Exploratory study on chiral BVOC fluxes from tropical forests by REA method

NUCLEAR AND ENERGY RESEARCH INSTITUTE

Caroline Ostermann[1], Nora Zannoni[2], Elias Felipe de Carvalho[1], Jonathan Williams[2], Oscar Vega[1]

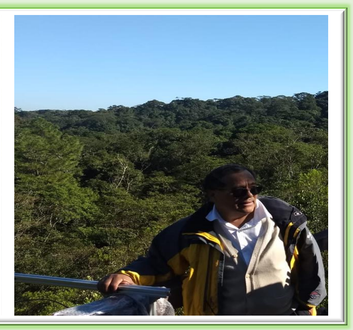
carol.kako@usp.br

1 Nuclear and Energy Research Institute, Center for Chemistry and Environment, 2242 São Paulo/SP, Brazil

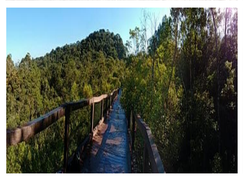
2 Air Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

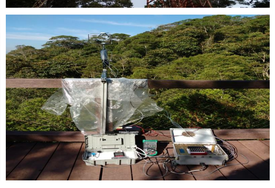
1.WHAT IS THE STUDY ABOUT?

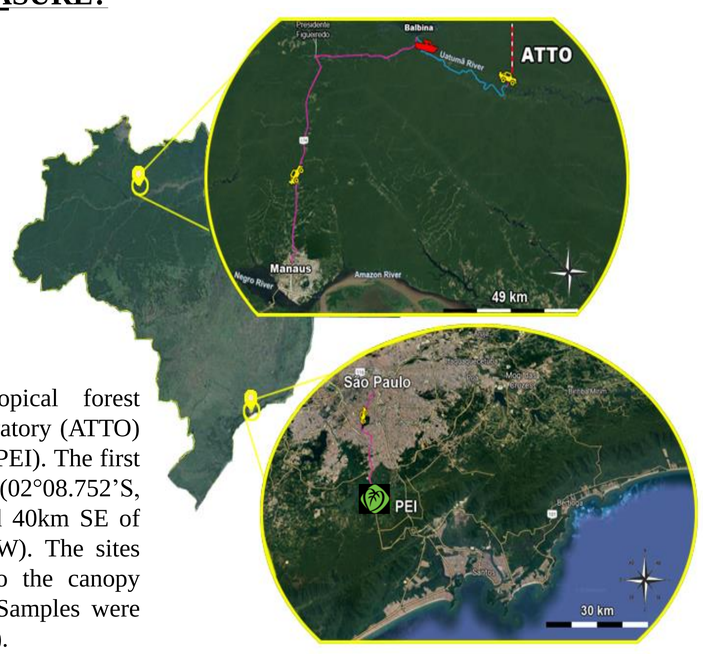
Many biogenic volatile organic compounds (BVOCs) are chiral, meaning they naturally occur as two mirror images of the same molecule. Past and current studies on chiral BVOCs have highlighted the existence of regiospecific patterns [1] and their variability with time of the day, season and height [2]. To better elucidate the role of the tropical forest as a source or a sink of chiral VOC we determined the fluxes of chiral molecules in two distinctive tropical forest environments: the Amazonian forest and the Atlantic forest. Fluxes were estimated by means of the *Relaxed Eddy Accumulation* (REA) method.



2. WHERE AND WHEN DID WE MEASURE?





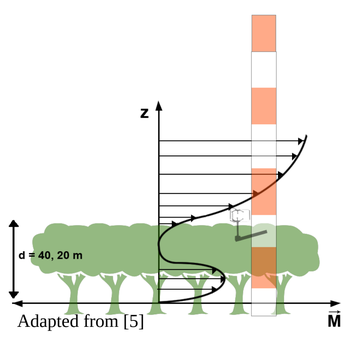


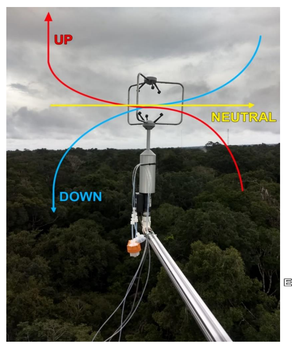
We took air samples in two distinct tropical forest environments: the Amazonian Tall Tower Observatory (ATTO) and Atlantic forest in Imigrants Ecological Park (PEI). The first site is located 150km NE of Manaus, Brazil (02°08.752'S, 59°00.335'W) [3] and the second one is located 40km SE of São Paulo, Brazil (23°50'39.86"S, 46°34'37.09"W). The sites were chosen for having a tower enclosed into the canopy allowing to measure above the canopy height. Samples were taken at 40m height during July/2019 (wet season).

