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## Supplement of

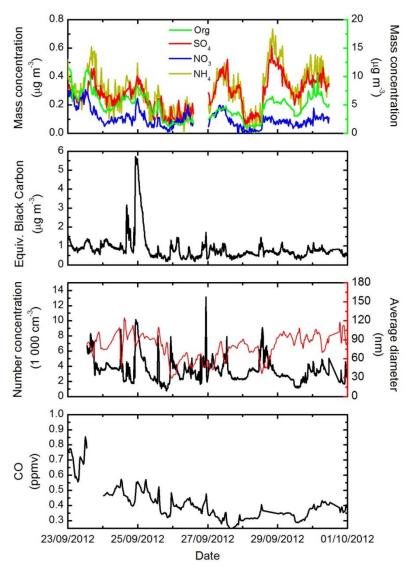
# Ground-based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment

J. Brito et al.

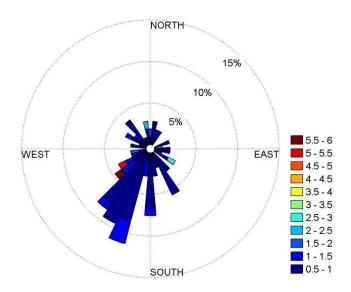
Correspondence to: J. Brito (jbrito@if.usp.br)

### Strong BC<sub>e</sub> enhancement observed during Phase II

The identified BBOA peaks are in good agreement with the strong enhancements of aerosol number, CO and BCe, shown in Fig. 5. BCe, however, shows other peaks throughout the campaign, in particular on 24 September, without a similar trend in organics and CO (Fig. 5, detailed view on Fig. S1). Given that BCe loading enhancement was observed for several hours and correlates precisely with southwesterly wind directions (Fig. S2), this BCe loading can be assigned to a point source, probably a brickyard. Despite the relatively important contribution to the BCe loading during this event, this source did not show up in the OA factor analysis as discussed below.



**Fig. S1.** Detailed view of concentration time series of the following species: Organics, SO4, NO3 and NH4 (a), Equivalent Black Carbon (b), particle number concentration and average diameter (c) and CO mixing ratio (d).



**Fig. S2.** Correlation between BCe concentrations (color, in μg m<sup>-3</sup>) and wind direction from 23 to 30 September 2012. Values below 0.5 μg m<sup>-3</sup> were removed to reduce noise.

#### Satellite identification of fire spots around the sampling area

As discussed in the site description section (Sec. 2.1), a state reservation is located north of the sampling site, thus most of the biomass burning is expect to take place outside this area, most notably in previously deforested areas south of the sampling site. Fig. S3 depicts fire spot locations as identified by the fire spot identification tool from the Brazilian National Institute of Space Research (<a href="http://queimadas.cptec.inpe.br">http://queimadas.cptec.inpe.br</a>) from 13 to 15 September 2012. This period of time comprises the peak of aerosol loading at the sampling site during SAMBBA.



Fig. S3. Fire spots identified in the sampling site region from 13 to 15 September 2012.

#### PMF Analysis of ACSM data

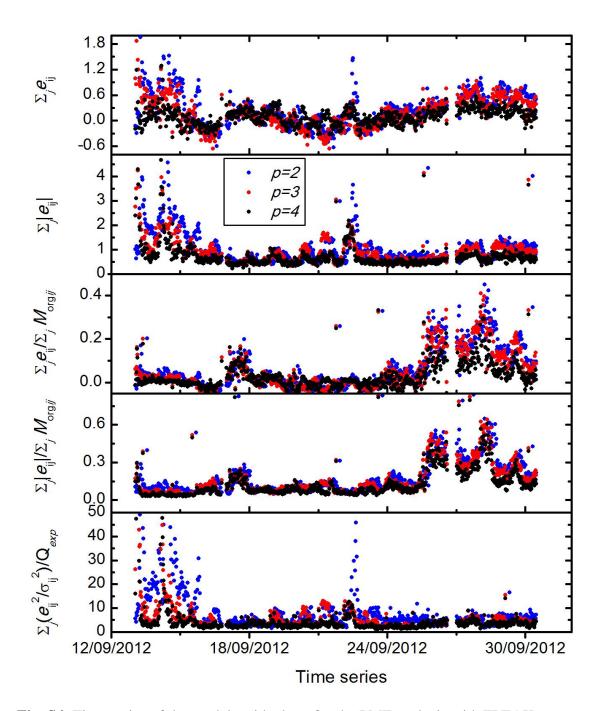
PMF analysis has been performed on the time series of the mass spectral intensities for  $12 \le m/z \le 100$  of the organic component (Ulbrich et al., 2009). Before applying PMF analysis on the ACSM data, the errors from incorrect and non-representative spikes had to be eliminated. Following Carbone et al. (2013), individual m/z's of such events were downweighted 100 times, decreasing their importance in the fit, instead of simply eliminating the data points. This procedure is especially important when treating ACSM data that has a 30 min time resolution.

