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

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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 <sub>2</sub>	Nitrogen dioxide
O <sub>3</sub>	Ozone
PM <sub>2.5</sub>	Particulate matter of aerodynamic diameter equal to or smaller than 2.5 μm
SO <sub>2</sub>	Sulfur dioxide
WHO	World Health Organization
XRF	X-ray fluorescence

## Contents

Executive Summary .....	iii
Acronyms and Abbreviations .....	v
1.0 Background.....	1
2.0 Notable Events or Highlights .....	2
3.0 Lessons Learned .....	2
4.0 Results .....	3
4.1 Gaseous Pollutants .....	3
4.2 Particulate matter.....	5
4.2.1 Weight Concentration .....	5
4.2.2 Black Carbon Content .....	6
4.2.3 Elemental Composition by X-Ray Fluorescence .....	6
4.2.4 Soluble Cation Concentrations .....	6
5.0 Public Outreach .....	9
6.0 GoAmazon 2014/5 Publications.....	9
6.1 Journal Articles/Manuscripts.....	9
6.2 Meeting Abstracts/Presentations/Posters .....	9
7.0 References .....	11

## Figures

Figure 1. Satellite image of the studied area with superimposed average concentrations of NO <sub>2</sub> , SO <sub>2</sub> , and O <sub>3</sub> for each sampling point during each sampling period. ....	5
Figure 2. Daily average weight concentration measured at T3 03 during IOP1. ....	6
Figure 3. Daily average black carbon concentration measured at T3 03 during IOP1. ....	7
Figure 4. Daily average black carbon concentration measured at T3 03 during IOP2. ....	7
Figure 5. Elemental concentration of the PM <sub>2.5</sub> filters collected at T3 03 during IOP1. ....	8
Figure 6. Soluble cation concentrations of the PM <sub>2.5</sub> filters collected at T3 03 during IOP1. ....	8
Figure 7. Soluble cation concentrations of the PM <sub>2.5</sub> filters collected at T3 03 during IOP2. ....	9

## Tables

Table 1. NO <sub>2</sub> concentrations measured at the five Manacapuru site sampling points. ....	3
Table 2. SO <sub>2</sub> concentrations measured at the five Manacapuru site sampling points. ....	4
Table 3. O <sub>3</sub> concentrations measured at the five Manacapuru site sampling points. ....	4

## 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  $\mu\text{m}$ , also called  $\text{PM}_{2.5}$ ) is the most harmful because it is able to penetrate the alveoli and therefore reach the bloodstream. For that reason, the  $\text{PM}_{2.5}$  fraction was selected for sampling. For gaseous pollution, the inorganic gases nitrogen and sulfur dioxides ( $\text{NO}_2$  and  $\text{SO}_2$ , respectively) and ozone ( $\text{O}_3$ ) 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  $\text{PM}_{2.5}$ , atmospheric oxidation potential ( $\text{NO}_2$  and  $\text{O}_3$ ), and rainfall acidity ( $\text{NO}_2$  and  $\text{SO}_2$ ).

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<sup>®</sup> 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).  $\text{PM}_{2.5}$  samples were taken by a Harvard impactor using 37-mm diameter polycarbonate filters from Nucleopore<sup>®</sup>.



All samples were analyzed in the Federal University of Paraná, Brazil. NO<sub>2</sub> and SO<sub>2</sub> samples were analyzed by ion chromatography (using an ion chromatograph Dionex Model ICS-5000 from Thermo Fisher, analytic column IonPac<sup>®</sup> AS19, eluent potassium hydroxide with concentration gradient, and 0.3 mL min<sup>-1</sup> flux with 100-μL loop), and O<sub>3</sub> samples were analyzed using ultraviolet-vis spectrophotometry. PM<sub>2.5</sub> 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 transmissometer SootScan Model OT 21 from Magee Scientific Company), soluble cation concentration was analyzed using an analytic column (IonPac<sup>®</sup> CS12, eluent methanesulfonic acid with isocratic concentration, 0.3-mL min<sup>-1</sup> 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<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>, 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<sub>2.5</sub> 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<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>, respectively, for all five sampling points. Further, Figure 1 shows the average NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub> concentrations graphically for each site superimposed onto a satellite image of the studied area.

