**Supplementary Information for: "Leaf phenology as one important driver of seasonal changes in isoprene emission in central Amazonia"**

## 1. Isoprene flux - Relaxed Eddy Accumulation system

### 1.1 Source of errors

According to Arnts et al. (2013), there are three main sources of errors that lead to uncertainties in the air sampling portion of the REA technique – (1) time lag, (2) non-constant flow achievement, and (3) chemical losses.

Since air sample segregation into the respective reservoirs – up, down, and neutral – should be performed without cross-contamination from the other direction, the time spent measuring wind velocity and direction and then computing and executing the respective command needs to be fast enough to avoid a time lag. Here, the REA sampling was carried out with two tubing lines for up (+w') and down (-w') and one tubing line for neutral sampling air ($\pm 0.6\sigma_w$ - deadband), each consisting of about 1.5 m long tubes (polytetrafluoroethylene, PTFE). Each inlet valve at the main REA box prevented air from entering the inactive tube (up- in the case of down sampling (-w') and down - in the case of up sampling (+w'), and both up and down in the case of deadband), which otherwise would compromise the concentration differences between up and down reservoirs and, consequently, the flux calculation.

By having separate inlet lines, there is an intrinsic one-sample time lag that cannot be corrected. The system measures the wind velocity from the sonic anemometer during the first 0.1 second, and then switches the valve for the following 0.1 second. Therefore, there is a mismatch of 0.1 second. However, this is not a significant problem over tall canopies, as in the Amazonian rainforest, where the main flux-carrying eddies are large. In addition, the use of the deadband helps since only large eddies are sampled, removing the contribution of small eddies.

To diminish the second source of error described by Arnts et al. (2013), the REA system had three sets of valves (upstream and downstream valves for up, down and neutral reservoirs) joined with a constant flow rate sampling (air samples were drawn by a pump and controlled by a mass flow controller at a rate of 200 ml $min^{-1}$) to minimize problems with non-equivalent pressure differential across the valve inlet(s) and exit, so that constant sample flow can be achieved through the correct placement of three way valves, mass flow controller and pump with adsorbent tube accumulators. To avoid the third problem, chemical losses, the inlets (up, down, and neutral) were installed at the sonic anemometer height (48 m) with a filter for ozone and particulate matter (Pall Corporation, Glass Fiber Acrodisc), and then connected to the main REA box containing the adsorbent cartridges for the respective up/down/neutral reservoirs.

When using cartridges as reservoirs, a non-constant flow rate has an even larger effect since it is necessary to know the gas volume that was sampled onto each cartridge. To verify the constant flow rate and chemical losses, the REA was tested by sampling a gas standard (isoprene and camphene) while using actual wind data to drive the valves. Isoprene and camphene were recovered on the cartridges quantitatively (to within ± 10%), indicating that sample volumes were correctly measured by the REA and that there were insignificant chemical losses for these two compounds.

**1.2 Uncertainties**

The REA system is parameterized by the *b*-coefficient, which is derived from the covariance of the vertical wind velocity (w') and air temperature (T') measured by the sonic anemometer. Therefore, the isoprene flux derived from the REA is relative to the heat flux. The heat flux measured by the REA sonic anemometer (at 48 m) and heat flux data measured simultaneously by an Eddy Covariance (EC) system (at 53.1 m) indicated a slope of 0.86 ($R^2$=0.72, $p$<0.05), suggesting the REA may have underestimated the heat flux by 14%. It is not clear why the REA heat fluxes were this much lower than those from the EC system.

In general, REA flux measurements have the same errors of Eddy Covariance flux measurements (e.g. statistical averaging, nonzero $\overline{w}$, etc.), which is typically around 10-15%. But, REA flux measurements have in addition a source of error in the compound concentration measured. Typically, the BVOC concentration measurement is the larger source of error. In this study, propagation of errors accounting for the $C_{up}$ - $C_{down}$ of isoprene concentrations ranged from 17.1% to 29.9 % for all measurements. Therefore, assuming errors in turbulence measurements and in isoprene concentration measurements, the uncertainties of these REA flux measurements ranged from 27.1% to 44.9%.

**1.3 Sample analysis at the National Center for Atmospheric Research (NCAR)**

Samples from June 2013 and July 2013 were analyzed in a TD/GC-MS-FID system from the Atmospheric Chemistry Division of the NCAR. For this system, thermal desorption was carried out via a two-stage process, where the adsorbent cartridge was initially desorbed at 275 $^{o}$C while passing a flow of ultra-high purity through using a commercial TD-autosampler (Model Ultra1, Markes International, UK). The sample was transferred via a heated line to a cold trap that was packed with Tenax-TA and cooled to 0 $^{o}$C via peltier (Unity Series1, Markes International, UK). Once the entire sample was transferred to this intermediate trap, it is rapidly heated to 300 $^{o}$C and injected into the GC column (DB-5 column, Restek, 250 micron). The GC column was cryofocused to -30 $^{o}$C and then temperature programmed up to 275 $^{o}$C. After separation, the sample was split between the two detectors (FID and Mass Spectrometer - MS). This system is calibrated daily by filling adsorbent cartridges with a secondary standard consisting of isoprene and camphene. This isoprene/camphene standard was calibrated relative to a NIST-certified butane/benzene gas standard as well as a NIST-certified neohexane gas standard. The FID was used to quantify isoprene.

