# TES SFA: Tropical Research as Part of GoAmazon (GECO)

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## ABSTRACT


- This LBNL TES SFA research on biogenic volatile organic compound (BVOC) emissions from Tropical Forests is being conducted as part of the DOE ARM Program's GoAmazon campaign.
- Emissions of BVOCs from Amazon forests affect key atmospheric processes including aerosol and cloud lifecycles, which in turn influence terrestrial physiological processes through changes in precipitation, temperature, and the quality of incoming light for photosynthesis (**Fig.1**).
- Our ability to represent these coupled biosphere-atmosphere processes in Earth system models (ESMs) is constrained by an extremely poor understanding of the identities, quantities, and seasonal patterns of BVOC emissions from tropical forests, and a mechanistic understanding of the plant physiological and environmental controls over BVOC emissions.
- The Green Ocean Amazon Terrestrial Ecosystem project (Geco) is designed to evaluate and improve leaf and ecosystem-scale BVOC emission algorithms for forests near Manaus, Brazil.


## BACKGROUND, HYPOTHESIS & APPROACH

Thousands of BVOCs are known to be emitted from plants into the atmosphere where they fuel atmospheric chemistry (Guenther *et al*., 1995) and impact the hydrologic cycle (Kulmala *et al*., 1994). However, the identities, amounts, and biological and environmental controls over BVOC emissions from tropical ecosystems remain highly uncertain as only a limited number of short duration studies have been conducted (Barkley *et al*., 2008). Using advanced analytics (proton transfer reaction-mass spectrometry: PTR-MS and thermal desorption gas chromatography-mass spectrometry TD-GC-MS) together with emission model development (MEGAN-CLM), we will conduct a multiyear field study near Manaus, Brazil to characterize emissions of targeted BVOCs below whose oxidation products will be observed in aerosols by the GOAmazon2014 deployment.

**Volatile isoprenoids:** isoprene, monoterpenes, and sesquiterpenes
**Oxidation products:** methyl vinyl ketone, methacrolein, nopinone
**Green leaf volatiles:** 3-hexenal, 3-hexenol, 3-hexen-1-yl acetate, nonanal, decanal
**Oxygenated VOCs:** methanol, acetone, acetaldehyde, ethanol, formic acid, acetic acid
**Alkenes and Alkanes:** ethene, propene, ethane, propane
**Sulfides:** hydrogen sulfide, dimethyl sulfide, methyl mercaptan
**Aromatics:** benzene, toluene, phenol, cresol, benzaldehyde

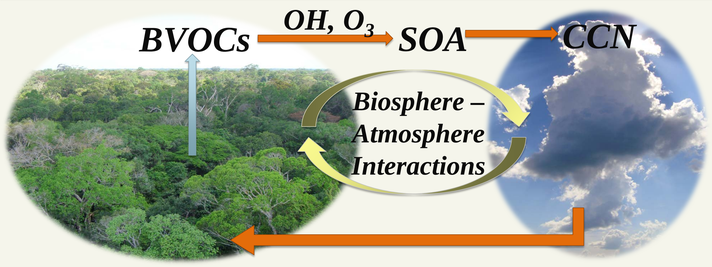


**Fig. 1.** Schematic of biosphere-atmosphere interactions between BVOCs and the hydrologic cycle in the Amazon Basin. BVOCs are released to the atmosphere and are oxidized forming secondary organic aerosols (SOA) which may serve as cloud condensation nuclei (CCN). By improving the representation of BVOC emissions within the CESM model with field observations, we will evaluate the impacts of BVOC emissions on aerosol and cloud lifecycles and their associated climate feedbacks to the biosphere.

