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Observations and Modeling of the Green Ocean Amazon (GOAMAZON): Particulate Matter and Gases Final Campaign Summary

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Executive Summary

Because of their proven adverse effects on human health and vegetation, and also considering their influence over the local and regional climate, inhalable fine particles ($PM_{2.5}$) and NO_2, SO_2, and O_3 have been collected at the ARM site located in Manacapuru, Amazon, Brazil, as a part of the GoAmazon 2014/5 project. $PM_{2.5}$ samples were analyzed through gravimetry, black carbon transmittance, elemental composition by energy dispersive x-ray fluorescence, and ionic concentration (cations) by ion chromatography. NO_2 and SO_2 samples were analyzed by ion chromatography, whereas O_3 samples were analyzed through ultraviolet-vis spectrophotometry. Sampling of both particulate and gaseous pollutants took place during the two intensive operation periods (IOP1 from February to March 2014, and IOP2 from August to October 2014). Results are interpreted both separately and as a whole with the specific goal of identifying compounds that could affect the population's health and/or could act as cloud condensation nuclei. Chemical analysis supports the elucidation of the possible origins, transport mechanisms, health effects, and main effects of the assessed pollutants in those environments.

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement (program)
GoAmazon 2014/5	Green Ocean Amazon 2014//2015 project
IOP1	First Intensive Operation Period, February to March 2014
IOP2	Second Intensive Operation Period, August to October 2014
NO_2	Nitrogen dioxide
O_3	Ozone
$PM_{2.5}$	Particulate matter of aerodynamic diameter equal to or smaller than 2.5 μm
SO_2	Sulfur dioxide
WHO	World Health Organization
XRF	X-ray fluorescence

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1.0 Background

Industrial and urban development; growth of the automotive fleet; current patterns of consumption; deforestation, agriculture, and fertilizer use; and recurrent forest burning are some of the factors that have contributed to the increase of atmospheric pollutant emissions. The scientific literature agrees that this air pollution is a significant threat to the health of the world population, especially in developing countries (WHO 2006, Bruce et al. 2000, Pope et al. 2004, Urdea et al. 2006, Freitas et al., 2013; Watson, 2014; Kessler, 2014; Fowler et al., 2013), where regulations and inspections in general are less stringent. In recent decades, a strong correlation indicates the association between a high level of air pollution and its effects on human health, such as mortality rates, hospitalization for respiratory problems and cardiovascular diseases, worsening of asthma attacks, adverse effects on lung function, low weight of newborns, high infant and perinatal mortality, tuberculosis, cataract, and nasopharyngeal, larynx, and lung cancer (Bruce et al., 2000; Pope et al., 2004, Pope et al. 2002, Delfino et al. 2003, Valavanidis et al. 2008, Watson 2014, Kessler, 2014).

All of the main sources of atmospheric pollutants—industrial activity, vehicular exhaust, and biomass burning (forest fires and deforestation)—are present in the Amazon region of Brazil. Prevailing northwest winds carry a large portion of the pollution arising from Manaus, the capital city of the state of Amazonas, to the ARM sampling site in Manacapuru, which is located in a rural area nearly 70 km southwest of Manaus,. Manacapuru has no well-developed urban center; thus, local anthropogenic sources of air pollution can be excluded from measurements taken at the ARM site. Therefore, this site allows the assessment of anthropogenic influences in a place where urban development is minimal and pollutants that are present are mainly transported by wind.

For this campaign, both particulate and gaseous pollutants were assessed. For particulate pollution, the finest fraction of particulate matter (i.e., particulates with an aerodynamic diameter equal to or smaller than 2.5 μm, also called $PM_{2.5}$) is the most harmful because it is able to penetrate the alveoli and therefore reach the bloodstream. For that reason, the $PM_{2.5}$ fraction was selected for sampling. For gaseous pollution, the inorganic gases nitrogen and sulfur dioxides (NO_2 and SO_2, respectively) and ozone (O_3) were selected because of their proven harmful effects on human health and vegetation. There also is evidence that these pollutants influence climate processes such as cloud formation for $PM_{2.5}$, atmospheric oxidation potential (NO_2 and O_3), and rainfall acidity (NO_2 and SO_2).

Particulate and gaseous samples were taken at the ARM site in Manacapuru, Brazil, as a part of the GoAmazon 2014/5 project, which is commonly called T3. Gaseous samples were taken weekly during both the wet season from February 1, 2014, to March 31, 2014 (during the first Intensive Operation Period, or IOP1) and the dry season from August 15, 2014 to October 15, 2014 (during the second Intensive Operation Period, or IOP2). Sampling was carried out using passive diffusive samplers from Radiello® at five points (hereby called T3 01, T3 02, T3 03, T3 04 and T3 05) distributed along a 5 km straight line perpendicular to the Manacapuru-Manaus axis (the point in the middle, T3 03, was located inside the Manacapuru ARM site, and two points were located at each side from the center). Particulate sampling was taken daily also during the wet season (March 3, 2014, to April 22, 2014) and the dry season (September 4, 2014 to October 18, 2014), but at only one point at the site (T3 03). $PM_{2.5}$ samples were taken by a Harvard impactor using 37-mm diameter polycarbonate filters from Nucleopore®.

All samples were analyzed in the Federal University of Paraná, Brazil. NO_2 and SO_2 samples were analyzed by ion chromatography (using an ion chromatograph Dionex Model ICS-5000 from Thermo Fisher, analytic column IonPac® AS19, eluent potassium hydroxide with concentration gradient, and 0.3 mL min^{-1} flux with 100-µL loop), and O_3 samples were analyzed using ultraviolet-vis spectrophotometry. $PM_{2.5}$ filters were analyzed by gravimetry (using an analytic microscale Sartorius with 0.1-µg resolution), black carbon content was analyzed by transmittance (using an optic transmisometer SootScan Model OT 21 from Magee Scientific Company), soluble cation concentration was analyzed using an analytic column (IonPac® CS12, eluent methanesulfonic acid with isocratic concentration, 0.3-mL min^{-1} flux with 100-µl loop), and elemental composition was analyzed by X-ray fluorescence (XRF) (using a Minipal 4 from Panalytical). Filters from IOP1 were analyzed by all four techniques mentioned, while IOP2 filters were analyzed only for black carbon content and soluble cations concentration.

