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GoAmazon 2014/15 Particle Sampling Field Campaign Report

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Executive Summary

As a part of the GoAmazon 2014/15 field deployments, samples of atmospheric particles were collected at the T3 field site (3° 12' 46.70" S, 60° 35' 53.0, Manacapuru, Brazil) established in the Amazonian region. The site was located downwind from Manaus and therefore, experienced clean conditions when winds were from northwest and polluted conditions when winds were from Manaus. During the second intensive operational period of GoAmazon 2014/15 (09/06/2014-10/02/2014), multiple samples of particles were collected using a cascade Multi-Orifice Uniform Deposition Impactor (MOUDI-110). Size-resolved samples by MOUDI (0.056-0.1, 0.1-0.18, 0.18-0.32, 0.32-0.56, 0.56-1.0, 1.0-1.8 μm) were collected for 6-12 hours. A variety of substrates, compatible with different spectro-microscopy methods of analysis, were arranged on the impactor stages. Collected aerosol samples are now stored pending laboratory analysis using multi-modal methods of chemical imaging. Our approach is to analyze only the samples of specific interest. We use the field campaign records and data on meteorology, as well as in situ measurements of gases and aerosols, to select the subset of samples for the in-depth laboratory analysis for selected episodes where changes in chemical composition of particles can be correlated with other data recorded at the site. Hence, we do not expect to perform detailed measurements on all samples—rather, only those samples with the greatest potential to provide scientific insight into aerosol chemistry.

Acronyms and Abbreviations

CCSEM/EDX	Computer Controlled Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy
CNPq	Brazilian National Council for Scientific and Technological Development
EMSL	Environmental Molecular Science Laboratory at PNNL
GoAmazon 2014/15	Green Ocean Amazon 2014/15 campaign
INPA	Instituto Nacional de Pesquisas da Amazonia
LBA	Large Scale Biosphere Atmosphere Experiment in Amazonia
LBNL	Lawrence Berkeley National Laboratory
MOUDI	Multi-Orifice Uniform Deposition Impactor
QCM-D	Quartz Crystal Microbalance with Dissipation Monitoring
PNNL	Pacific Northwest National Laboratory
RH	relative humidity
SOA	secondary organic aerosol
STXM	Scanning Transmission X-ray Microscopy
STXM/NEXAFS	Scanning Transmission X-ray Microscopy with Near-Edge X-Ray Absorption Fine Structure spectroscopy
UEA	Universidade do Estado do Amazonia

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1.0 Background

Contemporary models of secondary organic aerosol (SOA) formation and aging assume condensed-phase diffusion rates sufficiently rapid to maintain equilibrium with the gas phase and that the SOA is liquid.[1, 2] However, recent studies examining particle bounce behavior,[3] response to physical manipulation,[4] evaporation,[4-6] thermal desorption,[7] particulate nitrate uptake,[8] ammonia uptake,[9] and diffusion[5] provide evidence that both laboratory and ambient particles can have higher viscosities. One objective of our study is to correlate particle composition, chemical bonding, and mixing state with phase in selected particle samples collected during the U.S. Department of Energy's Atmospheric Radiation Measurement (ARM) Climate Research Facility GoAmazon 2014/15 campaign.

The oxidation of biogenic and anthropogenic gas-phase species produces a complex suite of organic products with a range of volatilities.[10, 11] These products often contain a variety of ketone, alcohol, and numerous carboxylic acid functional groups. When atmospheric particles encounter different relative humidities in the atmosphere they can undergo shifts in equilibrium bonding configuration, deliquescence, efflorescence, phase changes, and liquid-liquid phase separation. Changes in phase may govern the competition between reactions occurring at the particle gas/liquid (or gas/ solid) interface and diffusion of reactant or product species within the particle.[4, 12] During these changes the optical properties and the reactive uptake of gaseous species are affected, with important impacts on climate predictions. During transport, as aerosols are exposed to a range of relative humidity their viscoelastic properties as well as glass transition temperature can change.[13] Relative humidity (RH) can affect properties such as viscosity or glass transition temperature. Absorption isotherms for water uptake depend upon the material studied[14] as well as whether the material is porous or not.[11, 15] Crystalline salts absorb a monolayer at the surface, and little additional water is absorbed until reaching the relative humidity for deliquescence. At this humidity a direct deliquescence, or phase transformation from solid to liquid, occurs. In contrast, as relative humidity is increased, amorphous materials continue to absorb water beyond monolayer formation. Multilayers of water grow and begin to incorporate as multilayers and then water molecules embed between molecules (plasticization). Plasticization is well documented in plastics and food industries.[16] Plasticization increases the distance between molecules and generally decreases the viscosity as well as the glass transition temperature,[13] and may result in the release (outgassing) of previously trapped less volatile components in multicomponent polymers or secondary organic aerosols.

We use samples of particles collected to investigate the relationship between chemical composition, water vapor absorption, and phase states of atmospheric aerosols. Objective 1) focuses on determining compositional differences between "rebound" and 'no rebound" particles collected at the T3 site from the GoAmazon 2014/15 campaign and employs analysis techniques established by the combined Environmental Molecular Science Laboratory (EMSL)/Lawrence Berkeley National Laboratory (LBNL) groups. Objective 2) focuses on the chemical speciation and mixing state of particles. Objective 3) focuses on Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) experiments to monitor H_2O absorption, viscosity, and phase transformations of ensembles of particles. The laboratory experiments with collected particle samples combine chemical speciation, morphology, particle types, and mixing state with water vapor uptake measurements and the resulting viscosity/phase changes.