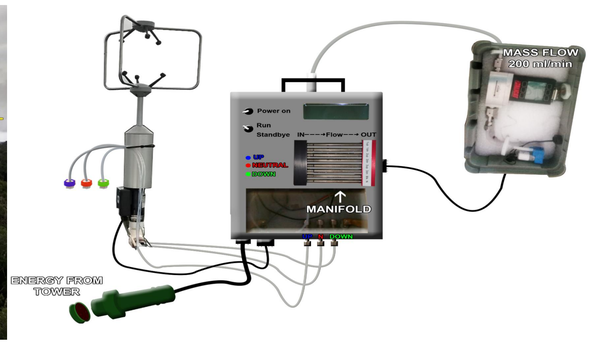
3. HOW DID WE MEASURE?

The sampling :

The sampling was done with cREA (*REA Cartridge Sampler*) which is a data recorder with 3 cartridge pairs up and down, 1 blank and 1 neutral: home-built cartridges made of Tenax TA followed by Carbograph sorbent [4] coupled to a sonic anemometer that determines wind speed and direction.







The method applied was the REA, which determines the atmospheric flow (F) of VOCs in the tree canopy, discriminating the target species in air upward concentration currents (C_{up}) and downward (C_{down}).

$$F = \sigma_w b \, (C_{up} - C_{down})$$

In addition to VOC concentrations, for the flow calculation, we calculated the coefficient b, which is an empirical value that depends on atmospheric stability (temperature w and heat of flow) ranging from 0.3 to 0.45, and the standard deviation of vertical wind speed, σ_w [6].

$$b = \frac{W'T'}{\sigma_w \, (T_{up} - T_{down})}$$

How the cREA works?

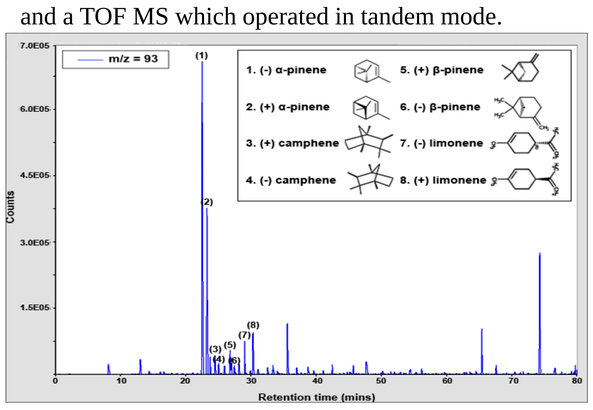
It requires two pieces of information at the beginning of each average flow period, every 30 minutes, in order to segregate the sample flow:

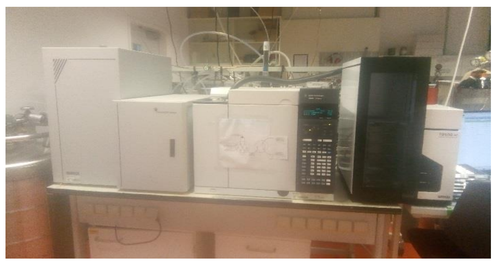
(1) $\overline{w}$, the average vertical wind speed, is required to determine the direction of the instantaneous vertical wind velocity $w' = w(t) - \overline{w}$

(2) σ_w: is used to calculate a "dead band" (is a range of small, centered values around which the sample air is sampled through the "neutral" line. The method uses a dead band from ± 0.6 σ_w [7].

The analysis:

