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Observations and Modeling of the Green Ocean Amazon 2014/15: Hydroxyl Radical (OH) Chemical Ionization Mass Spectrometer (CIMS) Field Campaign Report

S Kim

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Observations and Modeling of the Green Ocean Amazon 2014/15: Hydroxyl Radical (OH) Chemical Ionization Mass Spectrometer (CIMS) Field Campaign Report

S Kim, University of California, Irvine
Principal Investigator

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Executive Summary

The University of California, Irvine, science team (Dr. Saewung Kim, Dr. Roger Seco, Dr. Alex Guenther, and Dr. Jim Smith) deployed a chemical ionization mass spectrometer system for hydroxyl radical (OH) and sulfuric acid quantifications. As part of the GoAmazon 2014/15 field campaign. Hydroxyl radical determines tropospheric oxidation capacity and had been expected to be very low in the pristine rain forest region such as the Brazilian Amazon because of the presence of significant levels of highly reactive biogenic volatile organic compounds and very low levels of NO, which is an OH recycling agent. However, several recent in situ OH observations provided by a laser-induced fluorescence system reported unaccountably high OH concentrations. To address this discrepancy, a series of laboratory and theoretical studies has postulated chemical reaction mechanisms of isoprene that may regenerate OH in photo-oxidation processes. Along with these efforts, potential artifacts on the laser induced fluorescence system from isoprene and its oxidation products also have been explored. Therefore, the first chemical ionization mass spectrometer observations at the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility's T3 site in Manacapuru, Brazil, are expected to provide a critical experimental constraint to address uncertainty in constraining oxidation capacity over pristine rain forest environments. In addition, we deployed a National Center for Atmospheric Research (NCAR) proton transfer reaction time-of-flight mass spectrometer to characterize atmospheric volatile organic compound levels, especially isoprene and its oxidation products, which are critical input parameters for box modeling to simulate OH with different isoprene photo-oxidation schemes. As there has been no report on noticeable new particle formation events, our first in situ sulfuric acid observations in the Amazon rain forest were expected to constrain the reasons behind such observations.

The planned field observations during Intensive Observational Periods I and II, post-field campaign calibrations, and preliminary data reports have been completed. We presented preliminary data analysis results at the 2014 American Geophysical Union Fall meeting and the GOAmazon Science Meeting in Boston (May 2015). We are in the process of submitting two more abstracts to the 2015 American Geophysical Union fall meeting while we are preparing two manuscripts to be submitted to (tentatively) the GOAmazon special issue of *Atmospheric Chemistry and Physics*.

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement Climate Research Facility
BVOC	biogenic volatile organic compound
CIMS	chemical ionization mass spectrometry
CNPq	Brazilian National Council for Scientific and Technological Development
DOE	U.S. Department of Energy
INPA	Instituto Nacional de Pesquisas da Amazonia
INPE	Instituto Nacional de Pesquisas Espaciais
LBA	Large Scale Biosphere Atmosphere Experiment in Amazonia
LIF	laser-induced fluorescence
NCAR	National Center for Atmospheric Research
UTC	Coordinated Universal Time
VOC	volatile organic compound

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1.0 Background

GOAmazon 2014/15 is a large-scale research initiative that integrates field observation, process-level modeling, and regional climate modeling efforts to advance our understanding of how changes in natural and anthropogenic environmental factors affect the regional climate.[1]

The goal of the University of California, Irvine, research team to deploy a chemical ionization mass spectrometry (CIMS) system for hydroxyl radical (OH) quantification is to experimentally constrain an oxidant level that initiates volatile organic compound (VOC) oxidation. Photo-oxidation of VOCs, especially of biogenic origin (BVOC), is considered to significantly contribute to cloud condensation nuclei formation (Figure 1). However, recent field OH observations in pristine rain forest regions have consistently reported higher-than-expected OH levels (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 × 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) led us explore unidentified OH recycling processes related with 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 as 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. One most plausible speculation has been the possible presence of below-the-threshold, gas-phase sulfuric acid (H_2SO_4) levels, which is critical for the formation of gas molecule clusters (Spracklen et al. 2006).

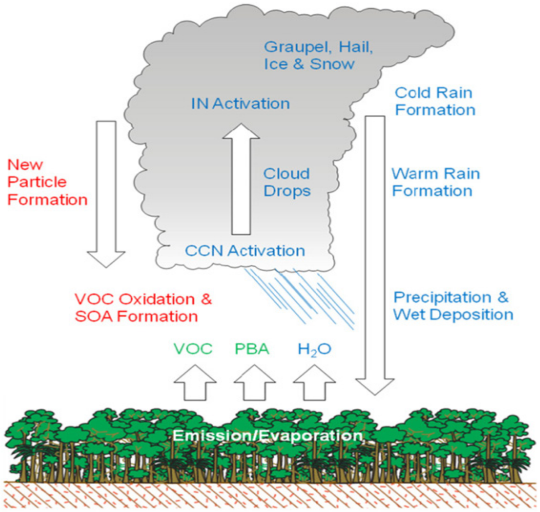

Figure 1. Schematic diagram showing interactions between chemistry-aerosol-precipitation over the tropical rain forest environment (Pöschl et al. 2010).

