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Harvard Bounce Apparatus GoAmazon 2014/15 Field Campaign Report

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Executive Summary

The effect of relative humidity (RH) on the physical state of particulate matter during the GoAmazon 2014/15 campaign was investigated through the use of particle rebound (or lack thereof) during impaction. The physics governing particle rebound have been previously modeled and can be attributed to the surface and material properties. The physical state of secondary organic material is regulated by several factors, including the local RH, the recent RH history in the case of hysteresis, and chemical composition. Across the range of atmospheric RH, hygroscopic water uptake can occur and transitions from higher to lower viscosity phases are possible.

By varying the particulate matter water content and observing particle rebound as a function of RH, the phase state of the organic material under investigation can be determined. Custom-made impactors were employed to study the effects of RH (up to 95%) on the particle physical state. Results inferred from the particle rebound measurements indicate that, under ambient conditions (RH >80%), particulate matter in Amazonia can be considered in a liquid phase state. However, during certain time periods, a fraction (10 to 30%) of particulate matter is found to rebound during the highest RH conditions, which indicates the presence of hydrophobic particles. The source of the hydrophobic particulates appears to be anthropogenic, from either biomass burning or the Manaus plume.

Acronyms and Abbreviations

AMF1	First ARM Mobile Facility
ARM	Atmospheric Radiation Measurement Climate Research Facility
CNPq	Brazilian National Council for Scientific and Technological Development
DOE	U.S. Department of Energy
INPA	Instituto Nacional de Pesquisas da Amazonia
IOP	intensive operational period
LBA	Large Scale Biosphere Atmosphere Experiment in Amazonia
PM	particulate matter
RH	relative humidity
SOM	secondary organic material
UEA	Universidade do Estado do Amazonia
UTC	Coordinated Universal Time

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1.0 Background

Particulate matter plays a key role in climate and air quality by scattering/absorbing radiation and serving as cloud condensation nuclei (Andreae and Rosenfeld 2008). The magnitude of climate-relevant perturbations depends on particle size, particle chemical composition, hygroscopic growth, and phase state, among other factors (Andreae and Rosenfeld 2008; Hallquist et al. 2009). Recent studies suggest that a particle phase transition from liquid to semisolid/solid phase states can alter chemical reaction pathways by shifting from absorption to adsorption mechanisms (Kuwata and Martin 2012; Shiraiwa et al. 2011; Tong et al. 2011; Zobrist et al. 2011). As a result, parameters that depend on rates of molecular diffusion in the particle and on the surface, such as particle growth mechanisms (Perraud et al., 2012), uptake of gas-phase species (Kuwata and Martin 2012; Shiraiwa et al. 2011), and transport of pollutants (Friedman et al., 2014; Zelenyuk et al. 2012), depend on the particle phase state.

The phase state of aerosol particles is a strong function of particle water content because of the hygroscopic nature of its constituents. Previous findings for measurements in a boreal forest of northern Europe reported semisolid/solid particles (Virtanen et al. 2010). It has recently been hypothesized that ambient particles in Amazonia, however, would be in a predominately liquid state because of the isoprene-dominant biogenic output and high ambient relative humidity (RH) (Bateman et al. 2014; Song et al. 2015). This hypothesis is supported by chamber-generated secondary organic material (SOM) measurements, while atmospheric particulate matter (PM) is far more complex. The most common chemical composition of sub-micrometer aerosol particles is an internal mixture of inorganic salts, organic compounds, and water (Chen et al. 2009; Murphy et al. 1998; Pratt and Prather 2010). Indirect literature evidence exists that supports the hypothesis of liquid particles in central Amazonia (Chen et al. 2014; Pöschl et al. 2010).

The GoAmazon 2014/15 campaign was carried out to determine the particle physical state in situ and the particle physical state above a tropical forest. The campaign was conducted at the Manacapuru, Brazil, site collocated with deployment of the U.S. Department of Energy's (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility's First ARM Mobile Facility (AMF1). The Harvard Bounce Apparatus was deployed during the time periods of February 1 through March 31, 2014 (intensive operational period [IOP]1) and August 15 through October 15, 2014 (IOP2). The campaign was a collaborative effort among DOE investigators and Brazilian co-investigators Paulo Artaxo (University São Paulo), Rodrigo Souza (Amazonas State University), and Antonio Mani (National Institute of Amazonian Research). The measurements were conducted by Adam Bateman, a postdoctoral associate in the research group of Principal Investigator Scot Martin (Harvard).