This work was financially supported by the National Council for Scientific and Technological Development, with additional support from the Fundação de Amparo à Pesquisa do Estado do Amazonas and the Financiadora de Estudos e Projetos. We also acknowledge the support from the Central Office of the Large Scale Biosphere Atmosphere Experiment in Amazônia, the Instituto Nacional de Pesquisas da Amazônia, and the Universidade do Estado do Amazonas. We want to give special recognition and express our appreciation to Bruno Takeshi and Professor Rodrigo Souza and his team for their extraordinary help during these campaigns.

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

2.0 Notable Events or Highlights

During the two sampling periods, we did not register any instrument issues, and we did not record unusual meteorological episodes.

3.0 Lessons Learned

In our initial plans for this project, we intended to analyze gaseous pollutants other than NO_2, SO_2, and O_3, namely acetic and formic acid, dioxins, and the mono-aromatic compounds benzene, toluene, ethylbenzene and meta-, orto- and para-xylenes. Because of logistical complications, sampling of dioxins was not possible, and was excluded from the project. The mono-aromatic compounds and organic acids were sampled at the site, but the samples are still being analyzed so those results are not included in this report.

Regarding particulate matter analysis, we initially intended to perform single-particle sampling, in addition to $PM_{2.5}$ sampling, and to perform additional analyses, namely single-particle elemental and molecular compositions by micro Raman spectrometry, and electron probe micro-analysis using facilities for low-Z element determination. These analyses and sampling of single particles were not performed because of unforeseen issues regarding the necessary equipment.

4.0 Results

The results obtained by the present project are divided into the following sections, the first one dealing with the gaseous pollutants and the second with particulate matter.

4.1 Gaseous Pollutants

Table 1, Table 2, and Table 3 present the results obtained for NO_2, SO_2, and O_3, respectively, for all five sampling points. Further, Figure 1 shows the average NO_2, SO_2, and O_3 concentrations graphically for each site superimposed onto a satellite image of the studied area.

Table 1. NO_2 concentrations measured at the five Manacapuru site sampling points.

		NO_2 ($\mu g\ m^{-3}$)				
	Sampling Periods	T01	T02	T03	T04	T05
IOP1	3/1-8/2014[a]	23.317 ±7.1323	0.100 ±0.1815	BDL[b]	12.199 ±0.7388	17.96 ±6.6433
	3/8-15/2014	8.935 ±0.23	0.162 ±0.0759	BDL	2.709 ±0.3424	9.257 ±0.1287
	3/15-24,/2014	7.411 ±0.429	1.72 ±0.0495	BDL	2.764 ±0.1055	0.124 ±0.0373
	3/24-31/2014	5.213 ±0.9308	2.17 ±0.3527	BDL	1.853 ±0.0604	1.186 ±0.0108
IOP2	8/27-9/3/2014	0.827 ±0.0237	2.121 ±1.4439	4.446 ±0.1872	6.132 ±0.4739	1.737 ±0.1023
	9/3-10/2014	BDL	1.512 ±0.0667	1.605 ±0.0718	1.137 ±0.442	0.514 ±0.341
	9/10-17/2014	BDL	1.336 ±0.5082	3.413 ±0.2997	2.129 ±0.0082	0.782 ±0.2625
	9/17-10/1/2014	--[c]	--	3.114 ±0.113	2.336 ±0.3611	1.801 ±0.1109
	10-1-8/2014	--	1.737 ±3.0825	1.109 ±1.6299	2.021 ±0.0244	1.477 ±0.5939
	10/8-15/2014	--	1.319 ±0.0476	2.959 ±0.5036	0.339 ±0.0935	2.631 ±0.576

[a] Date convention is month/day/year.
[b] Below Detection Limit
[c] Missing samples

Table 2. SO_2 concentrations measured at the five Manacapuru site sampling points.

		SO_2 (µg m^{-3})				
	Sampling period	T01	T02	T03	T04	T05
IOP1	3/1-8/2014[a]	0.276 ±0.0737	0.137 ±0.0156	0.079 ±0.0002	0.316 ±0.0028	0.436 ±0.0949
	3/8-15/2014	0.177 ±0.0098	0.156 ±0.01	0.152 ±0.0049	0.256 ±0.0164	3.675 ±0.0181
	3/15-24,/2014	0.197 ±0.0071	0.253 ±0.0022	0.166 ±0.0212	0.202 ±0.0183	1.078 ±0.0084
	3/24-31/2014	0.584 ±0.036	0.264 ±0.0019	0.196 ±0.0074	0.122 ±0.0014	0.622 ±0.0154
IOP2	8/27-9/3/2014	4.505 ±0.035	1.584 ±0.4433	8.963 ±0.1406	8.125 ±0.2396	14.88 ±0.3131
	9/3-10/2014	0.143 ±0.005	1.679 ±0.0056	1.259 ±0.037	1.17 ±0.1995	0.272 ±0.0375
	9/10-17/2014	--[b]	0.47 ±0.0756	0.815 ±0.0512	1.652 ±0.0106	0.284 ±0.0367
	9/17-10/1/2014	--	--	0.209 ±0.0056	0.303 ±0.0017	0.207 ±0.0189
	10-1-8/2014	--	0.215 ±0.1519	0.157 ±0.0626	22533 ±0.0426	0.216 ±0.0376
	10/8-15/2014	--	0.323 ±0.0459	0.453 ±0.0589	1,001 ±0.0107	0.33 ±0.0357

[a] Date convention is month/day/year.
[b] Missing samples

Table 3. O_3 concentrations measured at the five Manacapuru site sampling points.