**Table 1.** NO<sub>2</sub> concentrations measured at the five Manacapuru site sampling points.

		NO <sub>2</sub> (µg m <sup>-3</sup> )				
	Sampling Periods	T01	T02	T03	T04	T05
IOP1	3/1-8/2014 <sup>a</sup>	23.317 ±7.1323	0.100 ±0.1815	BDL <sup>b</sup>	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	-- <sup>c</sup>	--	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

<sup>a</sup> Date convention is month/day/year.  
<sup>b</sup> Below Detection Limit  
<sup>c</sup> Missing samples

**Table 2.** SO<sub>2</sub> concentrations measured at the five Manacapuru site sampling points.

		SO <sub>2</sub> (µg m <sup>-3</sup> )				
	Sampling period	T01	T02	T03	T04	T05
IOP1	3/1-8/2014 <sup>a</sup>	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	-- <sup>b</sup>	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

<sup>a</sup>Date convention is month/day/year.  
<sup>b</sup>Missing samples

**Table 3.** O<sub>3</sub> concentrations measured at the five Manacapuru site sampling points.

		O <sub>3</sub> (µg m <sup>-3</sup> )				
	Sampling period	T01	T02	T03	T04	T05
IOP1	3/1-8/2014 <sup>a</sup>	3.3265 <sup>b</sup>	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	-- <sup>c</sup>	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

<sup>a</sup>Date convention is month/day/year.  
<sup>b</sup>Standard deviation was not calculated for O<sub>3</sub> samples because the volume extracted during the analytical procedure was not enough to analyze replicates of each sample.  
<sup>c</sup>Missing samples

