

## **Green Ocean Amazon 2014/15 Manaus Pollution Study Field Campaign Report**

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## **Acronyms and Abbreviations**

ARM	Atmospheric Radiation Measurement Climate Research Facility
CNPq	Brazilian National Council for Scientific and Technological Development
DOAS	differential optical absorption spectroscopy
DOE	U.S. Department of Energy
GoAmazon2014/15	Green Ocean Amazon 2014/15
INPA	Instituto Nacional de Pesquisas da Amazonia
IOP	intensive operational period
km	kilometer
LBA	Large Scale Biosphere Atmosphere Experiment in Amazonia
LIF	laser-induced fluorescence
LIP	laser-induced phosphorescence
NO <sub>x</sub>	nitrogen oxides
SOA	secondary organic aerosol
UEA	Universidade do Estado do Amazonia
VOCs	volatile organic compounds

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## 1.0 Summary

This work was part of the larger Green Ocean Amazon 2014/15 (GOAmazon 2014/15) experiment, which extended through the wet and dry seasons from January 2014 through December 2015 and which took place around the urban region of Manaus, Brazil in central Amazonia. This work was conducted as part of this experiment at the main U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility ground research site “T3” circa 100 km west of Manaus during two intensive operational periods, “IOP1” and “IOP2” (February 1 to March 31, 2014, and August 15 to October 15, 2014, respectively). Funding for this work was provided by the National Science Foundation AGS 1321987/1628491.

The GoAmazon experiment was designed to enable the study of how aerosols and surface fluxes influence cloud cycles under clean conditions, as well as how aerosol and cloud life cycles, including cloud-aerosol-precipitation interactions, are influenced by pollutant outflow from a tropical megacity. These observations provide a data set vital to constrain tropical rain forest model parameterizations for organic aerosols, cloud and convection schemes, and terrestrial vegetation components and how these are perturbed by pollution.

Research objectives specific to this work and the T3 ground site included studies of how outflow of pollution from Manaus modulated the photochemically driven conversion of emitted precursors to aerosol precursors and aerosol.

## 2.0 Results

During the Green Ocean Amazon campaign (GoAmazon 2014/15), we obtained formaldehyde and glyoxal measurements at the T3 site. These measurements were obtained using the Harvard formaldehyde laser-induced fluorescence (LIF) and glyoxal laser-induced phosphorescence (LIP) instruments, both of which are in situ instruments. After quality control the data were submitted to the ARM Data Archive.

Oxidation of volatile organic compounds (VOCs), in particular biogenic VOCs, such as isoprene, and (sesqui)terpenes, is directly linked to the formation of secondary organic aerosol (SOA) and ozone, secondary pollutants that affect climate and human health. In order to understand to what degree human influence on VOC oxidation, in particular via emissions of nitrogen oxides (NO<sub>x</sub>), changes formation of these secondary pollutants, observations of VOC oxidation products provide a powerful tool. Formaldehyde and glyoxal are VOC oxidation products often used as tracers for VOC oxidation and glyoxal has been proposed to directly contribute to SOA formation. However, only few observations of formaldehyde in pristine tropical environments exist and no previous observations of glyoxal using in situ observations have been reported, with the only previous report using differential optical absorption spectroscopy (DOAS) showing very high glyoxal concentrations. The T3 site therefore provided a unique opportunity to explore this VOC oxidation chemistry across a large range of NO<sub>x</sub> concentrations due to the regular influence from the Manaus pollution plume, which alternated with clean periods.

Our glyoxal measurements at the T3 site contrast strongly with the DOAS measurements from a tropical forest in Borneo, as we see low glyoxal concentrations. In fact, the ratio of glyoxal to formaldehyde that we observe is among the lowest ever reported. Based on extensive calibrations during the GoAmazon

campaign and additional quality control post-campaign, we have high confidence in both our observations. We are in the process of analyzing our results in combination with measurements of VOCs (precursors), oxidants (the OH radical and ozone), peroxy radicals (RO<sub>2</sub>+HO<sub>2</sub>), NO<sub>x</sub>, and other VOC oxidation products, as well as aerosol particle size distribution using a chemical box model. We will evaluate both our understanding of the fate of reactive carbon (VOCs) as well as whether current mechanisms are able to reproduce the (unique) formaldehyde and glyoxal observational data set.

The findings will provide important insight into how well current understanding is able to reproduce the conversion of emissions to SOA precursors over a large range of anthropogenic influence.

## 3.0 Publications and References

### 3.1 Publications

Martin, ST, P Artaxo, L Machado, AO Manzi, RAF Souza, C Schumacher, J Wang, T Biscaro, J Brito, A Calheiros, K Jardine, A Medeiros, B Portela, SS de Sá, K Adachi, AC Aiken, R Albrecht, L Alexander, MO Andreae, HMJ Barbosa, P Buseck, D Chand, JM Comstock, DA Day, M Dubey, J Fan, J Fast, G Fisch, E Fortner, S Giangrande, M Gilles, AH Goldstein, A Guenther, J Hubbe, M Jensen, JL Jimenez, FN Keutsch, S Kim, C Kuang, A Laskin, K McKinney, F Mei, M Miller, R Nascimento, T Pauliquevis, M Pekour, J Peres, T Petäjä, C Pöhlker, U Pöschl, L Rizzo, B Schmid, JE Shilling, MA Silva Dias, JN Smith, JM Tomlinson, J Tóta, and M Wendisch. 2016. "The Green Ocean Amazon Experiment (GoAmazon2014/5) observes pollution affecting gases, aerosols, clouds, and rainfall over the rain forest," *Bulletin of the American Meteorological Society* [doi: 10.1175/BAMS-D-15-00221.1](https://doi.org/10.1175/BAMS-D-15-00221.1).

Liu, Y, J Brito, MR Dorris, JC Rivera-Rios, R Seco, K H Bates, P Artaxo, S Duvoisin, FN Keutsch, S Kim, AH Goldstein, AB Guenther, AO Manzi, RAF Souza, SR Springston, TB Watson, KA McKinney, and S Martin. 2016. "Isoprene photochemistry over the Amazon rainforest." *Proceedings of the National Academy of Sciences of the United States of America* 113(22): 6125-6130, [doi: 10.1073/pnas.1524136113](https://doi.org/10.1073/pnas.1524136113).

### 3.2 Presentations

Impact of Anthropogenic Emissions on Isoprene Photochemical Oxidation Pathways in Central Amazonia. 2016 American Geophysical Union Fall Meeting, San Francisco, California, December, 2016. (Contributed).

Formaldehyde and Glyoxal Measurements as Tracers of Oxidation Chemistry in the Amazon Basin, 2015 American Geophysical Union Fall Meeting, San Francisco, California, December, 2015. (Contributed).

Tracking anthropogenic influence on isoprene chemistry over Amazonia, 2014 American Geophysical Union Fall Meeting, San Francisco, California, December, 2014.

Tracking anthropogenic influence on isoprene chemistry over Amazonia, 13th IGAC Science Conference on Atmospheric Chemistry, Natal, Brazil, September, 2014. (Contributed).