		O_3 (µg m^{-3})				
	Sampling period	T01	T02	T03	T04	T05
IOP1	3/1-8/2014[a]	3.3265[b]	5.8898	1.5969	4.545	6.2578
	3/8-15/2014	8.6066	7.3148	1.8168	4.0788	13.5495
	3/15-24./2014	11.3441	5.4738	1.439	3.6268	11.9792
	3/24-31/2014	10.8555	6.5128	3.8097	3.1291	5.1396
IOP2	8/27-9/3/2014	6.7162	1.8587	1.4296	4.553	3.2996
	9/3-10/2014	--[c]	1.3384	1.0003	-	6.2148
	9/10-17/2014	--	1.6535	2.1597	18.4487	12.7573
	9/17-10/1/2014	--	1.7151	2.3724	40.213	36.0312
	10-1-8/2014	--	1.2657	1.3327	16.3307	19.4015
	10/8-15/2014	--	1.2584	1.557	1.5665	22.7877

[a] Date convention is month/day/year.
[b] Standard deviation was not calculated for O_3 samples because the volume extracted during the analytical procedure was not enough to analyze replicates of each sample.
[c] Missing samples

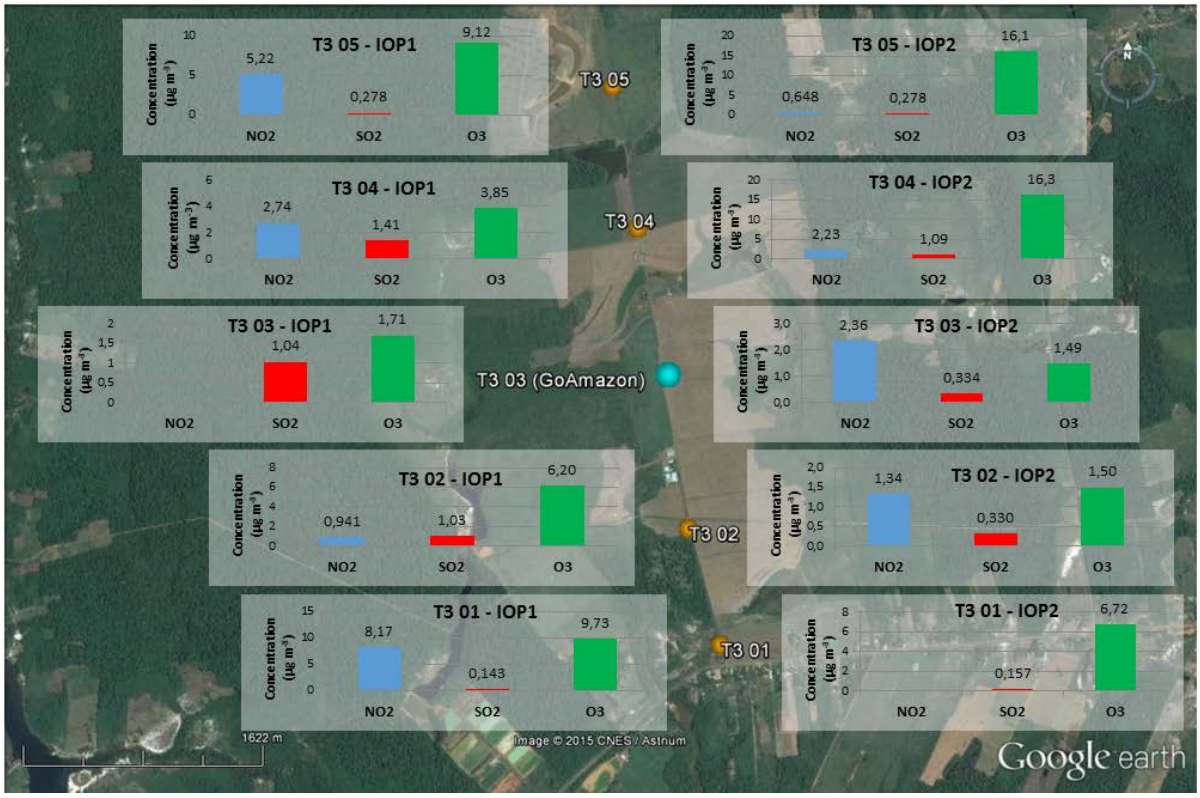

Figure 1. Satellite image of the studied area with superimposed average concentrations of NO_2, SO_2, and O_3 for each sampling point during each sampling period.

4.2 Particulate matter

The results from $PM_{2.5}$ analyses are provided in the following sections for sampling point T3 03 during both IOPs.

4.2.1 Weight Concentration

Figure 2 displays all the weight concentration data resulting from measurements taken at sampling point T3 03 during IOP1.