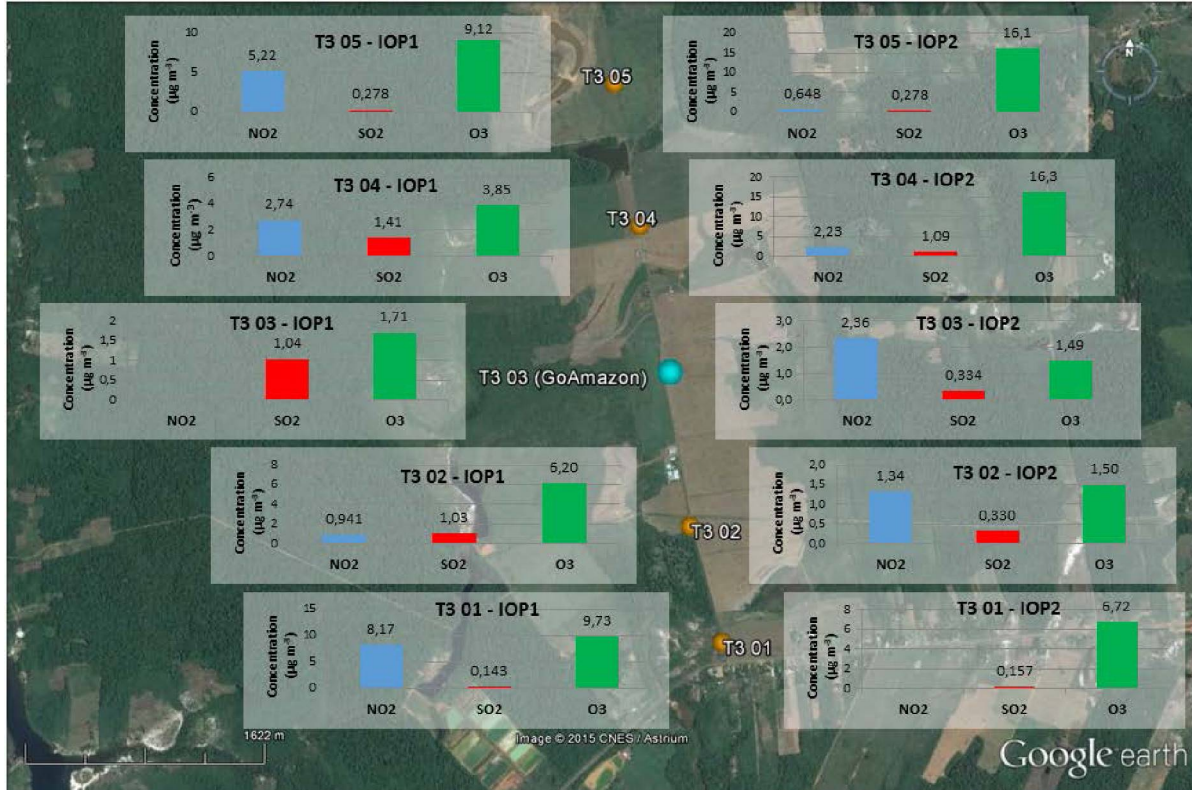


Figure 1. Satellite image of the studied area with superimposed average concentrations of NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub> for each sampling point during each sampling period.

## 4.2 Particulate matter

The results from PM<sub>2.5</sub> 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.

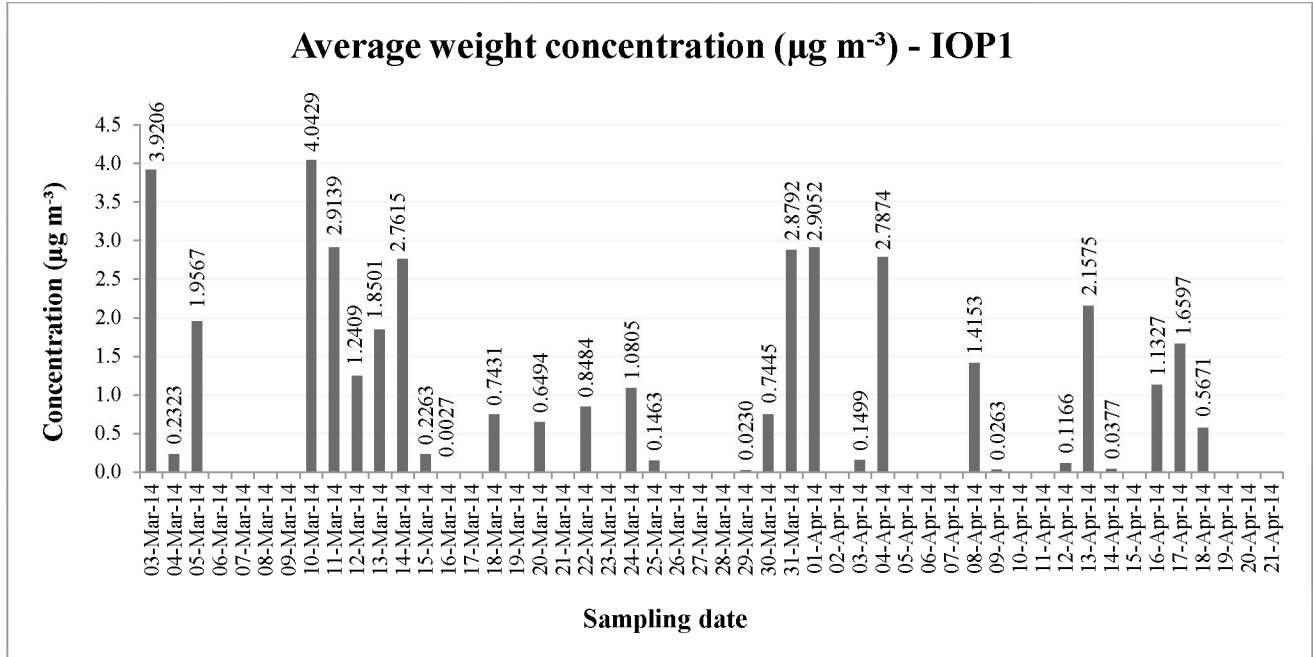


Figure 2. Daily average weight concentration measured at T3 03 during IOP1.

