MEASURING STABLES ISOTOPES OF CO_2 (^{13}C AND $^{17,18}O$) IN VERTICAL PROFILES OVER THE AMAZON

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1. Introduction

The most abundant Greenhouse gas (GHG) in our atmosphere is carbon dioxide (CO_2) and in 2017 its concentration reached 146% of pre-industrial levels[1]. In the period 2007-2016 around 44% of total CO_2 emissions from human activities accumulated in the atmosphere, while 22% was stored in the ocean and 28% on land[1], but important questions remain on the processes behind this partitioning, and their persistence under climate change. The study of the stable isotopologues of CO_2 – ^{13}COO, $C^{17}OO$ and $C^{18}OO$ – can provide new insights, for example on the efficiency of water use during photosynthesis[2].They also can be helpful in determining the temporal and spatial distribution of sources and sinks, and to estimate the contributions of C3 and C4 to total primary productivity[3].

2. Methodology

The Greenhouse gas measurements were started with vertical profiles using small aircrafts, since 2010 in SAN (2.86ºS; 54.95ºW), RBA (9.01ºS, 64.72ºW), ALF (98.80ºS, 56.75ºW) and TEF (3.31ºS, 65.8°W), which started in 2013 to replace TAB (5.96ºS, 70.06ºW), all these sites located in Brazilian Amazon Basin (Figure 1).

Samples from vertical profiles were collected, generally fortnightly, using a semi-automatic sampling system, which consists of separate compressor and flask units, developed by ESRL/NOAA. The first unit contains two rechargeable batteries and compressors, and remains at the sampling site. The second unit containing 17 glass flasks (used in SAN) or 12 flasks (used in ALF, RBA and TEF) (Figure 2), a microprocessor that controls the sampling and storage of information about it conditions. Small aircraft were used for collecting, in which were installed a collector tube (inlet), a temperature and relative humidity sensor and GPS (Global Positioning System) to record the position and altitude of each sample. Samples were taken between 12 pm and 2 pm local time, a period of greater stability in the troposphere, and therefore with better repeatability of atmospheric conditions, where the height of the boundary layer is close to its maximum height. The inlet was connected to the compressor unit that transfers the air to the unit containing the flasks which was connected to a device, called the pilot's display, indicating the pre-programmed altitude determined to sample the first to the last flask. The trajectory of the airplane was made in descending helical profile with a diameter of around 5 km, so there is no influence of the gas emitted by the engine of the aircraft in the sampling, starting at 4420 m and finishing at 427 m in ALF, 308 m in RBA, SAN and TEF.

Since June 2016, 700 ml of air from each flask has been used to extract pure CO_2 in glass vials, to determine $d^{13}C$ ratios in CO_2 at the stable isotope laboratory in Groningen, the Netherlands. We currently have close to 1500 vials ready for analysis. In addition, direct analysis on air in each flask started in Feb-2017 at LaGEE. CO_2 and its stable isotopes (d^{13}C, and Excess-^{17}O, derived from d^{17}O and d^{18}O) are measured on a TILDAS-D CO_2 Analyser from Aerodyne Inc (Figure 3), through a limited number (12-16) repeat measurements of 15ml aliquots of air, interspersed with a measurement of a known reference gas for normalization.

Note that a useful measurement of the oxygen isotopes necessitated rigorous drying (< 2 deg dewpoint T) of very humid tropical air (2-4% H_2O), using a custom built Nafion drying system (Paul et al., 2019, in preparation).

3. Results and discussion

Figure 4 shows the analysis system. The pressure in valve V2 is six times higher than in Sample Cell. The PFP is connected to a tube containing Magnesium Perchlorate Mg $(ClO_4)_2$ to minimize the amount of water present in the collected sample.

To inject the sample into valve V2, valves E9 and E12 must be opened. Then the sample should go to Sample Cell, where the analysis will be performed, for this the valves E20 and E23 must be opened. Synthetic air is used to open and close the valves. When the analysis is being performed on Sample Cell, a vacuum is made on the valve V2 line by opening valves E20 and E22. In addition to these, valves E9 and E12 must also be open to “clear” the line for a second sample to be analysed. The analysis of the sample is carried out simultaneously with a reference cylinder (REF), also calibrated in Germany with high accuracy, of 393.03 ppm concentration. 16 measurements are taken for each vial, totalizing 192 measurements for each PFP version III and 272 measurements for each PFP version II. The WS1, WS2, and WS3 standards are measured twice: once before starting the analysis and after analysis, for a 12-vial PFP. The TARGET is measured once during the analyse. The sample is taken together with reference so that any changes during the analysis can be tracked, which increases measurement accuracy. Two calibration curves are constructed, so the analysis of the standards is made. There are patterns with low, medium and high concentration, as already reported (WS1, WS2 and WS3). All this procedure is performed in order to verify the stability of the equipment and to give greater precision to the analysis results.

The calibration of TARGET (Table 1) shows a result similar to the observed by NOAA indicating a good precision and stability of the measurements.

4. Conclusion

The stables isotopes will help us to understand better the changes in forest function in Amazonia, since measuring CO_2 in the atmosphere, since it is not possible to separate CO_2 from anthropogenic source from natural, and also inside the natural sources: photosynthesis, respiration and decomposition.