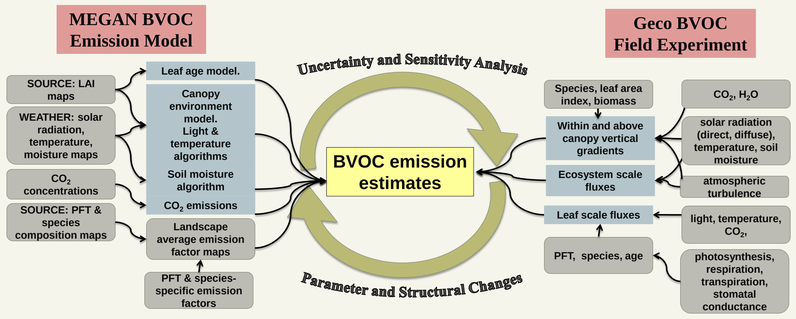


**Fig. 2**: Sensitivity and uncertainty analysis using MEGAN-CLM will be used to develop a detailed Geco field study near Manaus, Brazil which will, in turn, be used to develop parameter/structural changes to MEGAN-CLM.

## LEAF RESULTS

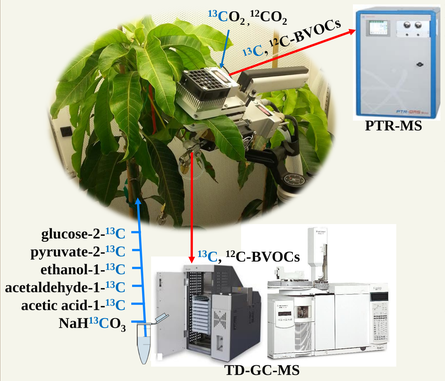


**Fig. 3:** At the ZF2 Forest Reserve;
- We will study individual leaves and a whole ecosystem for relationships between light and temperature, photosynthesis, transpiration, and emissions of BVOCs.
- We will apply positional specific $^{13}C$-labeled metabolite feeding to track intra and extra cellular carbon sources into BVOC biosynthesis and emission and their dependencies on environmental variables.
- Below are the results from a lab study on potted mango trees and leaf temperature data from ZF2.

### Temperature

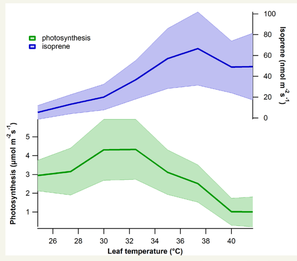


**Fig. 4**. Isoprene emissions decouple from photosynthesis at high temperatures.

### Light

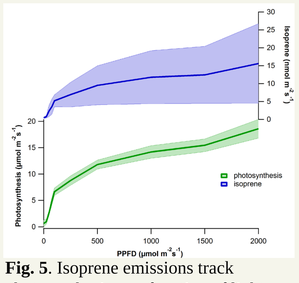


**Fig. 5**. Isoprene emissions track photosynthesis as a function of light.

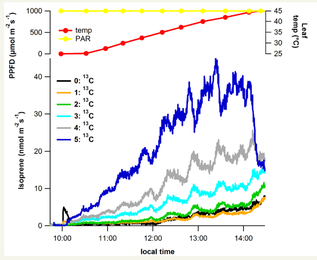


**Fig. 6**. Real-time PTR-MS isoprene emissions with 0-5 $^{13}C$ atoms as a function of temperature under $^{13}CO_2$. Note carbon source switch at high temperatures.

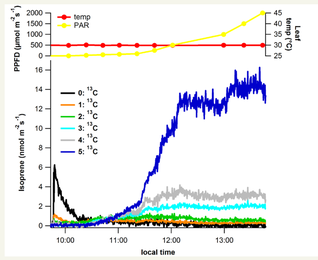


**Fig. 7**. Real-time PTR-MS isoprene emissions with 0-5 $^{13}C$ atoms as a function of light showing dominance of 'photosynthetic carbon' at high light.