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

There were a number of events when the generator was running and the wind direction brought the fresh emissions towards the inlet of our instrument. We were able to measure the fresh emissions and thus were

given an indication of how the instrument would respond to fresh soot emissions. The response included a large number of particles that passed the differential mobility analyzer that had aerodynamic diameters vastly different from the majority of the ambient particles. The presence of these particles likely were due to the contribution of fresh uncoated soot with fractal-like particle sizes. These particles also were highly hydrophobic.

3.0 Lessons Learned

During IOP1, the generator was of poor quality, and normal operations were routinely impacted by maintenance or adjustments that needed to be made to the generator.

4.0 Results

All data obtained in the wet and dry seasons are shown in Figure 1a and Figure 1b. The data points are colored according to the apparatus RH, which was routinely scanned from ~25 to 95% RH on a timescale of a few hours during IOP1 and less than 1 hour during IOP2.

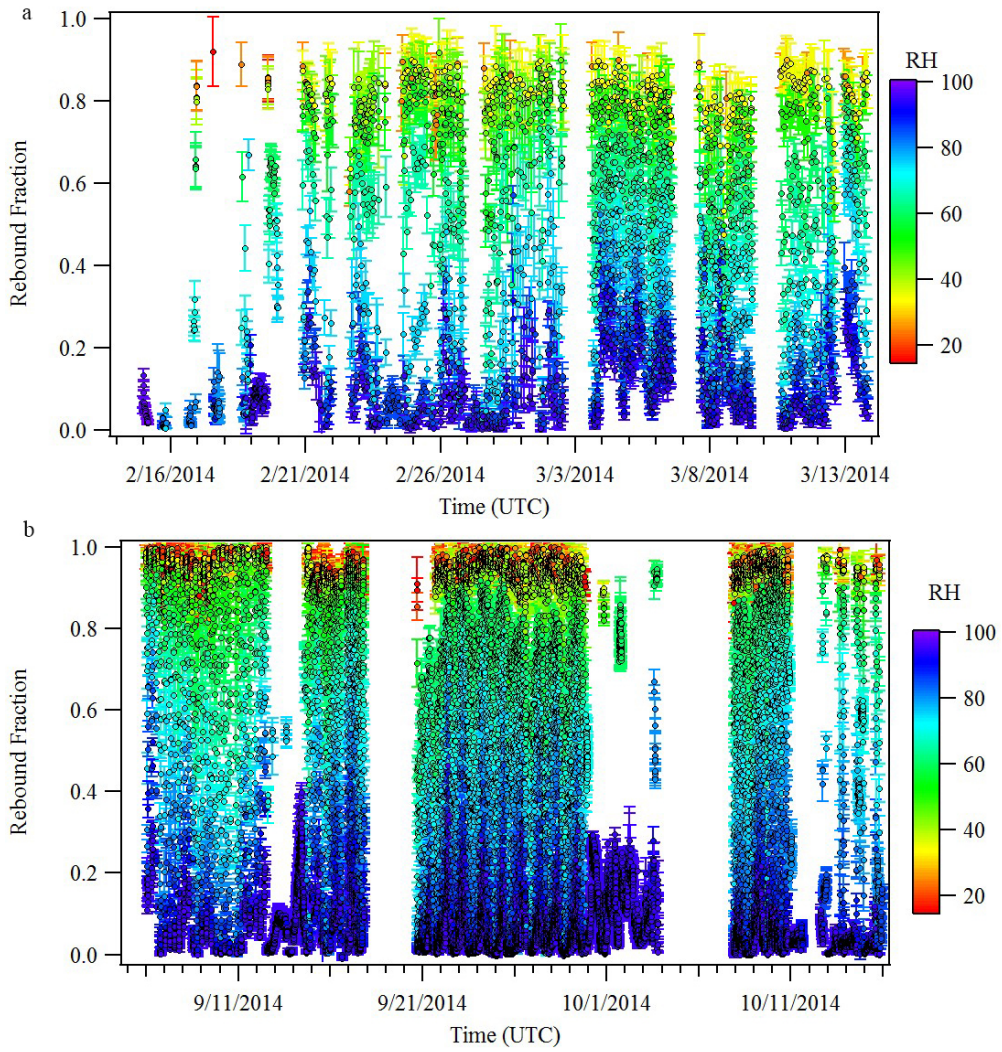

Figure 1. Rebound fraction data collected during (a) the wet season and (b) the dry season. The data were obtained by drying, sizing, re-humidifying, and then impacting particles. The reported RH is that measured from the apparatus after re-humidifying the particles

Figure 2a and Figure 2b show the measured rebound fraction as a function of ambient RH for the wet and dry seasons, respectively. Ambient RH is matched to the apparatus RH if within 5 RH percentage units and measured within 3 hours. The measured rebound fractions within the 3-hour window are then averaged to produce the values observed in Figure 2. From visual inspection, the wet season tends to favor the liquid phase state, primarily driven by higher RH values as compared to lower RH values observed during the dry season.

