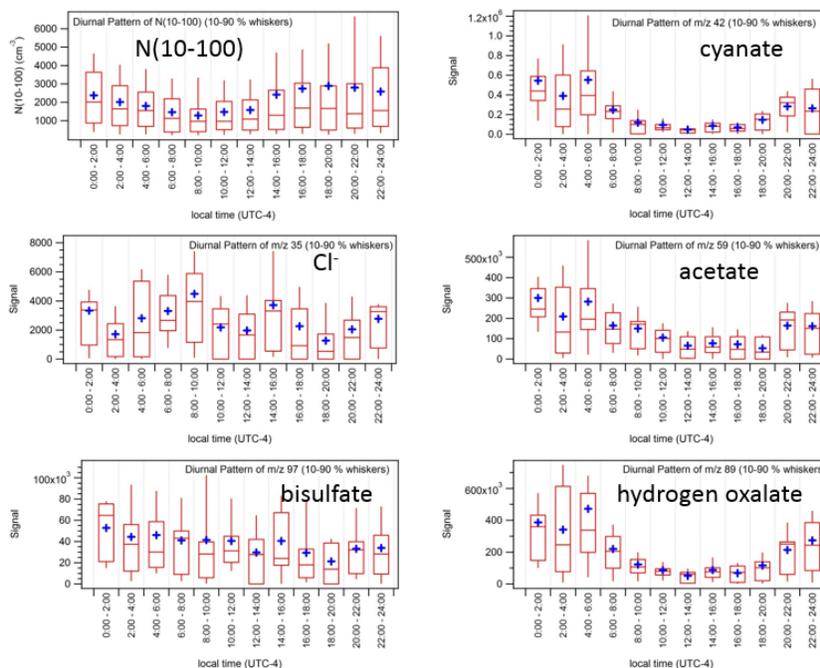


Figure 2. Diurnal variability of 10-100-nm-diameter particles (top left) and TDCIMS-measured negative ions abundance in particles during the wet season (IOP1, 10-30 March 2014).

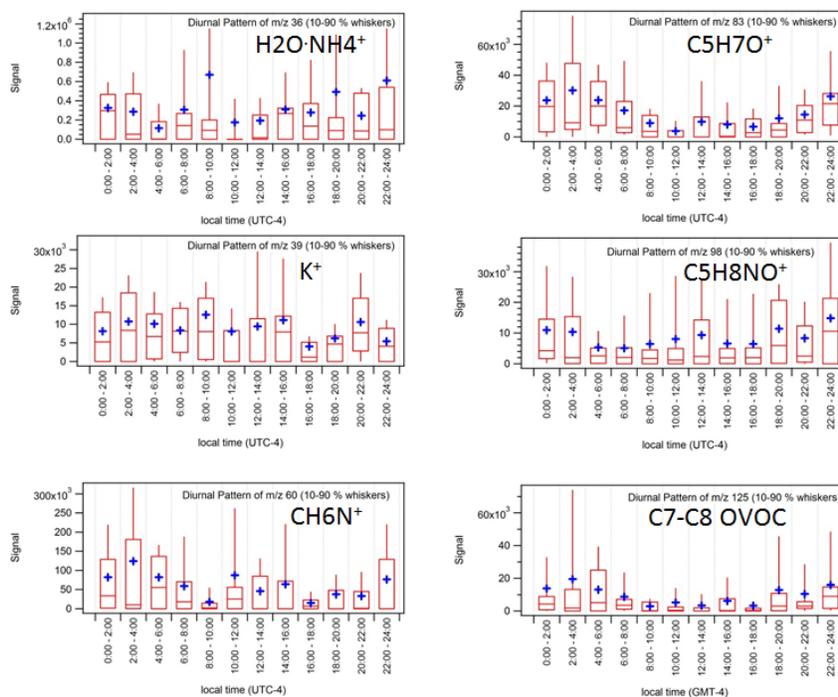


Figure 3. Diurnal variability of TDCIMS-measured positive ion abundance in particles during the wet season (IOP1, 10-30 March 2014).

