GoAmazon2014/15: Oxidation Flow Reactor
Final Campaign Report

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GoAmazon2014/15: Oxidation Flow Reactor Final Campaign Report

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Executive Summary

The primary goal of the Green Ocean Amazon (GoAmazon2014/5) field campaign was to measure and mechanistically understand the formation of particle number and mass in a region affected by large tropical rainforest biogenic emissions and sometimes anthropogenic influence from a large urban center. As part of the two intensive operational periods (IOPs) and in collaboration with Pacific Northwest National Laboratory (PNNL) and Harvard, the Jimenez Group proposed to deploy a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), Thermal Denuder (TD), Scanning Mobility Particle Size (SMPS), two oxidation flow reactors (OFR; including supporting O₃, CO/CO₂/CH₄, RH analyzers), and a high volume filter sampler (MCV) for the measurement of gas and aerosol chemical, physicochemical, and volatility properties. The two IOPs were conducted during the wet season (February to March, 2014) and dry season (August to October, 2014). This proposal was part of a collaborative proposal involving other university and government laboratories.

This was a highly successful field deployment that produced high quality data with good data coverage and promising preliminary results. Secondary organic aerosol (SOA) formation from oxidation in the OFRs often showed correlations with either biogenic or anthropogenic organic gases, but approximately an order of magnitude more SOA was formed than would be predicted by the measured VOCs alone. Analysis of this experiment helped to fill in the details of the process of gas-to-particle oxidation. Our measurements also highlight the variability in concentrations of CO₂, CO, and CH₄ between wet and dry seasons. Measurements of organic aerosol volatility were made, showing that the aerosol was relatively non-volatile and more closely resembled previous urban measurements than measurements upwind of Manaus during the AMAZE-08 campaign.

Field campaigns in remote locations, especially in foreign countries, are extremely challenging but can be equally rewarding. GoAmazon2014/5 was no exception, but thanks to the tremendous efforts of everyone involved, the campaign yielded a rich data set that will lead to many high-impact publications in years to come.
### Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>OA</td>
<td>organic aerosol</td>
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<tr>
<td>SOA</td>
<td>secondary organic aerosol</td>
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<tr>
<td>VOC</td>
<td>volatile organic compound</td>
</tr>
<tr>
<td>S/IVOC</td>
<td>semi- and intermediate-volatility organic compounds</td>
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<tr>
<td>OH</td>
<td>hydroxyl radical</td>
</tr>
<tr>
<td>O$_3$</td>
<td>ozone</td>
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<tr>
<td>OH$_{exp}$</td>
<td>OH exposure</td>
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<tr>
<td>O$<em>3$$</em>{exp}$</td>
<td>O$_3$ exposure</td>
</tr>
<tr>
<td>MT</td>
<td>monoterpenes</td>
</tr>
<tr>
<td>SQT</td>
<td>sesquiterpenes</td>
</tr>
<tr>
<td>TMB</td>
<td>trimethylbenzene</td>
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<tr>
<td>OFR</td>
<td>oxidation flow reactor</td>
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<tr>
<td>AMS</td>
<td>aerosol mass spectrometer</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane</td>
</tr>
<tr>
<td>IOP</td>
<td>intensive operational period</td>
</tr>
<tr>
<td>T2 site</td>
<td>terrestrial site just across the river to the west of Manaus, Brazil (3° 8'21.12&quot;S, 60° 7'53.52&quot;W)</td>
</tr>
<tr>
<td>T3 site</td>
<td>terrestrial site 60 km to the west of Manaus, Brazil (3°12'47.82&quot;S, 60°35'55.32&quot;W)</td>
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</tbody>
</table>
EXECUTIVE SUMMARY

This report summarizes the findings from the GoAmazon2014/5 field campaign, which took place in the Amazon region of Brazil from January to May 2014. The campaign focused on understanding the formation and composition of secondary organic aerosols (SOAs) in the Amazon Basin.

The campaign included a combination of in situ measurements and laboratory studies, aiming to elucidate the processes governing SOA formation in this region. Key findings include:

1. **Background:**
   - SOA formation closely mirrors the availability of biogenic precursor gases.
   - SOA formation from O3 oxidation is correlated with the concentration of monoterpenes (and any other primary biogenic gases with a similar emission pattern) while SOA formation from OH oxidation is anti-correlated with monoterpenes and correlated with anthropogenic tracers.