#### 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<sub>2.5</sub> 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<sup>+</sup>), sodium (Na<sup>+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), potassium (K<sup>+</sup>), magnesium (Mg<sup>2+</sup>), and calcium (Ca<sup>2+</sup>) in the PM<sub>2.5</sub> filters collected at sampling location T3 03 during IOP1 and IOP2, respectively (measured by ion chromatography).

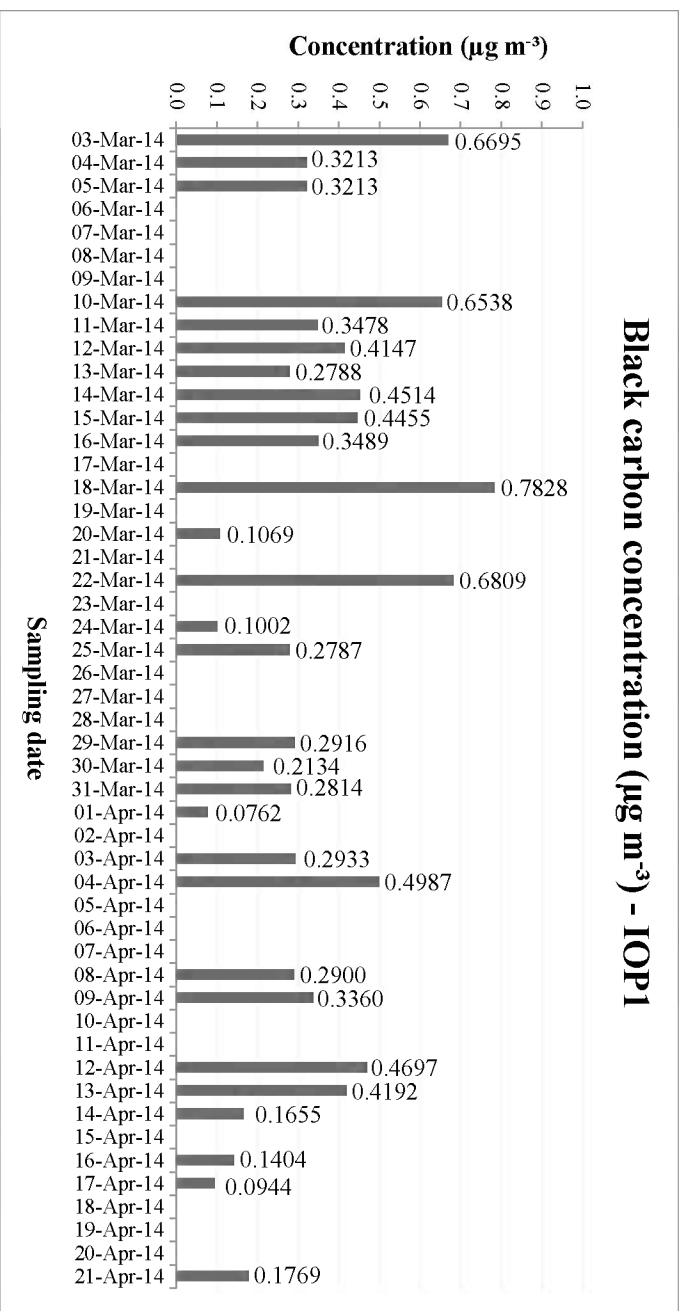


Figure 3. Daily average black carbon concentration measured at T3 03 during IOP1.