Figure 4 shows an overview of the dry season particle size distribution together with pertinent meteorological parameters. The meteorology of this period shared some similarities to that shown in Figure 1 during the wet season. For example, nighttime was characterized by a stagnant air mass at the T3 site, which has implications on the influence of locale emissions on our measurements. The most significant differences between the two seasons are: 1) high number concentrations of larger (>100nm)-diameter particles during the dry season, and (2) lower concentrations of sub-100nm-diameter particles due to scavenging of these small particles onto the larger particles. Regarding the latter, the difference in the peak concentrations was approximately an order of magnitude, which made ultrafine aerosol particle analysis by TDCIMS a challenge.

Figure 5 and Figure 6 show the diurnal patterns of ions observed by the TDCIMS from collected ultrafine particles using negative and positive ion chemistries, respectively. These data can be directly compared to Figure 2 and Figure 3; when possible, the y-axis is scaled the same for each ion to make differences more apparent.

The number concentration of 10-100 nm diameter particles during the dry season (Figure 5, upper left plot), shows a diurnal pattern similar to that of the wet season (Figure 2, upper left plot). The main difference, as mentioned above, is the much lower concentration during the dry season caused by scavenging to a large 100-200 nm-diameter mode. The most dramatic difference can be seen in the negative m/z 42 ion that we associate with cyanate (Figure 5, upper right plot), which was the major ion observed during the wet season. Unlike the wet season, a strong diurnal pattern is seen for the measure ions during the dry season. However, a weak diurnal pattern can be identified for some ions such as cyanate, acetate, $C_5H_8NO^+$, K^+ , and C7-C8 OVOC that can be characterized by small peaks in total concentration during the morning and evening hours.

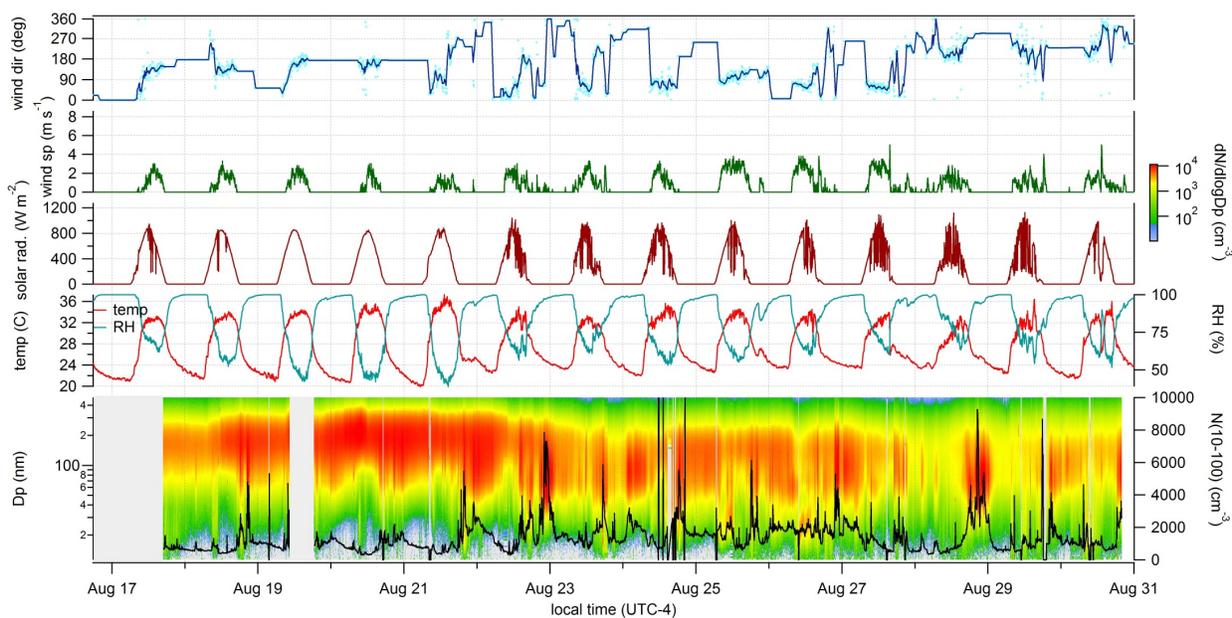


Figure 4. Meteorology (top panels) and particle size distribution with number concentration of 10-100-nm-diameter particles (bottom panel) during the dry season (IOP2, 17-31 August 2014).