References

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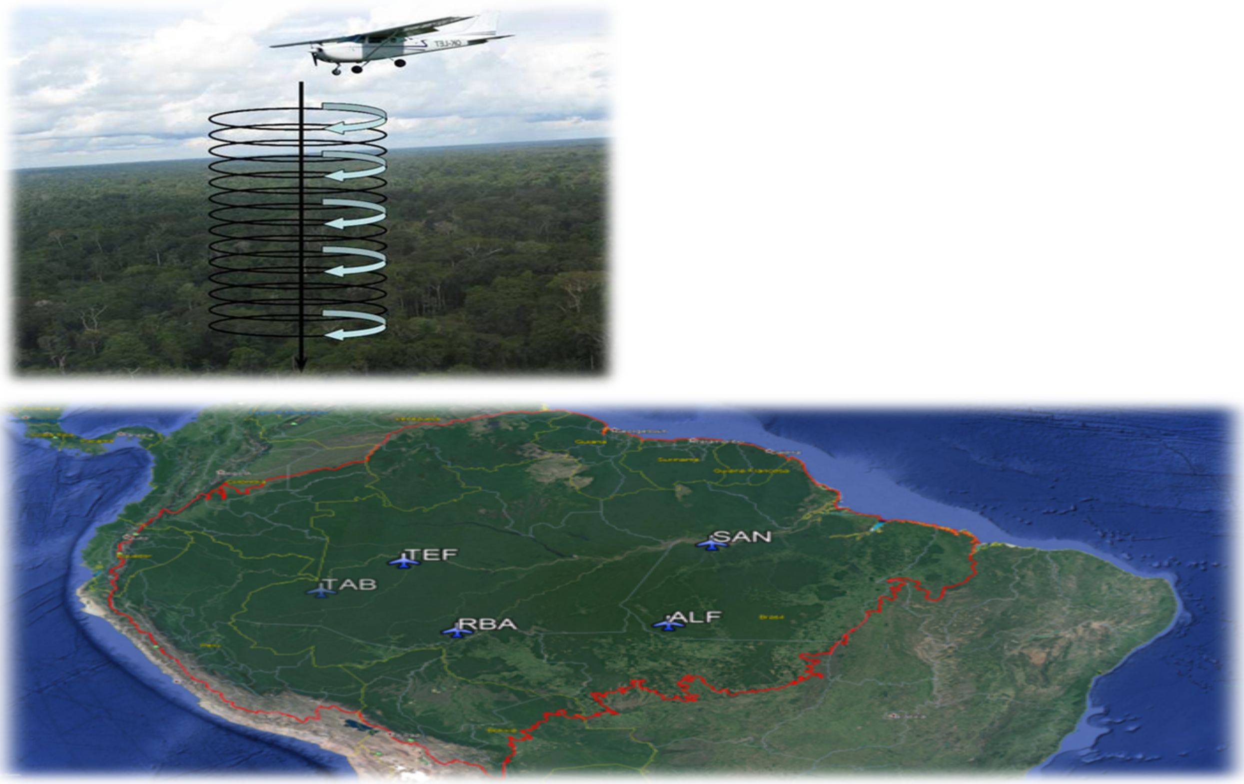

Figure 1. Vertical profiles and sampling sites

Figure 2. Portable Flask Package – PFP

Figure 3. TILDAS-D CO_2 Analyser from Aerodyne Inc connected in PFP (version II, with 12 flasks)

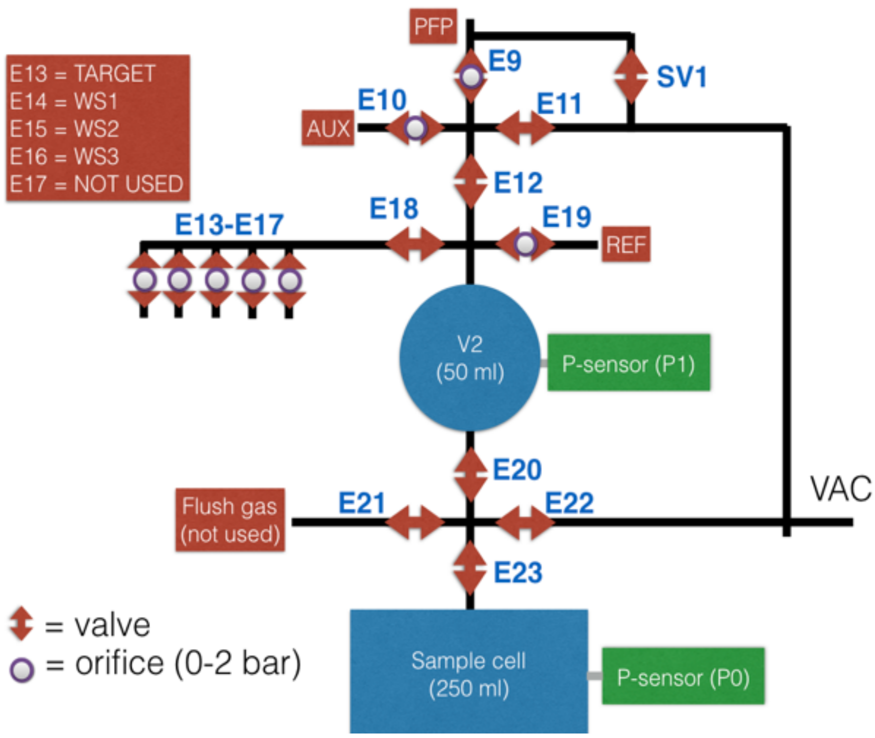

Figure 4. Analysis system

Table 1. Calibration TARGET TILDAS-D CO_2 and NOAA

ASICA_TARGET	*MEASURED*	*ASSIGNED NOAA*
CO_2	402.85±0.06 ppm	403.3 ppm