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[1] http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/WhitePaperonIrandubaManacapuruIOPGoAmazon2014.pdf

Therefore, the OH CIMS instrumentation, which is capable of quantifying both atmospheric OH and H_2SO_4 (Tanner et al. 1997), was deployed to address the current uncertainty regarding photochemical processes over the Amazon rain forest region. In addition, we deployed National Center for Atmospheric Research (NCAR) proton transfer reaction time-of-flight mass spectrometry manufactured by IONICON Analytik, GmbH, to quantify and identify isoprene, isoprene oxidation products, other BVOCs, and anthropogenic VOCs. The instrumentation was integrated in the ARM T3 site in Manacapuru, Amazonas, Brazil. This site is located ~80 km east of Manaus, which is the the most populated city in the Amazon; therefore, we expect to sample various anthropogenic influences in the pristine rainforest background. We participated in wet and dry season Intensive Operating Periods, IOP I (February through March 2014) and IOP II (late August through early October 2014), respectively. The preliminary data have been processed for IOP I. Processing of IOP II data has been just finished, and the analysis has just begun.

Team members are listed below:

- Saewung Kim (Principal Investigator; University of California, Irvine)
- Roger Seco (Co-Investigator; University of California, Irvine)
- Jim Smith (Co-Investigator; formerly NCAR, now at University of California, Irvine)
- Alex Guenther (Co-Investigator; formerly Pacific Northwest National Laboratory, now at University of California, Irvine).

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 Instituto Nacional de Pesquisas Espaciais (INPE). The work was conducted under 001262/2012-2 of the Brazilian National Council for Scientific and Technological Development (CNPq).

2.0 Notable Events or Highlights

The CIMS-observed OH during the wet season clearly shows much lower OH concentrations than previously reported by LIF observations ($3\text{-}5 \times 10^6$ molecules cm^{-3}), as shown in Figure 2. We just finalized our preliminary OH data set for IOP II, and it appears that OH levels were similar to, or slightly lower than, those observed during the wet season (IOP I). On the other hand, H_2SO_4 concentrations appeared to be higher than was expected from modeling exercises (5×10^5 molecules cm^{-3}). The H_2SO_4 level during the dry season also was observed to be at a similar level.

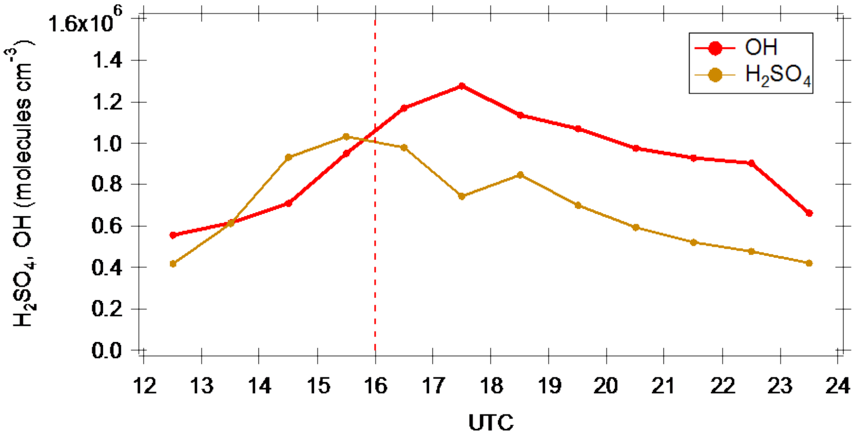

Figure 2. Averaged diurnal variations of OH and H_2SO_4 during IOP I.

As shown in Figure 3, OH concentrations appear to be highly dependent on anthropogenic influences. Hydroxyl was observed at more than 1 × 10^6 molecules cm^{-3} when CO was observed at concentrations more than 100 ppb. At about 4:00 p.m. (UTC), a clean air intrusion was observed with lower CO and ozone levels. During that time period, OH also was observed to be at a significantly suppressed level (~ 5 × 10^5 molecules cm^{-3}). This observation strongly indicates that CIMS OH observations do not support the previous findings of enhanced OH levels when the LIF technique was used.

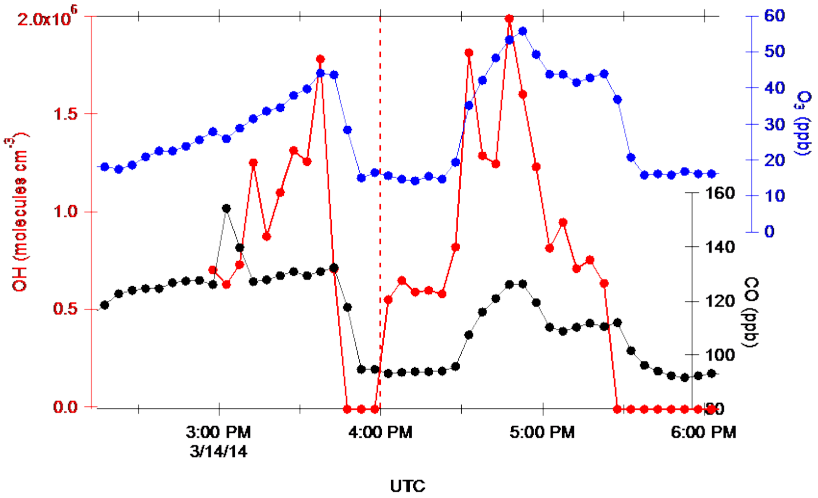

Figure 3. Temporal variations of CO, O_3, and OH on March 14, 2014, during IOP I showing sharp contrast between pristine and pollution-influenced air masses.