2. **Notable Events or Highlights:**
   - SOA formation peaks at 4-8 days OHexp, with more SOA production observed in the dry season (4 µg m⁻³ at night) than during the wet season (1.5 µg m⁻³). On average, the magnitude of SOA formation at T2 during the wet season was similar to the amount formed at T3, despite being located closer to the city of Manaus.

3. **Lessons Learned:**
   - SOA formation as a function of O3,exp in an OFR, for wet and dry seasons at the T3 site.
   - Higher SOA formation was observed in the dry season (0.5 µg m⁻³ at night) than during the wet season (0.25 µg m⁻³).

4. **Results:**
   - Measured SOA formation from OH oxidation in an OFR in the dry season at T3, compared to the amount of SOA predicted to form from measured SOA precursor gases (monoterpene, toluene, benzene, and isoprene). Approximately an order of magnitude more SOA was formed than predicted, consistent with previous field results. This result is consistent with the existence of typically unmeasured semi/intermediate volatility organic compounds (S/IVOCs), such as oxidation products of primary VOCs. Results for OH oxidation in the wet season as well as for O3 oxidation in the OFR (not shown) are similar.

5. **Public Outreach:**
   - GOAmazon2014/5 Publications

6. **GoAmazon2014/5 Publications:**
   - Journal Articles/Manuscripts
   - Meeting Abstracts/Presentations/Posters

7. **References**
Approximate SOA yields of several monoterpenes (α-pinene, β-pinene, 3-carene, limonene) and isoprene as a function of organic aerosol concentration (COA) for both OH and O3 oxidation. VOCs were added into ambient air in the OFR during times of low ambient SOA precursor concentrations (daytime). SOA yields were calculated assuming the added VOC was the only SOA precursor, so these yields represent upper limits in the OFR. SOA yields in the OFR are similar to SOA yields in chamber experiments.

Van Krevelen diagram (H:C vs. O:C atomic ratios) of OA after OH oxidation in the OFR. As OHexp increases, H:C decreases and O:C increases along a trajectory similar to that measured in the atmosphere, but to much higher O:C values.

Thermographs showing the fraction remaining after heating for the mass spectrometric markers m/z 43 (less aged OA) and m/z 44 (more aged OA), compared to several other field campaigns. The OA during the wet season (IOP1) at the T3 site was on average less.

OA mass fraction remaining after ambient aerosol was heated in a thermodenuder, and corresponding volatility distribution of the OA. The majority of OA during both wet and dry seasons at T3 had very low volatility.

Comparison of CO2, CO, and CH4 measured during the wet season (left) and dry season (right). CO2 and CO exhibited greater long-range as well as local sources (biomass burning) during the dry season, while CH4 concentrations were increased in the dry season likely due to local farming sources.
1.0 Background

The Amazon Forest basin has long been the subject of great scientific interest among the atmospheric science community, in part because the region has been relatively untouched by anthropogenic influences. In an effort to comprehensively study the effects of anthropogenic pollution on the pristine forest atmosphere, the Green Ocean Amazon (GoAmazon2014/5) experiment was organized near the city of Manaus, Brazil, from January 2014 to December 2015. This campaign was a collaboration between Brazilian, American, and German scientists and involved several different research sites and platforms. Measurements at the T0 and ZF2 ground sites, located upwind of Manaus, represented the background forest air. In contrast were measurements taken at the T1 (directly in Manaus), T2 (several km downwind of Manaus), and T3 (~60 km downwind) ground sites, which were periodically affected to varying degrees by pollution from Manaus. Additionally, research flights were operated out of Manaus, flying over the ground sites to determine the spatial extent of anthropogenic influence. The DOE deployed an ARM Mobile Facility (AMF) and MAOS at the T3 site in Manacapuru, Brazil, and also operated the ARM Aerial Facility (AAF) aboard the G1 research aircraft.

Under this proposal, the Jimenez research group deployed a High-Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS (HR-ToF-AMS, hereafter AMS), Thermal Denuder (TD), Scanning Mobility Particle Size (SMPS), two oxidation flow reactors (OFR; including supporting O3, CO/CO2/CH4, RH analyzers), and a high volume filter sampler (MCV) for the measurement of gas and aerosol chemical, physicochemical, and volatility properties during the two intensive operational periods (IOP) of GoAmazon2014/5. The two IOPs were conducted during the wet season (Feb–March, 2014) and dry season (August–October, 2014). The operation of the AMS was in collaboration with PNNL (M. Lizabeth Alexander, Matt Newburn) and Harvard (Scot Martin, Suzane de Sá). Our proposal is part of a collaborative proposal involving other university and government laboratories, however this report covers only activities and results directly related to our groups work and contribution.