For the analysis, a range of factor solutions was explored with different seeds, with the SEED parameter varying from 0 to 100 in steps of 5. The rotational ambiguity of the solutions was explored by varying the FPEAK parameter from -0.5 to 0.5, while keeping SEED=0, since little impact was observed from this parameter on the mass spectra and time series. PMF factor identification was conducted by comparing time series (TS) and mass spectra (MS) of each factor with external gas and particle tracers from collocated measurements and reference spectra from the AMS spectra database. For each dataset, PMF analysis was performed for

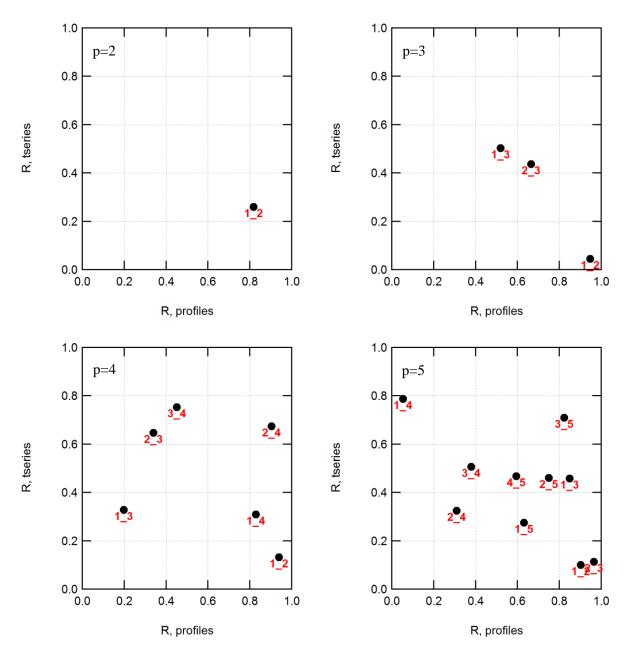
one to 8 factors. The time series of the model residuals  $e_{ij}$  for the PMF analysis is shown in Fig. S4. The solutions are described in Table S1 and Figures S4-S6.

Table S1. Summary of PMF solutions obtained for SAMBBA dataset.

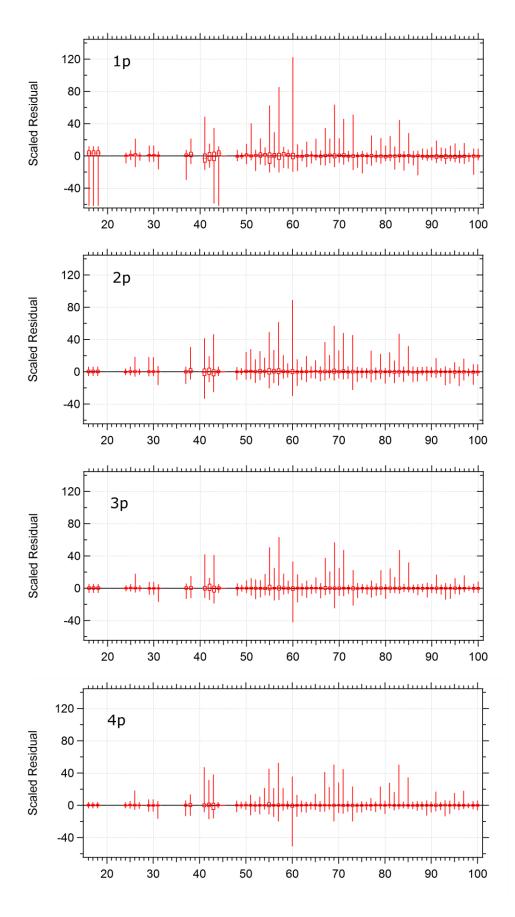
# Factors	FPEAK	SEED	Q/Q <sub>expected</sub>	Solution Description
1	0	0	8.40	One-factor resulted in large residuals at some time periods and $m/z$ 's
2	0	0	5.67	Two-factors linked to BBOA shows significantly reduced residuals. However with large residual at specific masses, in particular $m/z$ 60.
3	-0.5 to 0.5	0	4.29-4.31	In this range, factor time series and MS changing indicating a possible optimum solution for rotation.
3	0	0	4.29	Optimum number of factors (Fresh BBOA, Aged BBOA and LV-OOA) and FPEAK. The time trend and mass spectra compare well with independent particles and/or gaseous measurements and reference MS.
3	0	0-100 in steps of 5	4.29	All three factors are nearly identical for all different seed.
4 to 8	0	0	3.25-1.93	Although $Q/Q_{\rm exp}$ is reduced, factor splitting appears as shown by unrealistic zeroes in factor time series, a single $m/z$ peak in factor MS, and similar time trends with each other.