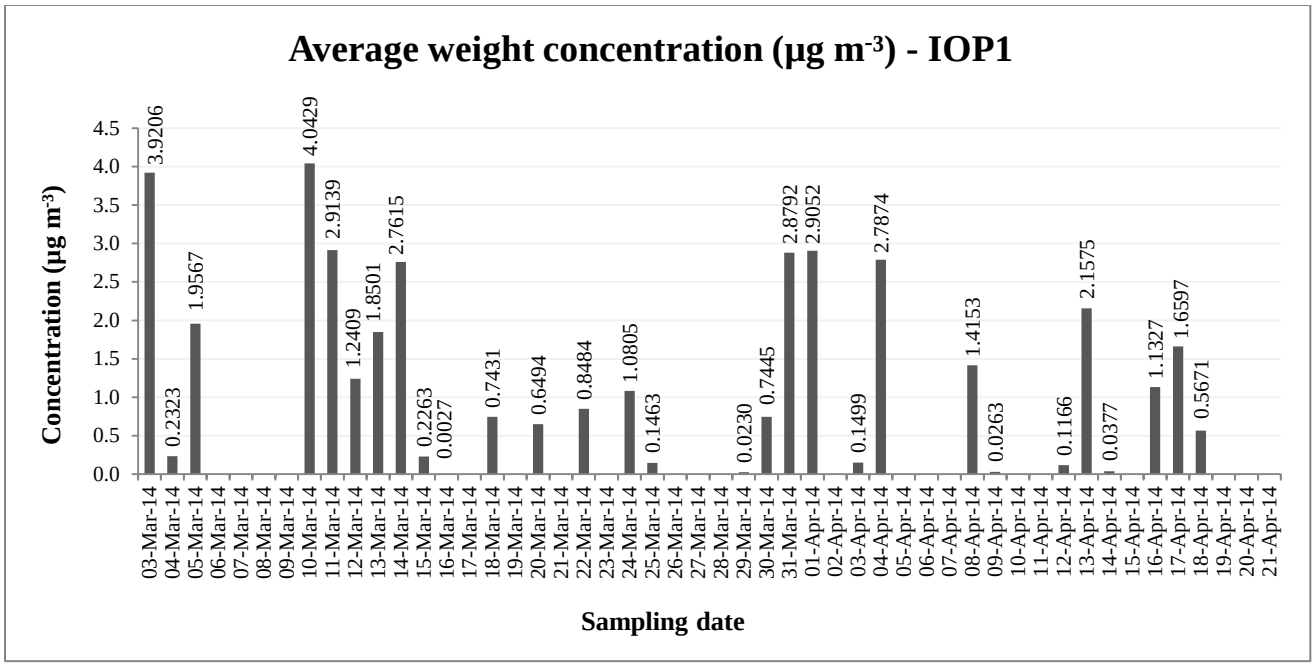

Figure 2. Daily average weight concentration measured at T3 03 during IOP1.

4.2.2 Black Carbon Content

Figure 3 and Figure 4 display all the black carbon concentration data resulting from measurements taken at sampling point T3 03 during IOP1 and IOP2, respectively.

4.2.3 Elemental Composition by X-Ray Fluorescence

Figure 5 shows the content of silicon (Si), sulfur (S), potassium (K), iron (Fe), calcium (Ca) and titanium (Ti) present in the $PM_{2.5}$ filters collected at sampling location T3 03 during IOP1 (measured by means of XRF).

4.2.4 Soluble Cation Concentrations

Figure 6 and Figure 7 show the content of the soluble cations lithium (Li^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) in the $PM_{2.5}$ filters collected at sampling location T3 03 during IOP1 and IOP2, respectively (measured by ion chromatography).

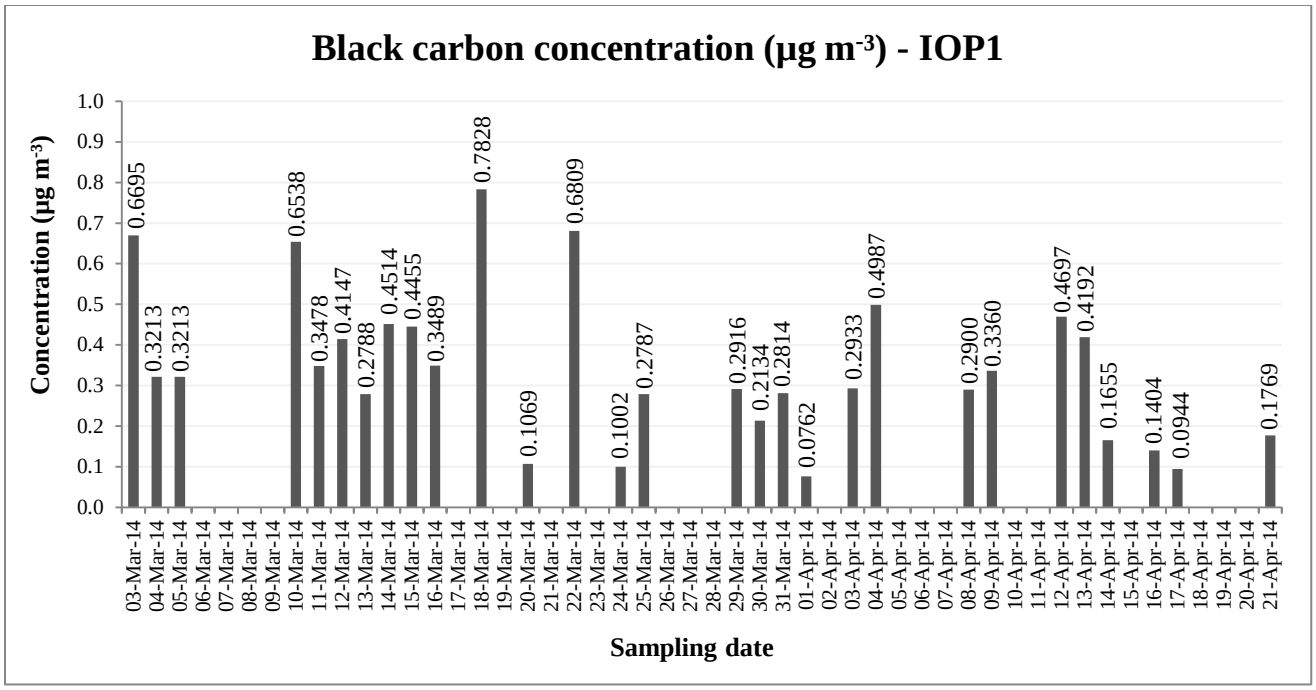

Figure 3. Daily average black carbon concentration measured at T3 03 during IOP1.