## 2. Tower-camera derived leaf phenology and demography

### 2.1 Camera setup

Two Red-Green-Blue (or RGB) imaging systems were installed at the K34 site and the ATTO site, respectively, for continuous monitoring of tropical leaf phenology. Both imaging systems used the Stardot IP camera, model Netcam XL 3MP. The K34 system used the native CMOS resolution of 1024 x 768 pixels, while the ATTO camera was configured to an interpolated resolution of 2048 x 1536 pixels, to reduce JPEG artifacts and allow use of crowns occupying few pixels. At K34, we used a varifocal lens (Stardot reference LEN-MV4510CS), adjusted to about 66$^o$ HFOV. A fixed-iris 96$^o$ HFOV lens (LEN-3.5MMCS) was installed on the ATTO camera. Views were fixed with south and west azimuths respectively, toward plateau forest areas and excluding the sky. Cameras were set to automatic exposure and to not apply automatic color balance. They were locally controlled by a Compulab microcomputer (model Fit-PC2i), which stored the images *in situ*. After one year of operation, ATTO images were stored on the tower server, and samples were sent daily by Internet, improving system monitoring and reducing data gaps. More details about the camera setup can be found in Lopes et al. (2016) and Wu et al. (2016).

## 2.2 Camera-based tree inventories

Using only diffusely lit images taken around local noon to avoid lighting artifacts, we tracked the temporal trajectory of each tree crown´s green chromatic coordinate (gcc) and assigned it to one of three classes: "leaf flushing" (abrupt greening due to massive emission of new leaves), "leaf abscising" (large abrupt greying – the color of exposed bare branches) or "no change". Different methods for detecting leaf flushing and leaf abscising crowns were used. Visual detection and classification of flushing and abscising crowns were used for the K34 inventory (as in Nelson et al., 2014, Lopes et al., 2016; Wu et al., 2016). For the ATTO inventory, due to the much larger number of trees, we used an automatic approach validated by visual classification.

To estimate the monthly fractions of all crowns that abruptly flushed or abscised at ATTO, we calculated each crown's gcc value at daily interval over the one-year timeline, and automatically assigned the phenophase by adopting thresholds for slope, slope duration and final height of peaks (massive leaf flush) or valleys (massive leaf abscission) of their gcc time series (see Lopes et al., 2016 for more details). As shown by Lopes et al. (2016), this method is highly correlated with the visual detection method (correlation coefficient, $R^2$=0.98).

For the K34 inventory, bare abscised crowns were visually classified and arranged in monthly counts. The fraction of all crowns classified to the abscised state has previously been shown to be linearly and inversely proportional to total canopy LAI at seasonal timescales (Wu et al., 2016), so was used at K34 to provide a camera-based estimate of temporal variation in canopy LAI. For the ATTO dataset, we obtained the fraction of each crown´s illuminated pixels (i.e. excluding shade) that were classified as woody pixels. When a crown contained a woody fraction higher than a certain threshold (see below), it was treated as the bare abscised state. We surveyed all the crowns through time, and consequently derived the time series of the fraction of bare abscised crowns, by which we further derived camera-based LAI time series, as at K34, using the relationship as shown in Wu et al. (2016). Automated woody (bare branch) pixel detection is described below.

**2.3 Bare branch detection at ATTO**

Upper canopy branches are grey or white, so an illuminated branch pixel has similar digital numbers (DN) across the three RGB bands. We first identified and masked shade areas by a threshold of the total DN brightness, as $R+G+B<250$. Then we obtained the Normalized Dissimilarity for non-shade areas:

$$\text{Dissimilarity} = \frac{|R-G| + |R-B| + |G-B|}{R + G + B}$$

Normalized Dissimilarity varies from zero to one and pixels occupied by bare wood are closer to zero. A threshold to obtain the fraction of each crown´s non-shade pixels having low Normalized Dissimilarity ($\leq 0.22$, for this dataset) identifies the illuminated fractional area of that crown occupied by bare branches (the complement of this is the illuminated green leaf fraction). Results are comparable to using the second principal component transform of the three RGB bands, as described by Wu et al. (2016; see section 5.3 of their Supplementary Materials), with the advantage that the same threshold can be applied to all images over time. Using the second principal component (or PC2) to measure wood area would require that a different threshold be selected for each image. A reference area with constant wood amount is therefore required to iteratively determine the correct PC2 threshold. Such a reference area containing a fixed wood amount was not available in the ATTO camera images.

We thus processed individual timelines of the percentage of woody pixels over the illuminated crown area. As previously noted, a tree crown was counted as deciduous for those days in its timeline when the fraction of its illuminated crown pixels classified as wood was >= 0.20. From this we obtained the monthly mean count and mean fraction of all crowns that were classified to the bare abscised state.

## References


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