Because of technical difficulties in quantifying the H_2SO_4 levels, there have been some attempts to deduce H_2SO_4 level from the SO_2 level. However, as shown in Figure 4, the previous H_2SO_4 and SO_2 observations in different rural environments show the highly non-linear relationship. This reflects that process-level understandings of the photochemical fates of H_2SO_4 are critical to assess the roles of H_2SO_4 in new particle formation

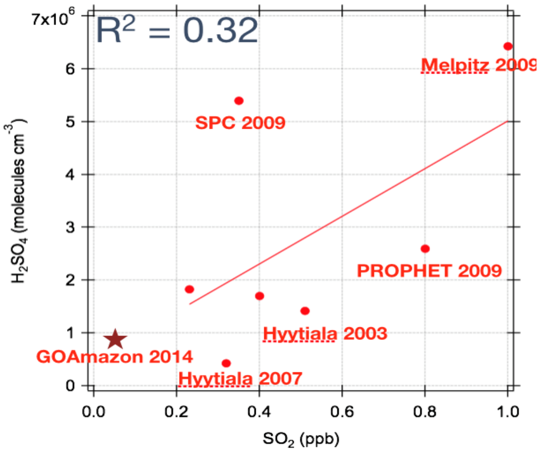

Figure 4. Correlation between SO_2 and H_2SO_4 in various forest environments. The result from IOP I is indicated as a star.

The star in Figure 4 represents SO_2 and H_2SO_4 levels during IOP I from the GOAmazon field campaign. Although it is in a very low SO_2 environment (~50 ppt), observable H_2SO_4 still exists. We are currently working with aerosol scientists to explore implications of these observations.

3.0 Lessons Learned

Our instrumentation requires ultra-high-purity nitrogen as a buffer gas. We found a significant amount of artifacts in the ultra-high-purity nitrogen obtained from a Manaus supplier for IOP II. The duty cycle for IOP II was significantly compromised because of this issue. The ultra-high-purity nitrogen for IOP I was supplied by a vendor in San Paulo and did not cause any notable issues.

The ARM shipment for the hazardous material arrived in 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 United States. In summary, it appears that knowledgeable shippers are capable of getting things through Brazilian customs. If ARM is committed/interested in future field observations in the Brazilian Amazon region, compiling lessons learned from each investigator regarding shipping would be highly beneficial for future missions.

4.0 Results

Our scientific findings are briefly described in Section 2.0. We are developing at least three collaborative research journal manuscripts at this time. The fact that this was the first deployment of a CIMS system to quantify OH and H_2SO_4 is scientifically important as these two reactive gas species govern the tropospheric oxidation capacity and new particle formation processes. In addition, we expect that our observational results could constrain uncertainty in our understanding of tropospheric photochemical processes such as 1) the discrepancy between modeled and observed OH when the LIF technique was used, and 2) the reason the new particle formation event was not observed over the Amazon rain forest environment.

5.0 Public Outreach

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

6.0 GOAmazon Publications

6.1 Journal Articles/Manuscripts

Kim et al. “Measurements of OH in the Amazon rain forest environment with various anthropogenic influences.” In preparation.

Kim et al. “Measurement of H_2SO_4 in the Amazon rain forest- implications towards new particle formation.” In preparation.

Seco 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

6.2.1 AGU Fall Meeting December 2014, San Francisco, California

Seco and Kim et al. “Isoprene and its oxidation products in the rural atmosphere of the Amazon during the GOAmazon 2014/15 campaign.” Poster presentation.

Kim and Seco et al. “A comprehensive evaluation of H_2SO_4 formation from OH and sCI pathways in high BVOC environment.” Oral presentation.

6.2.2 GOAmazon Data Meeting, May 2015, Cambridge, Massachusetts

Seco and Kim et al. “Isoprene and its oxidation products in the rural atmosphere of Amazon during the GOAmazon 2014/15.” Oral presentation.

Kim and Seco et al. “Hydroxyl and sulfuric acid observations.” Oral presentation.

6.2.3 AGU Fall Meeting December 2015, San Francisco, California

Kim and Seco et al. “OH observations in a tropical rain forest environment using a chemical ionization mass spectrometry technique during GOAmazon intensive.”

Seco and Kim et al. “Volatile organic compound and oxidation capacity of the atmosphere in the Brazilian Amazon during the GoAmazon campaign.”

7.0 References

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