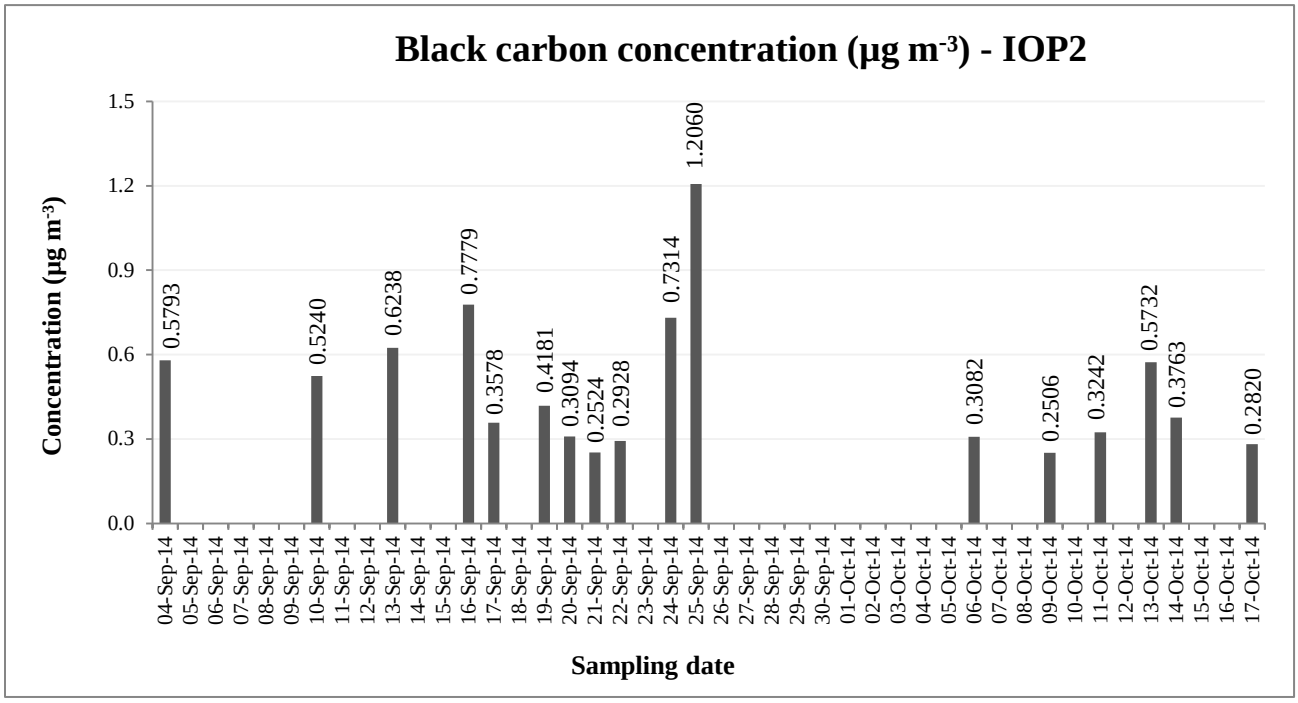

Figure 4. Daily average black carbon concentration measured at T3 03 during IOP2.

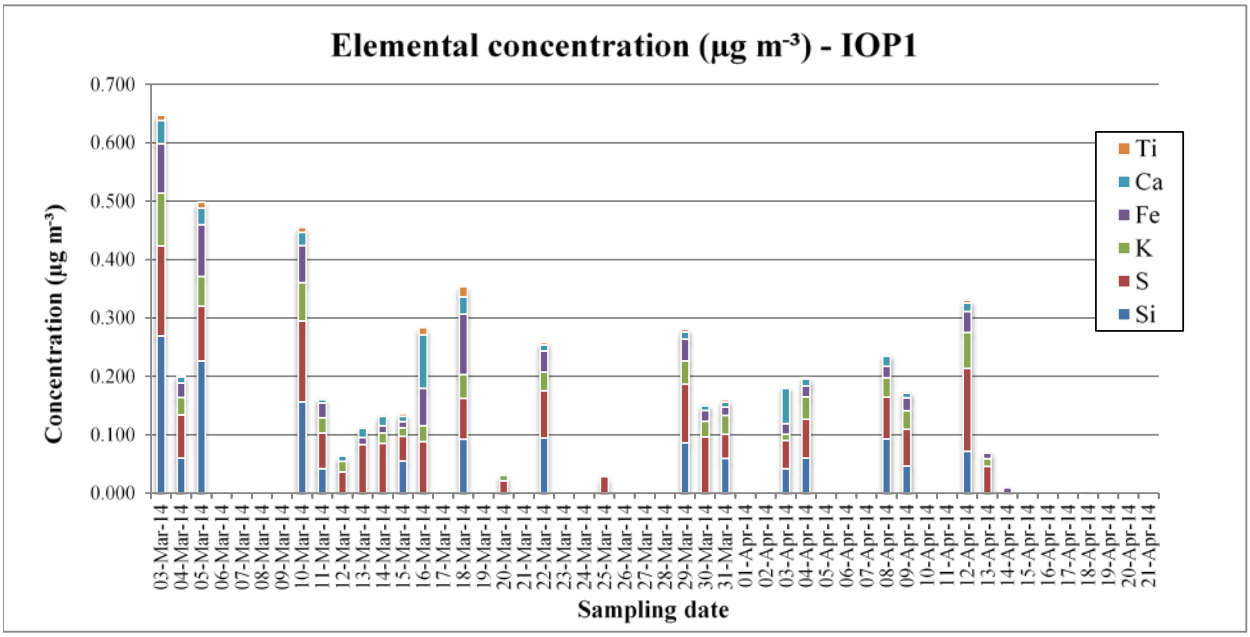

Figure 5. Elemental concentration of the $PM_{2.5}$ filters collected at T3 03 during IOP1 (XRF measurements).