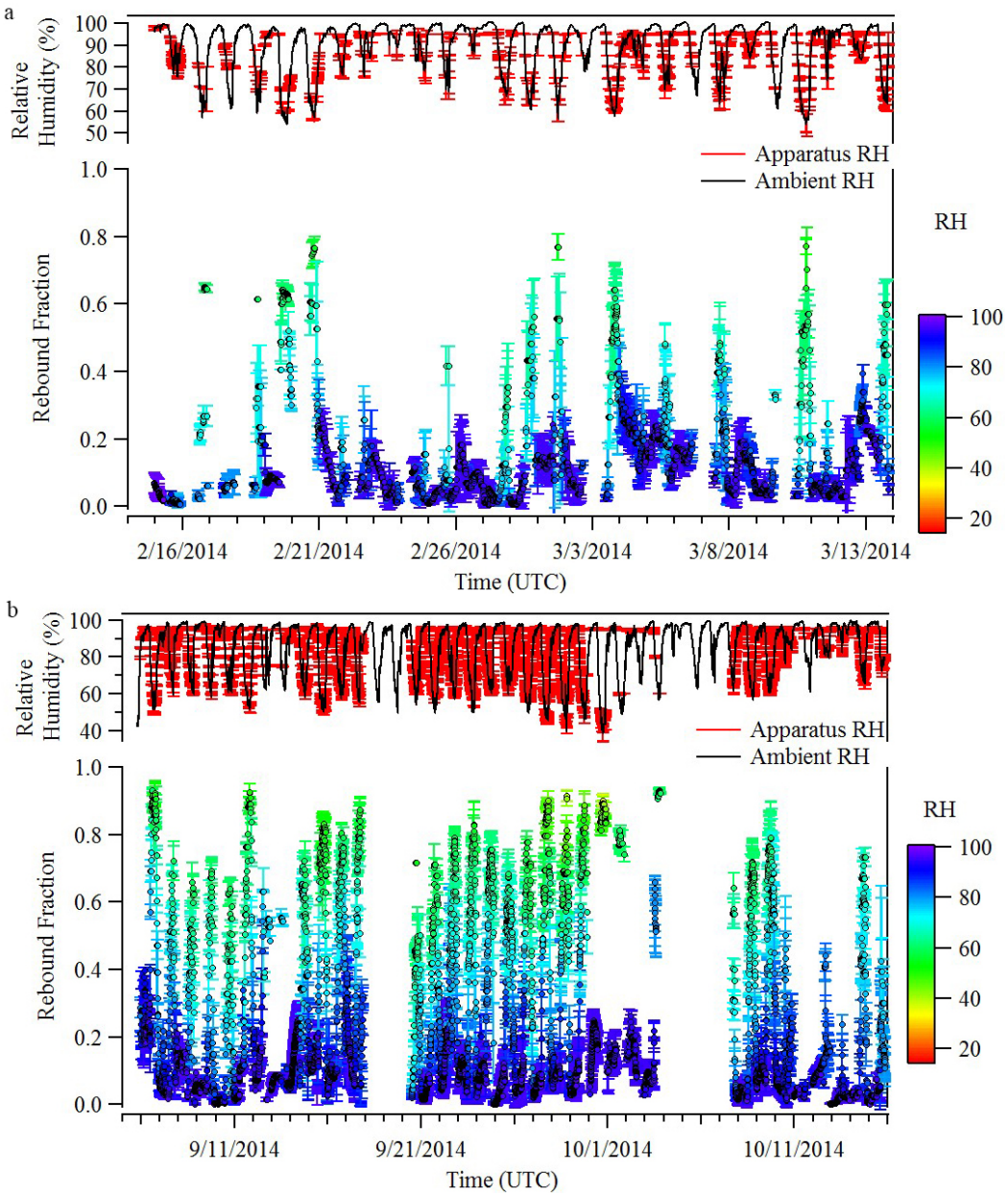

Figure 2. Measured rebound fraction for both (a) the wet season and (b) the dry season as a function of ambient RH. The ambient RH was matched to the apparatus RH if within 5%, and the average values over 1 hour are reported.