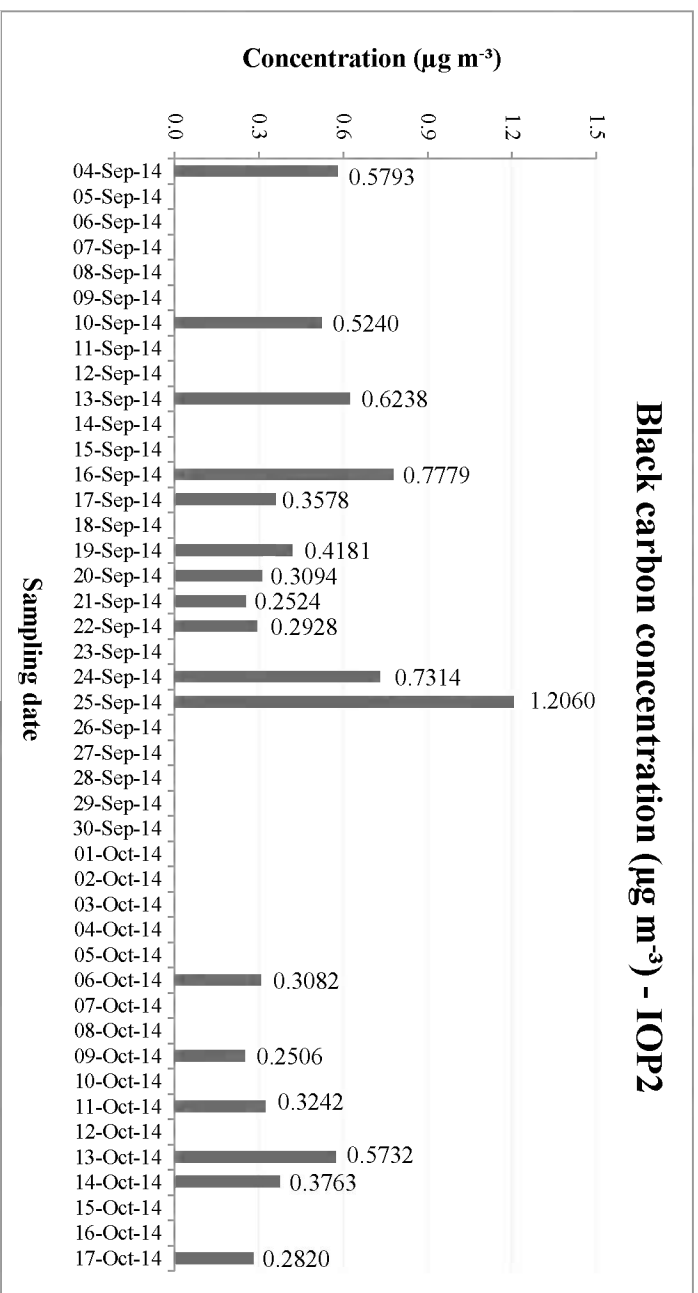
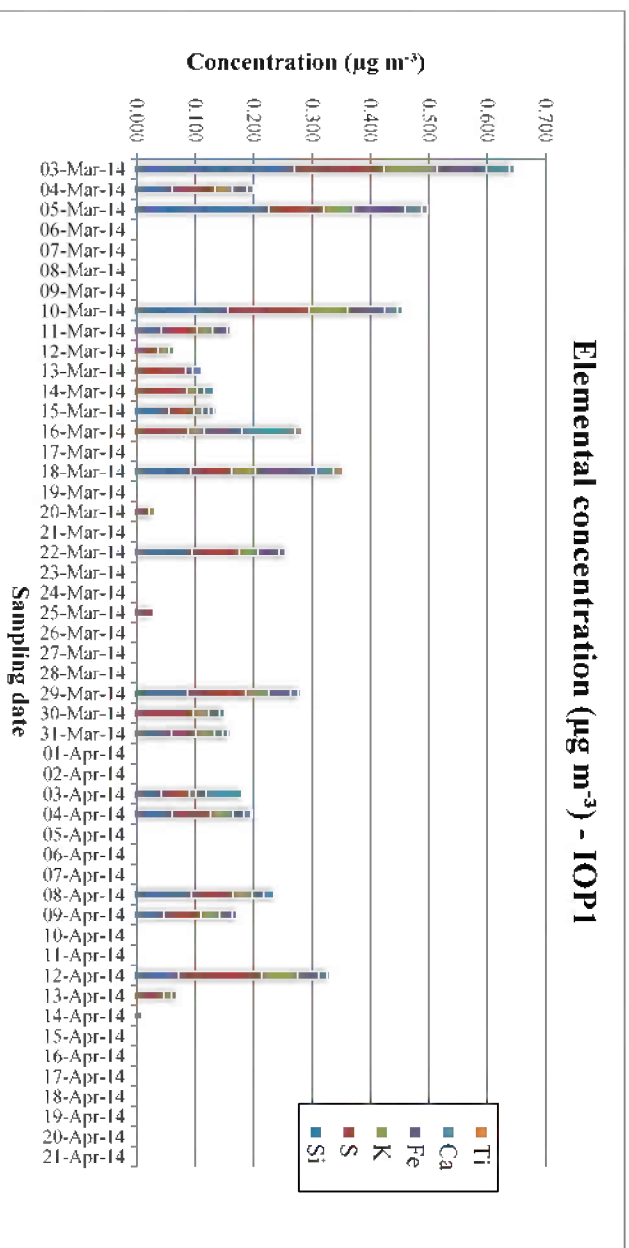
