Biogeosciences

EGU

Supplement of

Leaf phenology as one important driver of seasonal changes in isoprene emissions in central Amazonia

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S1. Isoprene flux - Relaxed Eddy Accumulation system

S1.1 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 (±0.6σ_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.

S1.2 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%.

S1.3 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.

References

Arnts, R. R., Mowry, F. L. and Hampton, G. A.: A high-frequency response relaxed eddy accumulation flux measurement system for sampling short-lived biogenic volatile organic compounds, J. Geophys. Res. Atmos., 118(10), 4860–4873, doi:10.1002/jgrd.50215, 2013.