The hygroscopic response curves associated with all data obtained in the wet and dry seasons are shown in Figure 3a and Figure 3b, respectively. The data points are color-coded according to the hour of day (coordinated universal time—UTC) of measurement. Also displayed in both panels of Figure 3 is the hygroscopic response curve for chamber-generated SOM (Bateman et al. 2015).

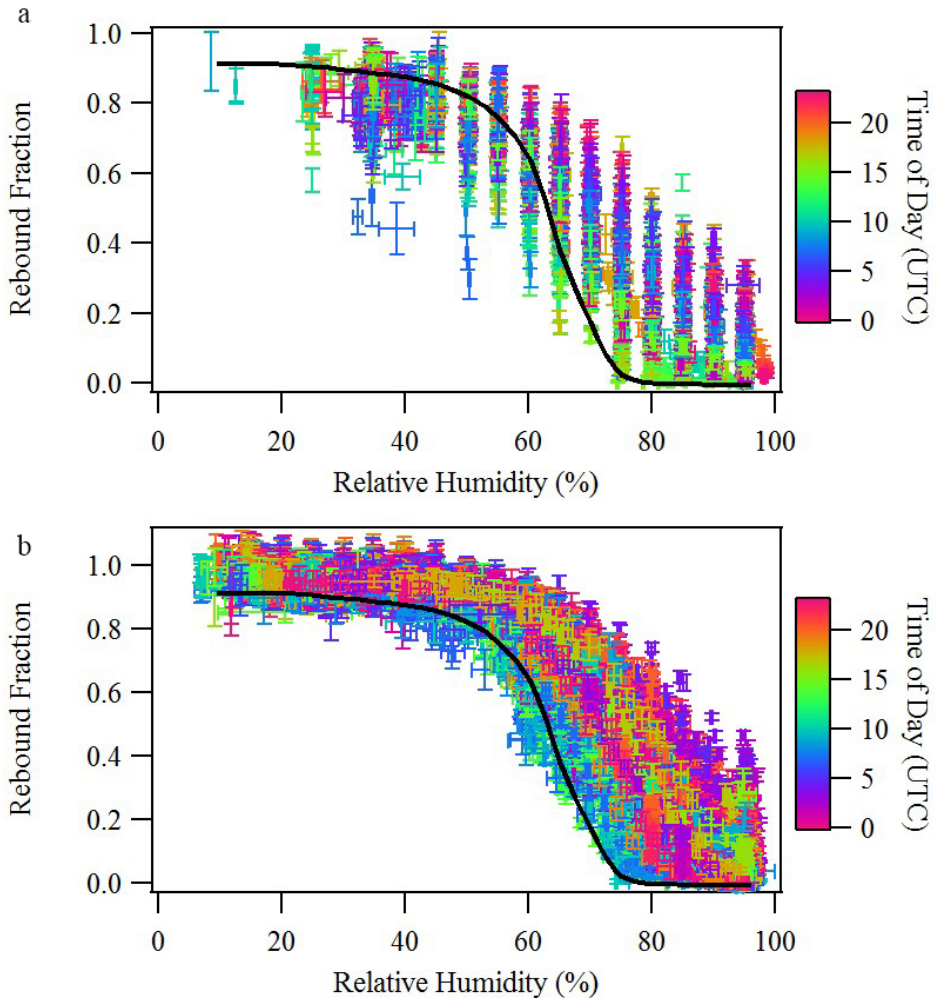

Figure 3. Hygroscopic response of particulate matter for (a) the wet season and (b) the dry season. The measured rebound fraction is displayed versus RH and color-coded for the time of day (UTC) during measurement. The hygroscopic response of chamber-generated SOM is also displayed.

The majority of daytime hygroscopic response curves for the wet and dry seasons follow the same response as the chamber-generated SOM. The majority of nighttime hygroscopic response can be described by less hygroscopic PM. Further research opportunities include identifying the chemical composition of the less hygroscopic PM measured during the nighttime and explaining the diurnal variation of the hygroscopic response curves.

5.0 Harvard Bounce Apparatus GoAmazon 2014/15 Campaign Publications

5.1 Meeting Abstracts/Presentations/Posters

May 19, 2015 GoAmazon 2014/15 Science Meeting, Harvard University, Cambridge, Massachusetts.

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