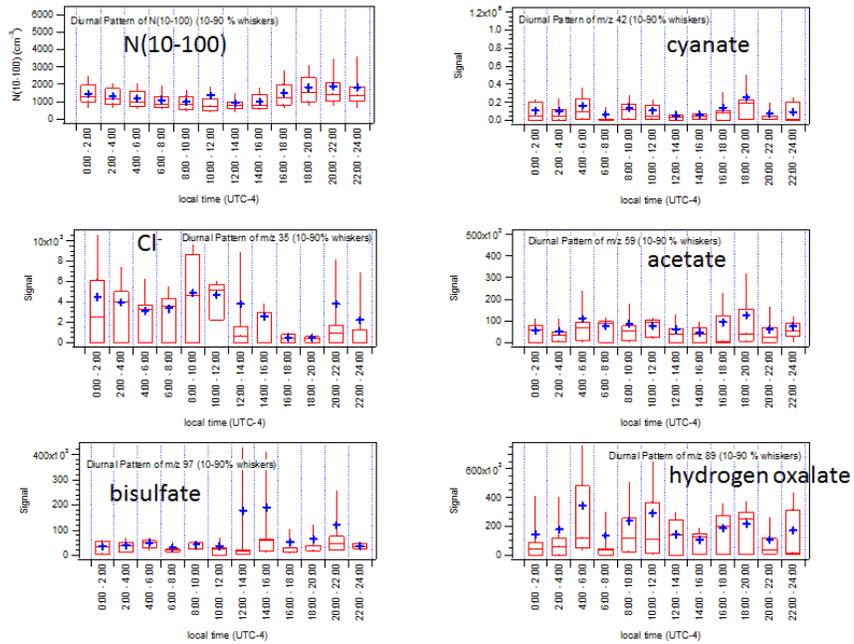


Figure 5. Diurnal variability of 10-100-nm-diameter particles (top left) and TDCIMS-measured negative ions abundance in particles during the dry season (IOP2, 17-31 August 2014).

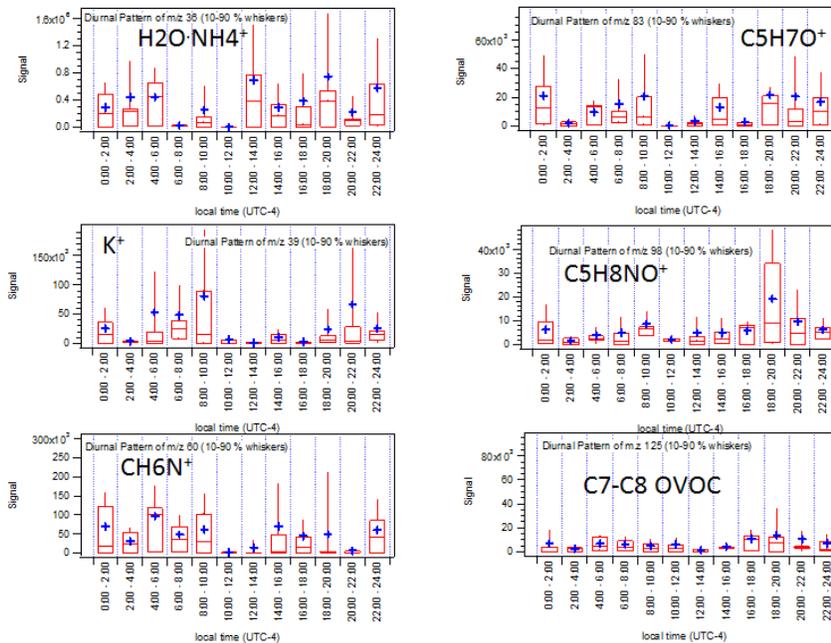


Figure 6. Diurnal variability of TDCIMS-measured positive ion abundance in particles during the dry season (IOP2, 17-31 August 2014).