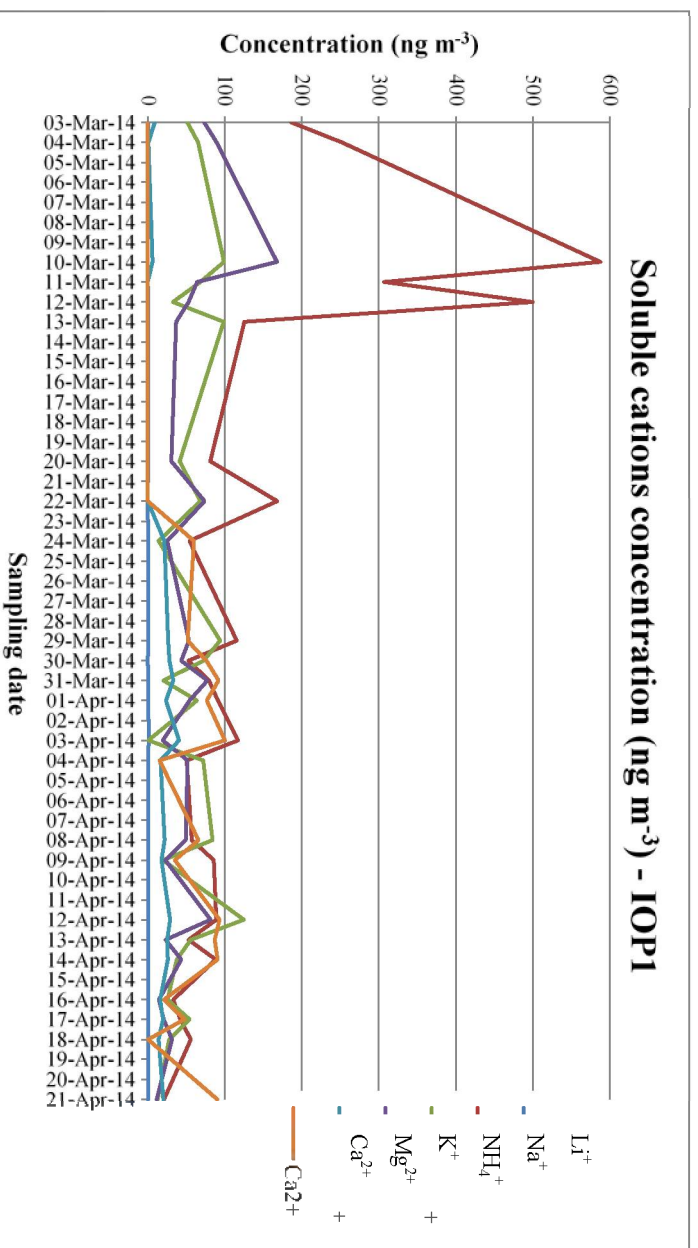