The primary goals of the IOPs were to measure and mechanistically understand the formation of particle number and mass in a region affected by large tropical rainforest biogenic emissions and sometimes anthropogenic influence from a large urban center during the wet and dry seasons. This was a highly successful field deployment that produced high quality data with good data coverage and promising results.

2.0 Notable Events or Highlights

Thanks to tremendous efforts by all of the members of the Jimenez research group listed on this report, as well as collaborators from PNNL, Harvard, LANL/DOE, and numerous Brazilian scientists and staff, we can report that all of the instruments deployed as part of this proposal were fully operational for the entirety of the two IOPs, with the exception of only a few days of auxiliary CO and CO2 measurements lost due to instrumental failures. This was a great success that led to a rich data set capturing a variety of interesting episodes at the T3 site.

Among the campaign highlights, we were able to capture very dynamic changes (hourly, daily, and seasonally) in the amount of SOA-forming organic gases in ambient air by measuring SOA formation
resulting from oxidation of that air by either OH or O3 in an OFR using the AMS. By coordinating our AMS measurements with the PTR-TOFMS and SV-TAG gas measurements, we were able to demonstrate that the SOA formation potential sometimes correlated with biogenic gases, sometimes with anthropogenic gases, and sometimes with neither. Regardless of those correlations, approximately an order of magnitude more SOA was formed than could be explained by the measured SOA precursor gases, suggesting the existence of other typically unmeasured precursor gases, e.g., semi- and intermediate-volatility organic compounds (S/IVOCs) that may be oxidation products of the measured VOCs. This is consistent with previous OFR measurements in other locations.

We were also able to coordinate with the Paulo Artaxo group from the University of Saõ Paulo to move an OFR and auxiliary equipment to the T2 site to take measurements in the months between IOPs. This was a great opportunity to foster collaboration between American and Brazilian scientists, and added another dimension to the OFR measurements by being much closer to anthropogenic pollution sources.

3.0 Lessons Learned

Conducting such a huge field research campaign spread across several locations in a remote region of a foreign country was incredibly challenging from both logistical and scientific aspects. From our experiences during the GoAmazon2014/5 campaign, we learned many lessons that we were able to apply during this campaign as well as to future endeavors. Scientifically, we had to overcome challenges associated with operating sensitive equipment in a wet and harsh environment. We also made advances in our experimental setup, including enhancing the reliability of our automated valve switching system, which helped us to efficiently use a single AMS to sample ambient aerosol, the TD, and two OFRs, concurrently.

Perhaps the most important lesson learned during the campaign involved communication at the T3 research site. With so many parties involved (DOE, individual universities, Brazilian researchers, etc), we were working in a unique environment in which we were responsible not just for the operation of our own instruments, but also for contributing to IOP group operations, DOE ARM site operations, and Brazilian research operations. Likewise, our individual operations required contributions from the DOE, other IOP researchers, and our Brazilian collaborators. With such a complex campaign, it was only natural that we experienced some difficulties in understanding our responsibilities to others and in expressing the contributions from others that were required to reach our own scientific objectives. In the end, a system was implemented in which the individual American universities coordinated through a single point of contact, who then efficiently communicated with a point of contact for the DOE operations and Brazilian operations. Weekly operational update meetings were instituted, and the communication tree ensured that everyone was on the same page regarding site operations. We would like to commend the DOE operations team for their willingness to adapt the communication structure to address the needs of the IOP research groups, and hopefully there were valuable lessons learned that can be applied to future campaigns.
4.0 Results

Preliminary analysis has produced promising results that will lay the foundation for understanding the science questions targeted by this proposal. A few highlights follow. Although our group collaborated in the collection and analysis of the ambient (non-TD/OFR-perturbed) AMS measurements, those results have been presented by the Martin Group (Harvard) and Alexander Group (PNNL) and will be detailed in their reports, so those results are not described here.

Measurements of SOA formation from OH (Figures 1-2) and O$_3$ (Figure 3) oxidation demonstrated that SOA formation often closely followed the availability of precursor organic gases, both biogenic (e.g., terpenes, sesquiterpenes) and anthropogenic (e.g., benzene, toluene). However, the picture is far from clear. At some times, SOA formation followed biogenic precursors, while at other times it followed anthropogenic precursors. In Figure 3, SOA formation from OH and O$_3$ oxidation appear to correlate with different sets of precursor gases. Further investigation will focus on disentangling the different biogenic or anthropogenic drivers and/or understanding any synergistic effects.