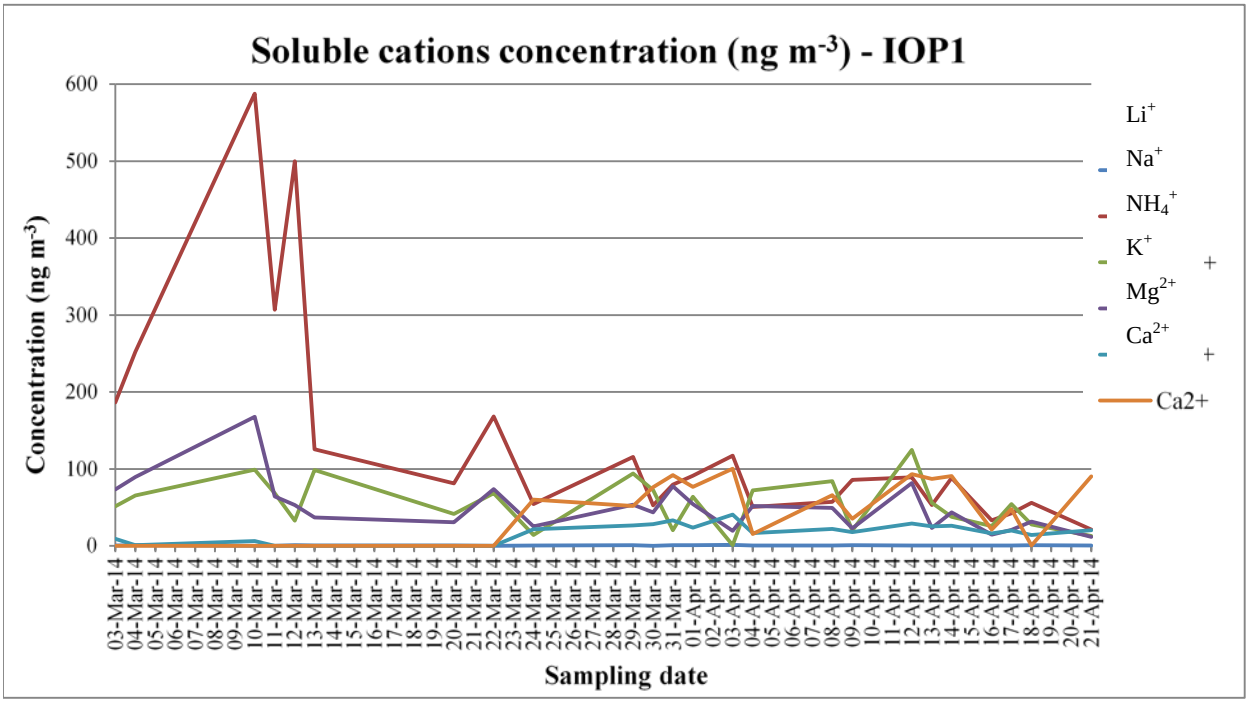

Figure 6. Soluble cation concentrations of the $PM_{2.5}$ filters collected at T3 03 during IOP1 (ion chromatography measurements).

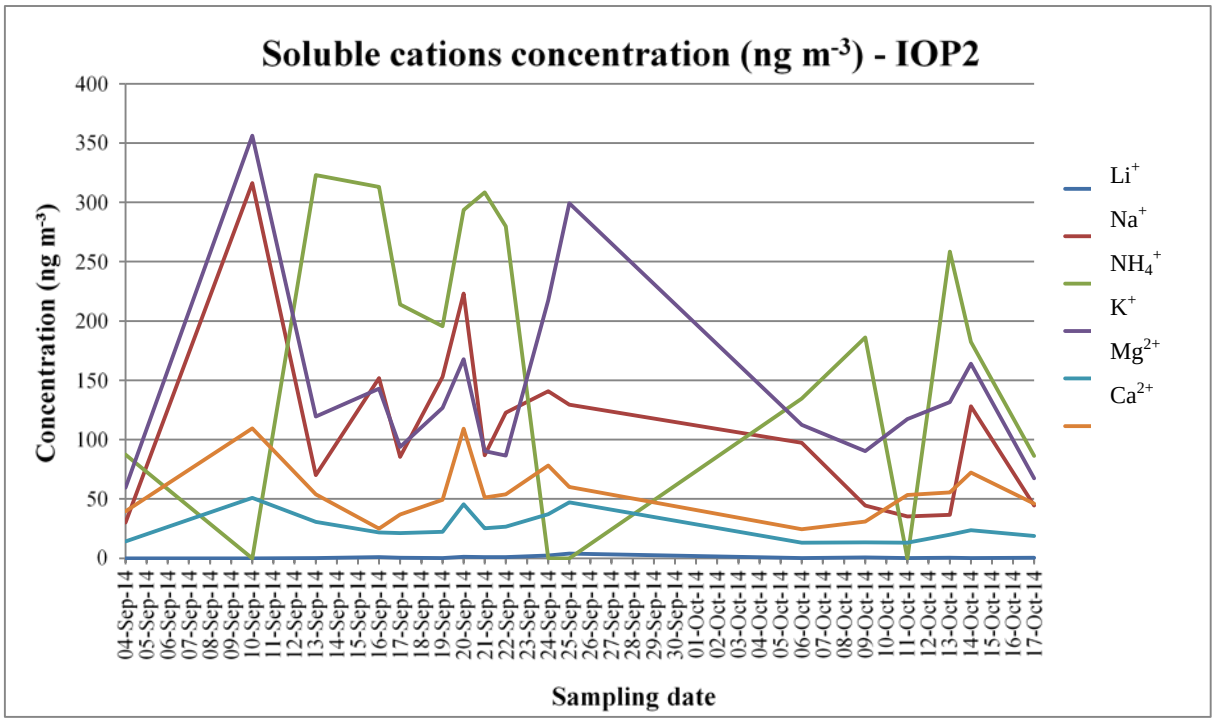

Figure 7. Soluble cation concentrations of the $PM_{2.5}$ filters collected at T3 03 during IOP2 (ion chromatography measurements).