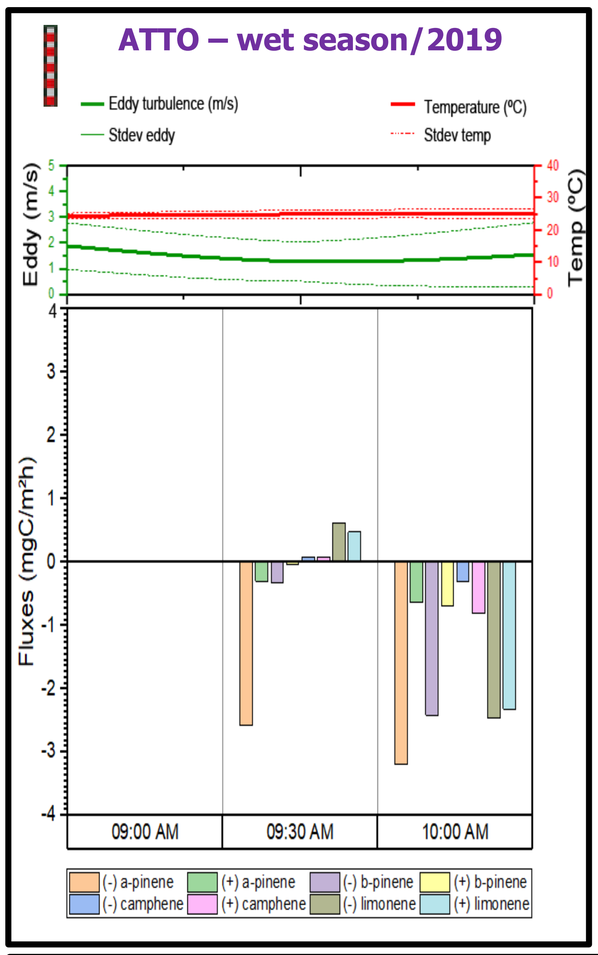
The concentration of VOC in each sample was determined through GC-TOF-MS (Markes International, UK) at the Max Planck Institute for Chemistry. The GC-TOF-MS is equipped with a thermodesorption unit, a chiral column and a TOF MS which operated in tandem mode.