5.0 Public Outreach

Our activities during GoAmazon2014/15 included close collaborations with our Brazilian colleagues and the education and mentoring of Brazilian students associated with their research groups. These are expected to develop further during the remaining years of the project and beyond.

Three Brazilian graduate students have played a particularly active role in this work thus far: Sarah Batalha of the Federal University of Western Pará (UFOPA), Eliane Alves of UEA and INPA, and Marinete Souza of UEA.

6.0 Publications

6.1 Journal Articles/Manuscripts

Wang J, R Krejci, S Giangrande, C Kuang, HMJ Barbosa, J Brito, J Comstock, M Krüger, J Lavric, K Longo, HE Manninen, AO Manzi, F Mei, C Pöhlker, B Schmid, RAF Souza, S Springston, J Tomlinson, T Toto, D Walter, D Wimmer, JN Smith, M Kulmala, LAT Machado, P Artaxo, MO Andreae, T Petaja, and ST Martin. “Vertical transport during rainfall sustains aerosol concentration in Amazon boundary layer.” *Nature*, submitted 2015.

Martin ST, P Artaxo, L Machado, R Souza, C Schumacher, J Wang, MO Andreae, HMJ Barbosa, J Fan, G Fisch, A Goldstein, A Guenther, J Jimenez, MA Silva Dias, JN Smith, and M Wendisch. “Introduction: Observations and modeling of the Green Ocean Amazon (GoAmazon2014/5).” *Atmospheric Chemistry and Physics*, submitted 2015.

6.2 Meeting Abstracts/Presentations/Posters

“Mechanisms for the formation and growth of nanometer-sized particles in the Amazon: Insights from GoAmazon2014 and the Tapajós Upwind Forest Flux Study (TUFFS).” Aerosol Physics Seminar, Kuopio, Finland, June 3, 2015.

“What are GoAmazon measurements telling us about the sources of ultrafine aerosol particles in the Amazon?” GoAmazon Science Team Meeting, Boston, MA, May 18, 2015.

“Recent research and future plans involving land ecosystem atmosphere processes.” Land Ecosystem—Atmosphere Processes Workshop, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, WA, March 9, 2015.

Smith, JN, JH Park, C Kuang, JOV Bustillos, RAFD Souza, KT Wiedemann, JW Munger, SC Wofsy, LV Rizzo, P Artaxo, ST Martin, R Seco, S Kim, AB Guenther, SSA Batalha, EG Alves and J Tota.

“Mechanisms for the formation and growth of nanometer-sized particles in the Amazon: Insights from GoAmazon2014 and the Tapajós Upwind Forest Flux Study (TUFFS).” American Geophysical Union Fall Meeting, San Francisco, CA, December 15, 2014.

<http://adsabs.harvard.edu/abs/2014AGUFM.A13O..08S>

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Pohlker, C, KT Wiedemann, B Sinha, M Shiraiwa, SS Gunthe, M Smith, H Su, P Artaxo, Q Chen, Y Cheng, W Elbert, MK Gilles, ALD Kilcoyne, RC Moffet, M Weigand, ST Martin, U Poschl, and MO Andreae 2012. "Biogenic potassium salt aerosols as seeds for secondary organic aerosol in the Amazon." *Science* 337(6098): 1075-1078, [doi:10.1126/science.1223264](https://doi.org/10.1126/science.1223264).

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Smith, JN, KF Moore, PH McMurry, and FL Eisele. 2004. "Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry." *Aerosol Science & Technology* 38(2): 100-110, [doi:10.1080/02786820490249036](https://doi.org/10.1080/02786820490249036).



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