5.0 Public Outreach

Not applicable.

6.0 GoAmazon 2014/5 Publications

6.1 Journal Articles/Manuscripts

Not applicable.

6.2 Meeting Abstracts/Presentations/Posters

The results presented here were also presented as a poster during the GoAmazon2014/5 Science Conference in Cambridge, MA, 18-20 May 2015. The poster presented there is reproduced below:

MONITORING AIR POLLUTANTS AT T1 MANAUS AND T3 MANACAPURU DURING GOAMAZON2014/5 IOPS

Rodrigo A. F. de Souza[2], Cybelli G. G. Barbosa[1], Sarah L. Paralovo[1], Priscila S. Kurzlop[1], Isabela P. S. Carneiro[1], Scot T. Martin[3], Antonio O. Manzi[4], Carlos I. Yamamoto[1], Ana F. L. Godoi[1], Ivan Kourtchev[6], Sarah Connors[5], James G. Levine[6], Neil Harris[5], Markus Kalberer[5], Ricardo H. M. Godoi[1*] - rhmgodoi@gmail.com

[1]Federal University of Paraná (UFPR), Brazil, [2]University of State of Amazon (UEA), Brazil, [3]Harvard University, USA, [4]National Institute of Amazonian Research (INPA), [5]University of Cambridge, [6]University of Birmingham.

SUMMARY

In the present study, 4 additional sites were selected for sampling nearby the T3 site, forming a straight line with 5 sampling points, being the original T3 in the center. This strategy was pursuit in order to provide an unprecedented spatial gradient of concentration of several air pollutants, namely NO_2, SO_2, O_3, H_2S, $PM_{2.5}$ and BC.

SAMPLING SITES

Sampling was carried out at five sites near T3 (the GoAmazon experiment) during the Intense Operation Periods 1 and 2 (IOP1 and 2. The location of the five sites, along with their coordinates, is shown in Figure 1, whereas Table 1 details the periods when the samples were taken.

Samples of PM2.5 were taken by means of a Harvard impactor, and analyzed for gravimetry and BC content. Gaseous pollutants were sampled using passive diffusive samplers, provided by Radiello®, as shown in Figure 2, which were later analyzed by ion chromatography (NO_2 and SO_2) or UV-spectrophotometry (O_3 and H_2S). *Compounds under analysis:* BTEX, Acetic Acid and Formic Acid.

A state-of-the-art direct-infusion nano-electrospray (nanoESI) ultrahigh resolution mass spectrometry was used to determine hundreds of individual constituents of organic aerosol influenced by biogenic-anthropogenic interactions. Comprehensive mass spectral data evaluation methods (e.g., Kendrick Mass Defect and Van Krevelen diagrams) were used to identify compound classes and mass distributions of the detected species.

Table 1. Sampling period of particulate matter.

Particulate daily sampling		
Period		
03 Mar 2014 to 31 Mar 2014 (18 samples)	IOP1	Wet Season
04 Sep 2014 to 14 Oct 2014 (16 samples)	IOP2	Dry Season

Table 2. Sampling period of gaseous compounds.

Gases weekly sampling		
Period		
01 Mar 2014 to 08 Mar 2014	IOP1	Wet Season
08 Mar 2014 to 15 Mar 2014		
15 Mar 2014 to 24 Mar 2014		
24 Mar 2014 to 31 Mar 2014		
29 Aug 2014 to 03 Sep 2014	IOP2	Dry Season
03 Sep 2014 to 10 Sep 2014		
10 Sep 2014 to 17 Sep 2014		
17 Sep 2014 to 01 Oct 2014		
01 Oct 2014 to 08 Oct 2014		
08 Oct 2014 to 15 Oct 2014		

Ultrahigh Resolution MS Analysis

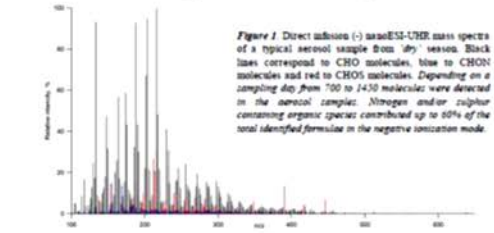

Figure 1. Direct infusion (-) nanoESI-UHR mass spectra of a typical aerosol sample from 'dry' season. Black lines correspond to CHO molecules, blue to CHON molecules and red to CHOS molecules. *Depending on a sampling day, from 700 to 1450 molecules were detected in the aerosol samples. Nitrogen and/or sulphur containing organic species contributed up to 60% of the total identified formulae in the negative ionization mode.*

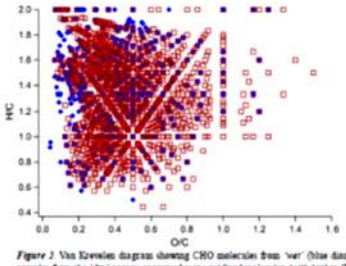

Figure 3. Van Krevelen diagram showing CHO molecules from 'wet' (blue diamonds) and 'dry' (red squares) seasons. *Aerosol samples from the 'dry' season contained more oxidized molecules (with higher O/C ratio) compared to that from the 'dry' season suggesting that wet deposition significantly affects molecular composition at the site.*

Table 3. Median concentrations (in μg m^{-3}) of $PM_{2.5}$ and BC at T3 03.