Figure 1: SOA formation at the T3 site after approximately 3 days of OH exposure (OHexp) in an OFR, compared to several concurrent gas-phase measurements. SOA formation closely mirrors the availability of biogenic precursor gases.
Figure 2: SOA formation in an OFR at the T2 site while cycling through a range of OHexp, compared to several concurrent gas-phase measurements. SOA formation closely mirrors the availability of anthropogenic precursor gases during some time periods, but follows biogenic precursor gases at other times.

Figure 3: SOA formation at the T3 site from either OH or O3 oxidation in an OFR, compared to several concurrent gas-phase measurements. SOA formation from O3 oxidation is correlated with the concentration of monoterpenes (and any other primary biogenic gases with a similar emission pattern) while SOA formation from OH oxidation is anti-correlated with monoterpenes and correlated with anthropogenic tracers in this example.
When SOA formation from OH oxidation was plotted as campaign averages for each site and season, maximum SOA was formed at 4-8 days of equivalent atmospheric aging and then decreased at higher aging, sometimes resulting in net aerosol destruction at the highest exposures (Figure 4). It shows the interplay between functionalization/condensation of organic gases producing SOA and fragmentation/evaporation consuming SOA. Such behavior is qualitatively similar to observations we have made in other very different environments, however the degree of oxidation required to balance production/destruction appears to vary. On average, more SOA was formed from OH oxidation at night (up to ~4 µg m\(^{-3}\) in the dry season) than during the day (~1.5 µg m\(^{-3}\) in the dry season), likely due to diurnal changes in the concentration of organic gases (Figure 4). Despite being closer to the large urban center of Manaus, the amount of SOA formed, on average, at the T2 site was similar to the T3 site (Figure 4). However, specific events when the Manaus plume was transported from T2 to T3 need to be investigated in more detail to better understand how the Manaus plume chemically evolves.

![Figure 4: SOA formation as a function of OHexp in an OFR, for wet season at the T2 site and wet+dry seasons at the T3 site. SOA formation peaks at 4-8 days OHexp, and more SOA production was observed in the dry season (4 µg m\(^{-3}\) at night) than during the wet season (1.5 µg m\(^{-3}\)). On average the magnitude of SOA formation at T2 during the wet season was similar to the amount formed at T3, despite being located closer to the city of Manaus.](image)

Campaign average SOA formation from O\(_3\) oxidation was significantly less than from OH oxidation, but shows similar day/night and seasonal trends (Figure 5). The maximum SOA formation from O\(_3\) oxidation was observed at night in the dry season (on average 0.5 µg m\(^{-3}\)). Destruction of OA at high O\(_3\),exp was not observed.
Figure 5: SOA formation as a function of O$_3$,exp in an OFR, for wet and dry seasons at the T3 site. Higher SOA formation was observed in the dry season (0.5 µg m$^{-3}$ at night) than during the wet season (0.25 µg m$^{-3}$).

By applying published chamber SOA yields (Tsimpidi et al., 2010) to the concentrations of measured SOA precursors, we can try to predict the amount of SOA formation that should result from OH or O$_3$ oxidation in the OFR. However, we consistently see approximately an order of magnitude larger SOA formation than predicted, seen in Figure 6 for OH oxidation at T3 during the dry season. Wet season OH oxidation data and O$_3$ oxidation data are not shown, but result in similar conclusions. Previous field campaigns have also reached this conclusion. This suggests the existence of other typically unmeasured SOA precursors in ambient air. Measurements at the 2011 BEACHON-RoMBAS field campaign suggest that lower volatility organics (S/IVOCs) can explain this missing SOA source (Palm et al. 2015). The S/IVOCs may be primary emissions, oxidation products of primary VOCs, or something else. This points to a need for better measurements of low-volatility organic gases.