**Fig. S4.** Time series of the model residuals  $e_{ij}$  for the PMF analysis with FPEAK = zero.



**Fig. S5.** Pearson's R for the correlations between the time series and the mass spectra of any two factors for the PMF solutions with different number of factors.

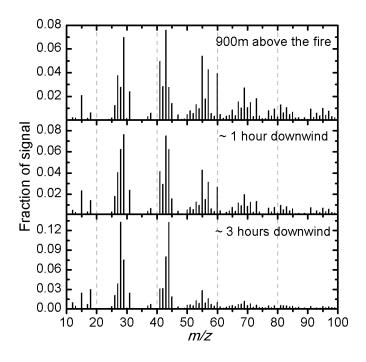


**Fig. S6.** Scaled residuals for all m/z's for 1-4 factor solutions.

Despite the relative proximity to the city of Porto Velho, factor analysis did not resolve an urban emissions factor. This probably arises from three reasons: a) Taking into account both wind speed and wind direction, the prevailing wind during the studied period comes from the north, the opposite direction from Porto Velho; b) The spectrum signature of primary organic aerosols from vehicular sources resembles closely those of BBOA (Ng et al., 2010) and c) the most human-impacted areas are located south of the sampling site (as well as Porto Velho), whereas north is a vast forest preserve.

#### AMS spectra obtained during plume chasing during SAMBBA

The Figure S7 below shows the organic spectra obtained from plume chasing in Rondônia/Brazil using the airborne AMS during flight B737 on 20 September 2012.

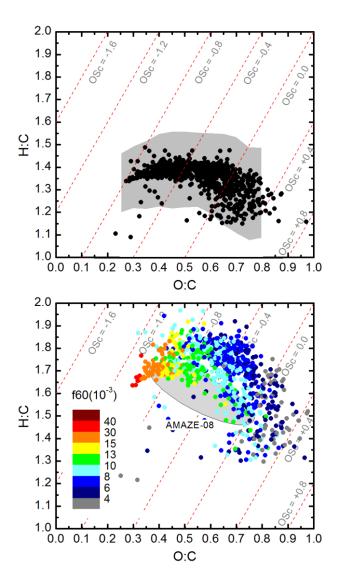


**Fig. S7.** Spectra obtained from the airborne AMS during plume chasing – flight B737.

#### Van Krevelen diagram using newly proposed O:C and H:C estimation methods

Based on the uncertainties reported by (Ng et al., 2011) on the H:C estimation from f43, an uncertainty area has been calculated increasing 10% of the 90<sup>th</sup> percentile and decreasing 10% of 10<sup>th</sup> percentile of the H:C values (Fig. S8, top panel). Such area indicates that the slope of the V-K diagram could deviate significantly and be still within considered uncertainty.

Recent laboratory measurements suggest that O:C and H:C ratios measured from HR-AMS are substantially underestimated for usual ambient measurements (Canagaratna et al., 2014). The newly proposed correlations directly impact O:C and H:C as estimated by the ACSM. As such, O:C and H:C were recalculated according using the relationship, still under validation, and shown in Fig. S8 bottom panel, below.



**Fig. S8.** Top: Results obtained here with uncertainty range (+10% above 90<sup>th</sup> percentile and -10% for 10<sup>th</sup> percentile) indicated in the gray area. Bottom: Similar to Fig. 07, taking into consideration the newly proposed corrections for HR-AMS O:C and H:C ratios according to Canagaratna et al., (2014). For consistency the AMAZE-08 V-K area based on Heald et al., (2010), shown here, has been corrected by similar factors.

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