Particulate Matter at T3 03 (GoAmazon) (in μg m^{-3})		
	IOP1	IOP2
$PM_{2.5}$	0.964	15.9
BC	0.335	0.397

MEDIAN CONCENTRATION OF GASEOUS POLLUTANTS AT T3

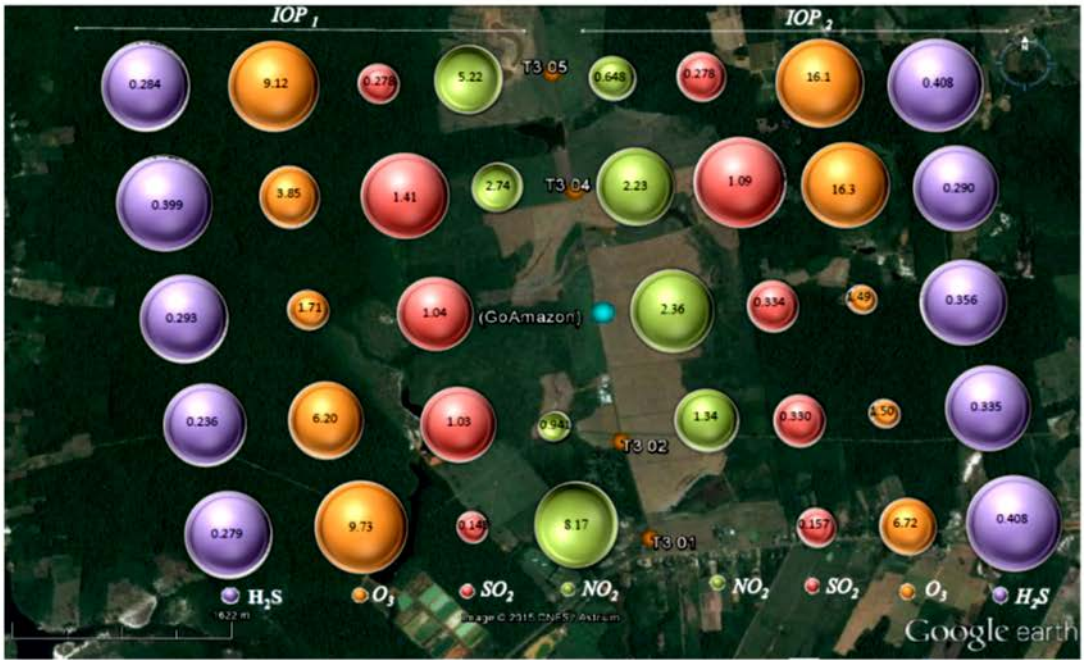

Figure 3. Median concentration (in μg m^{-3}) of various gaseous compounds at T3 and 2.5 km far from there (scales differ from dataset to dataset).

FAPESP CNPq

7.0 References

Bruce N, R Perez-Padilla, and R Albalak R. 2000. "Indoor Air Pollution in Developing Countries: A major environmental and public health challenge." *Bulletin of the World Health Organization*. 78(9):1078-1092.

Delfino, RJ, H Gong, WS Linn, Y Hu, and ED Pellizzari. 2003. "Respiratory Symptoms and Peak Expiratory Flow in Children with Asthma in Relation to Volatile Organic Compounds in Exhaled Breath and Ambient air." *Journal of Exposure Analysis and Environmental Epidemiology* 13(5):348-363.

Fowler, D, M Coyle, U Skiba, MA Sutton, JN Cape, S Reis, LJ Sheppard, A Jenkins, B Grizzetti, JN Galloway, P Vitousek, A Leach, AF Bouwman, K Butterbach-Bahl, F Dentener, D Stevenson, M Amann, and M Voss. 2013. "The Global Nitrogen Cycle in the Twenty-First Century." *Philosophical Transactions of the Royal Society* B 368:20130165. doi:10.1098/rstb.2013.0165.

Freitas, CU, W Junger, AP Leon, R Grimaldi, MAFR Silva, and N Gouveia. 2013. "Poluição do Ar Em Cidades Brasileiras: Selecionando indicadores de impacto na saúde para fins de vigilância." *Epidemiologia e Serviços de Saúde* 22(3):445-454.

Kessler R. 2014. "Prevention: Air of danger." *Nature* 509:s62-s63. doi:10.1038/509S62a.

Pope, CA, RT Burnett, MJ Thun, EE Calle, D Krewski, K Ito, and GD Thurston. 2002. "Lung Cancer, Cardiopulmonary Mortality, and Long-Term Exposure to Fine Particulate Air Pollution." *Journal of the American Medical Association* 287(9):1132–1141. doi:10.1001/jama.287.9.1132.

Pope, CA, RT Burnett, GD Thurston, MJ Thun, EE Calle, D Krewski, and JJ Godleski. 2004. "Cardiovascular Mortality and long-Term Exposure to Particulate Air Pollution: Epidemiological evidence of general pathophysiological pathways of disease. *Circulation* 109:71–77. doi:10.1161/01.CIR.0000108927.80044.7F.

Urdea M, LA Penny, SS Olmsted, P Kaspar, A Shepherd, P Wilson, CA Dahl, S Buchsbaum, G Moeller, and DCH Burgess. 2006. "Requirements for High Impact Diagnostics in the Developing World." *Nature* 73-79. doi:10.1038/nature05448.

Valavanidis, A, F Konstantinos, and T Vlachogianni. 2008. "Airborne Particulate Matter and Human Health: Toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms." *Journal of Environmental Science and Health Part C Environmental Carcinogenesis & Ecotoxicology Reviews* 26(4):339-362. doi:10.1080/10590500802494538.

Watson, T. 2014. "Environment: Breathing trouble." *Nature* 513:s14-s15. doi:10.1038/513S14a.

World Health Organization (WHO). 2006. *Air Quality Guidelines: Global Update 2005. Particulate matter, ozone, nitrogen dioxide, and sulfur dioxide*. WHO Regional Office for Europe, Copenhagen, Denmark. ISBN 92 890 2192 6.

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