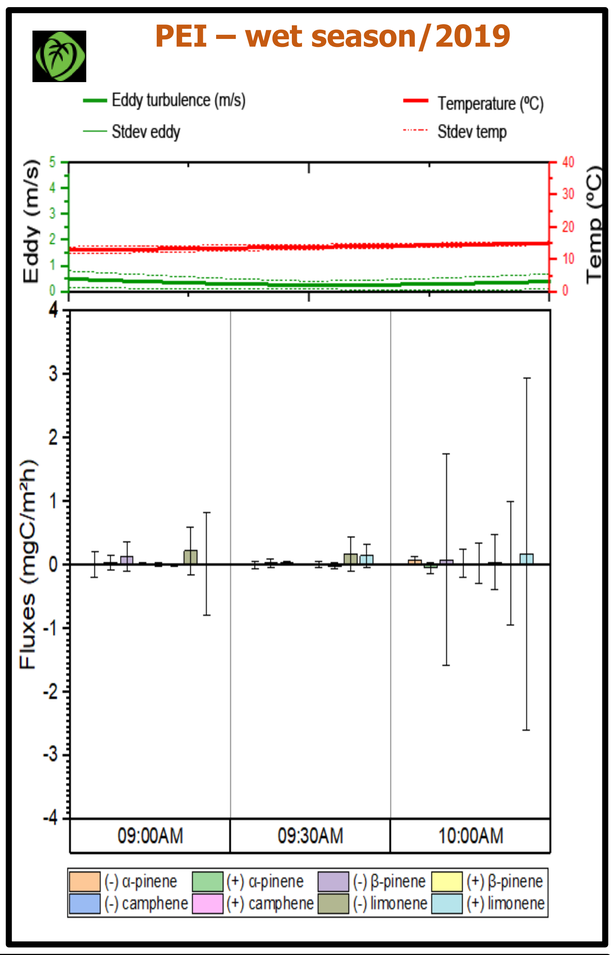


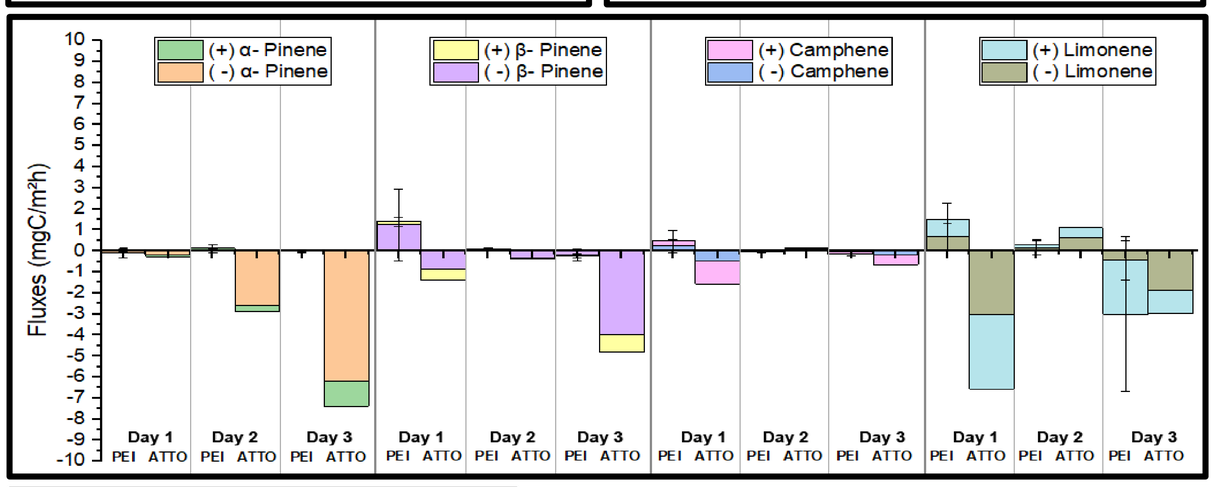


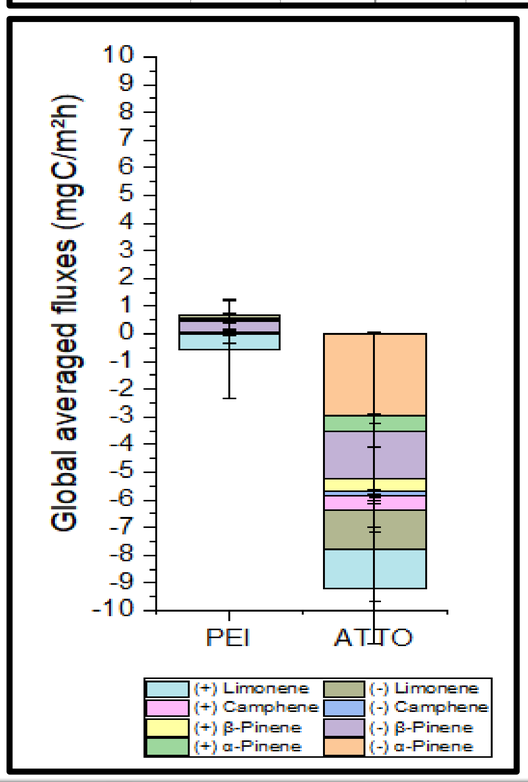
The GC-TOF-MS was operated as reported in the poster of Zannoni et al.

4. PRELIMINARY RESULTS









CONCLUSION POINTS:

ATTO

It is observed a larger BVOCs flux at 40m compared to Atlantic forest.

The BVOCs contributing to fluxes were (in decreasing order):

(-) α – Pinene;
(-) β – Pinene;
(-/+) Limonene;
(+) α – Pinene;
(+) Camphene;
(+) β – Pinene;
(-) Camphene.

We can notice that from 9:00AM to 10:00AM, in all days of campaing, the BVOCs fluxes were in their totally downward fluxes: ***i.e.*** **deposition.**

PEI

It is observed smaller BVOCs' fluxex at 20m compared to the Amazonian forest.

The BVOCs contributing to fluxes were (in decreasing order): (+) Limonene;
(-) β – Pinene;
(-) Limonene;
(+) Camphene;
(-) Camphene;
(-) β – Pinene;
(-) α – Pinene;
(+) α – Pinene.

We can notice that from 9:00AM to 10:00AM, in all days of the campaing, the magnitudes of BVOCs fluxes were close to zero, but in their total there were upward fluxes: ***i.e.*** **emissions.**

5. ACKNOWLEDGMENTS

We acknowledge Prof. Dr. Alex Gunther, to provide the 'cREA'. This study was partly financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

1. **Williams, J., et al.** "Mirror image hydrocarbons from Tropical and Boreal forests." Atmospheric Chemistry and Physics 7(3), 973-980., 2007.
2. **Zannoni N. et al.**, "Surprising chiral composition changes over the Amazon rainforest with height and time of day", manuscript in preparation.
3. **Andreae, M. O., et al.** "The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols." Atmospheric Chemistry and Physics 15,2015.
4. **Kesselmeier, J., et al**. Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia). Journal of Geophysical Research: Atmospheres, v. 107, n. D20, p. LBA 20-1-LBA 20-13, 2002.
5. **Stull, R. B**. An introduction to boundary layer meteorology. Springer Science & Business Media, 2012.
6. **Koppmann, R.,** (Ed.). Volatile organic compounds in the atmosphere. Blackwell Pub., 2007.
7. **Guenther, A., et al.** Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques. Journal of Geophysical Research: Atmospheres, v. 101, n. D13, p. 18555-18567, 1996.