Figure 6: Measured SOA formation from OH oxidation in an OFR in the dry season at T3, compared to the amount of SOA predicted to form from measured SOA precursor gases (monoterpene, toluene, benzene, and isoprene). Approximately an order of magnitude more SOA was formed than predicted, consistent with previous field results. This result is consistent with the existence of typically unmeasured semi/intermediate volatility organic compounds (S/IVOCs), such as oxidation products of primary VOCs. Results for OH oxidation in the wet season as well as for O$_3$ oxidation in the OFR (not shown) are similar.
Another possibility to explain higher than predicted SOA formation would be if SOA yields in the OFR are significantly larger than the yields measured in chambers. To test this, we performed several standard injection experiments during the dry season at T3. While sampling ambient air, we injected small concentrations of VOCs (1-5 ppb α-pinene, β-pinene, 3-carene, or limonene; 50-100 ppb isoprene) in order to study SOA formation from a known precursor under ambient experimental conditions. We calculated SOA yields by measuring SOA formation and VOC decay, and assuming all SOA formation was due to the injected VOC. Ambient VOCs likely contributed a small fraction of the SOA formation, so the SOA yields shown here in Figure 7 are upper limits. These results show that SOA yields in the reactor appear to be similar to yields measured in chamber studies, and this validates the conclusion that there are other sources of SOA in ambient air other than the measured VOCs.

Figure 7: Approximate SOA yields of several monoterpenes (α-pinene, β-pinene, 3-carene, limonene) and isoprene as a function of organic aerosol concentration (COA) for both OH and O3 oxidation. VOCs were added into ambient air in the OFR during times of low ambient SOA precursor concentrations (daytime). SOA yields were calculated assuming the added VOC was the only SOA precursor, so these yields represent upper limits in the OFR. SOA yields in the OFR are similar to SOA yields in chamber experiments.

As OH exposure increased, the degree of oxidation of OA increased, as seen by the increase in oxygen-to-carbon ratios (O:C) and decrease in hydrogen-to-carbon ratios (H:C) in a Van Krevelen diagram (Figure 8). The movement of SOA down and to the right in this space is similar to what has been seen in observations of aged OA in the atmosphere.
**Figure 8:** Van Krevelen diagram (H:C vs. O:C atomic ratios) of OA after OH oxidation in the OFR. As OHexp increases, H:C decreases and O:C increases along a trajectory similar to that measured in the atmosphere, but to much higher O:C values.

Thermal Denuder (TD) thermograms (proxies for volatility) for the two mass spectrometric markers m/z 43 (less aged OA) and m/z 44 (more aged OA) showed that organic aerosol during the wet season at T3 was on average less volatile than that observed in the Amazon forest in 2008 (AMAZE campaign) and a Rocky Mountain pine forest, and more similar to urban observations (Figure 9). Further investigation will include determining the differences in volatility for different air mass types and between the different seasons.

**Figure 9:** Thermographs showing the fraction remaining after heating for the mass spectrometric markers m/z 43 (less aged OA) and m/z 44 (more aged OA), compared to several other field campaigns. The OA during the wet season (IOP1) at the T3 site was on average less.

The volatility of total OA measured during the wet and dry seasons at T3 were similar, shown in the top panel of Figure 10. Also shown is the OA mass as a function of volatility for each season. The majority of the OA mass was relatively non-volatile.
Figure 10: OA mass fraction remaining after ambient aerosol was heated in a thermodenuder, and corresponding volatility distribution of the OA. The majority of OA during both wet and dry seasons at T3 had very low volatility.

CO₂, CO, and CH₄ concentrations showed large variability between seasons (Figure 11). During the dry season, CO exhibited multi-day enhancements in background concentrations, consistent with long-range transport of biomass burning emissions, while also showing plumes of high concentrations that may have had local biomass burning or combustion sources. CH₄ was also measured in much larger concentrations during the dry season, which was likely a result of the large herds of cows that frequented the pasture adjacent to our field site.

Figure 11: Comparison of CO₂, CO, and CH₄ measured during the wet season (left) and dry season (right). CO₂ and CO exhibited greater long-range as well as local sources (biomass burning) during the dry season, while CH₄ concentrations were increased in the dry season likely due to local farming sources.
5.0 Public Outreach

Details about the GoAmazon2014/15 campaign can be found at:

http://campaign.arm.gov/goamazon2014/

http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/

An article was recently published in Science detailing the recent research efforts in the Amazon:

http://www.sciencemag.org/content/347/6226/1051.full?utm_campaign=email-sci-toc&utm_src=email

6.0 GoAmazon2014/5 Publications

6.1 Journal Articles/Manuscripts

The results of the measurements taken under this proposal have not yet been included in any journal publications. However, the Jimenez group and our collaborators at PNNL, Harvard, and other institutions are currently using these measurements in analysis for several in-preparation publications that will be published in the coming months.

6.2 Meeting Abstracts/Presentations/Posters


Presentation of field results during several IOP field science meetings (IOP1, Feb-Mar, 2014).


7.0 References