Objectives

1. Chemical characterization of microscopy samples collected during “rebound” and “no rebound” periods (as reported by S. Martin and A. Bateman) to correlate differences in chemical composition and mixing state with phase.
2. Elemental composition and chemical bonding of ambient aerosol samples using scanning electron microscopy/energy dispersive x-ray spectroscopy (CCSEM/EDX) and scanning transmission X-ray microscopy (STXM) to enable the correlation of phase behavior and water vapor uptake to particle mixing states and composition.
3. QCM-D water vapor uptake experiments on samples collected at the same time as those in 2) to examine differences in phase changes (i.e., viscosity) during water vapor uptake of particle samples.

We acknowledge the support of the Atmospheric Radiation Measurement (ARM) Climate Research Facility, a U.S. Department of Energy Office of Science user facility sponsored by the Office of Biological and Environmental Research.

Further, 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

Collection of “rebound” and “no rebound” samples was coordinated at the T3 site with Dr. A. Bateman and Prof. S. Martin (Harvard University). In situ records from the extensive instrumentation deployed at the site during the GoAmazon 2014/15 study will provide complementary information.[17]

3.0 Lessons Learned

The only issue that we had to deal with during the field study was poor compatibility of the MOUDI rotating gear with the hot and humid environment in Amazonia. Research studies considering similar deployments of MOUDI need to have 3-5 spare gear motors for possible replacements.

4.0 Results

During the GoAmazon 2014/15 campaign, microscopy samples were collected at the T3 site by the A. Laskin (PNNL) and M. K. Gilles (LBNL) groups with the intent to capture the differences between pristine and urban areas of the Amazon basin. Micro-Orifice Uniform Deposit Impactors (MOUDI)[18] were deployed with different substrates for analysis. STXM and CCSEM experiments described here use Si3N4-coated Si frames and copper-grid-supported carbon B films. QCM-D experiments will use the Au-coated quartz crystal microbalance substrates that were simultaneously collected with the MOUDI. The QCM-D substrates were cleaned and resonant frequencies recorded prior to sampling. Hence, the mass of deposited aerosols on each substrate can be determined. While a suite of experiments on the size-fractionated samples have been previously reported (electron microscopy,[19] X-ray spectro-microscopy,[20] UV/Vis spectroscopy,[21] and high-resolution mass spectrometry,[22]), this was the first collection of field samples for complimentary QCM-D analysis.

STXM/NEXAFS and CCSEM/EDX are efficient methods to determine the relative contribution of the different particle types present in the sample. Scanning Transmission X-ray Microscopy with Near-Edge X-Ray Absorption Fine Structure spectroscopy (STXM/NEXAFS) is used to quantify the amount of organic, inorganic, and soot components in the particles. CCSEM/EDX is used to measure the elemental composition of individual particles. Combined, the two techniques provide complementary information on the composition of individual particles. For the GoAmazon 2014/15 particle samples, these techniques are used to determine the distribution of particle classes, composition, and morphology on samples collected at the times when QCM substrates were also collected. The goal is to correlate water vapor uptake, viscosity, and phase changes to specific aerosol types, composition, and morphology. By combining the compositional analysis of particles with the QCM-D results, we will correlate particle composition with water uptake and changes in viscosity. Hence, these experiments provide a unique opportunity to advance our understanding of the aging, and in particular the cycling, of relative humidity on composition and particle viscosity.

5.0 Public Outreach

Undergraduates who have performed laboratory experiments at LBNL relevant to this project include:

Simon Mueller, Physics M.S. University of Würzburg, Germany, 2015-2016

Johannes Weis, Physics M.S. University of Würzburg, Germany, 2015-2016

Tristan Harder, Physics M.S. University of Würzburg, Germany, 2014-2015

David Farland, August-December, 2014

Leah Tom, University of California, Berkeley Physics, summer, 2014

David Alspaugh, University of California, Berkeley Physics, summer, 2014

6.0 GoAmazon 2014/15 Particle Sampling Publications

6.1 Journal Articles/Manuscripts

Yet to be presented.

6.2 Meeting Abstracts/Presentations/Posters

MK Gilles. ”Spectromicroscopy of ambient aerosols particles: results from GoAmazon2014/15.” GOAmazon 2014/5/ Science Conference, Harvard University, Cambridge, MA, May 18-20, 2015.

A Laskin. “Molecular Characterization of Atmospheric Organic Particles Collected in the Amazonia*.”* GoAmazon 2014/5 Science Conference. Harvard University, Cambridge, MA, May 18-20, 2015.

A Laskin. “Molecular Characterization of Atmospheric Organic Particles Collected in the Amazonia”. 2015 ARM/ASR Joint User Facility PI Meeting, Washington, DC, March 16-19, 2015.

MK Gilles. “H_2O uptake on atmospheric aerosols from microscopy and quartz crystal microbalance methods.” Invited paper, 250th American Chemical Society meeting Boston, MA, August 16-20, 2015.

MK Gilles. “Atmospheric Particles: Viscosity, Phase, and Response to Relative Humidity.” Goldschmidt 2015, Prague, CZ, August 16-21, 2015.

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