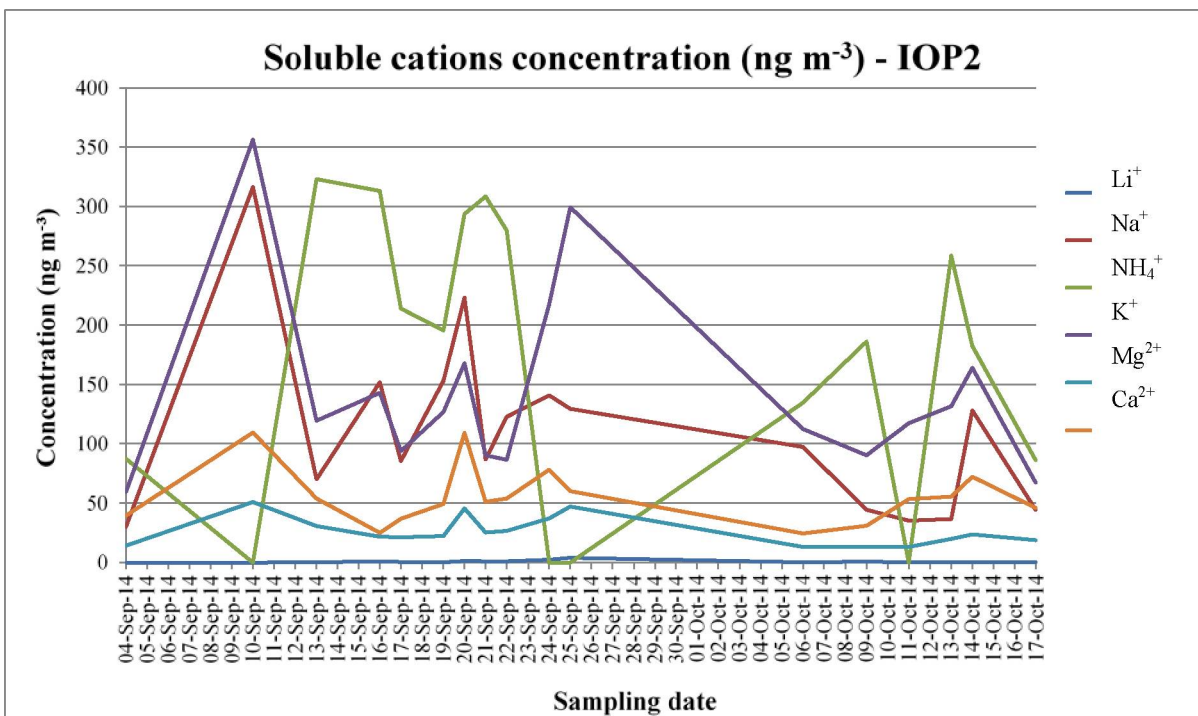
Figure 4. Daily average black carbon concentration measured at T3 03 during IOP2.



**Figure 5.** Elemental concentration of the  $\text{PM}_{2.5}$  filters collected at T3 03 during IOP1 (XRF measurements).



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



**Figure 7.** Soluble cation concentrations of the PM<sub>2.5</sub> filters collected at T3 03 during IOP2 (ion chromatography measurements).

## 5.0 Public Outreach

Not applicable.

## 6.0 GoAmazon 2014/5 Publications

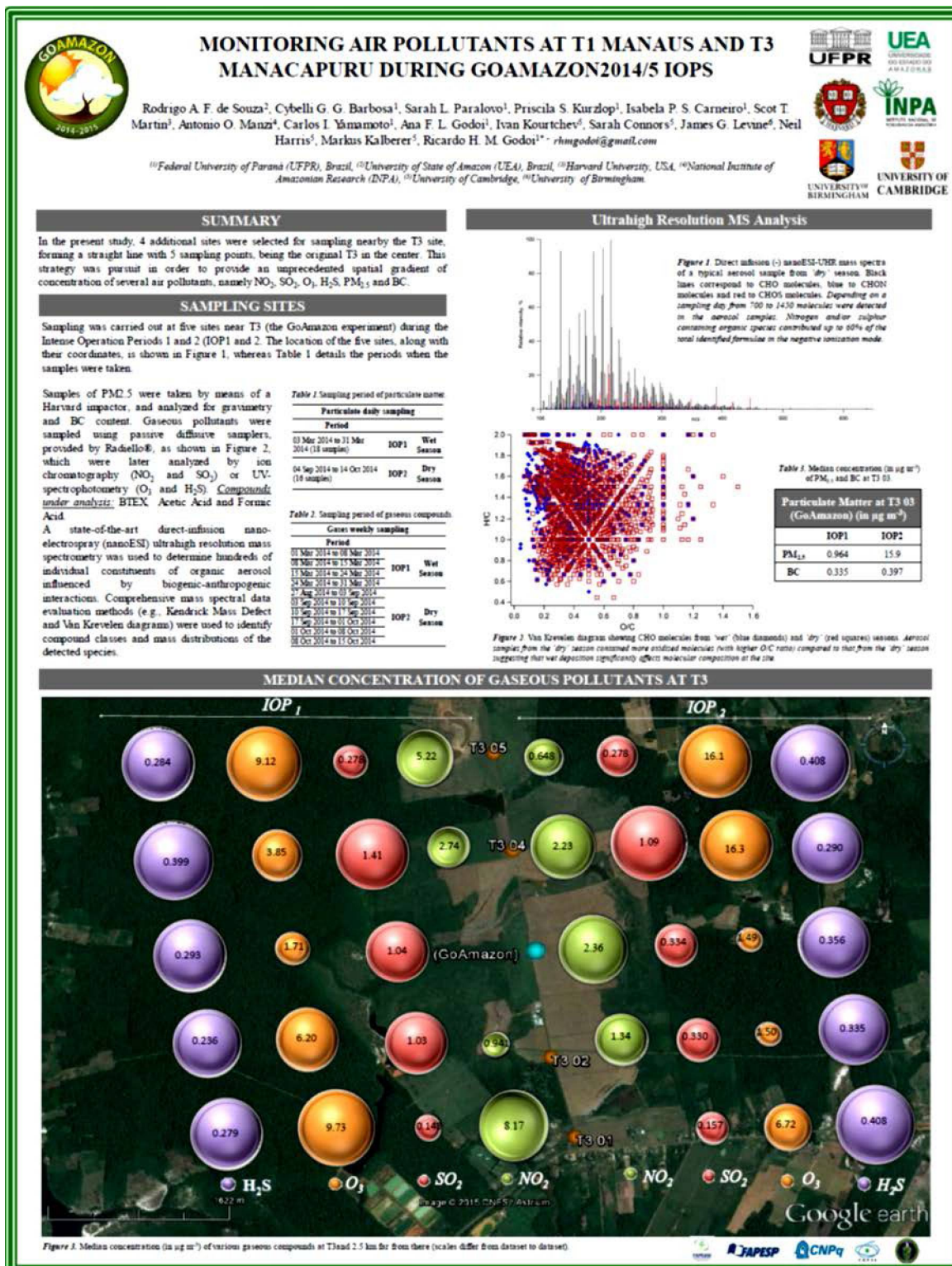
### 6.1 Journal Articles/Manuscripts

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:





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