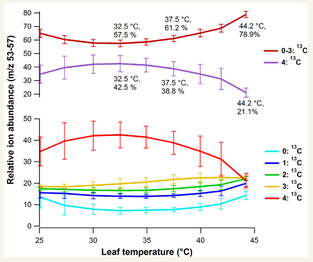


**Fig. 8**. Average relative abundances of a $C_4$ isoprene fragment (TD-GC-MS) with 0-4 $^{13}C$ atoms as a function of temperature under $^{13}CO_2$. Note carbon source switch at high temperature.

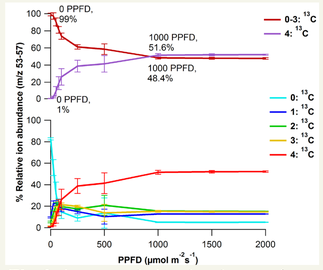


**Fig. 9**. Average relative abundances of a $C_4$ isoprene fragment with 0-4 $^{13}C$ atoms as a function of light under $^{13}CO_2$. Note dominance of 'photosynthetic carbon' at high light.

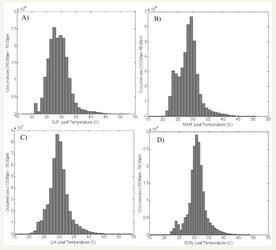

**Fig. 10.** Observed leaf temperature (by season) at the ZF2 field site in Brazil. These observations demonstrate that leaf temperatures above the maximum for photosynthesis (30-32 °C) are common in the upper canopy. This implies an important contribution of 'old carbon' to isoprene emissions from the Amazon Basin and an uncoupling from photosynthesis.

## Modeling RESULTS

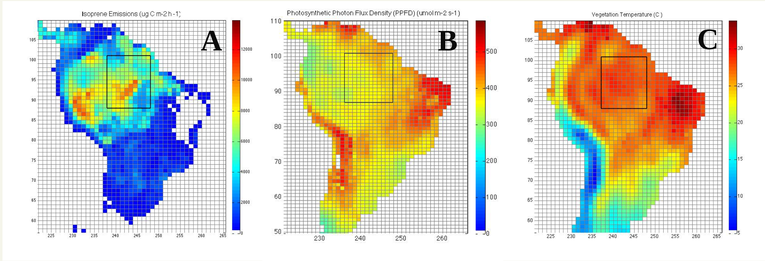


**Fig. 11**. **A)** Isoprene emission (ug C $m^{-2}$ $h^{-1}$), **B)** photosynthetic photon density flux (umol $m^{-2}$ $s^{-1}$), and **C)** leaf temperature (°C) for South America averaged over one year, simulated with MEGAN 2.1 using CLM4.

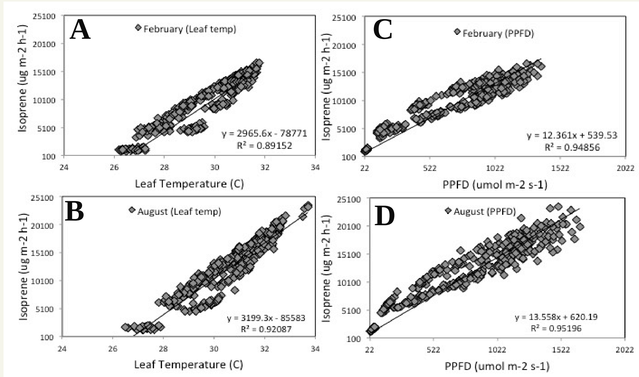


**Fig. 12**. **A & B)** Relationship between leaf temperature and isoprene emissions (ug C $m^{-2}$ $h^{-1}$) for one month in the wet season (February) and one month in the dry season (August). **C & D)** Relationship between photosynthetic photon density flux (PPDF, umol $m^{-2}$ $s^{-1}$) and isoprene emissions (ug C $m^{-2}$ $h^{-1}$) for one month in the wet season (February) and one month in the dry season (August) as simulated by MEAGN 2.1 using CLM4.

## SUMMARY

- Isoprene emissions track photosynthesis as a function of light but decouple from photosynthesis at high temperatures.
- Using $^{13}CO_2$ labeling, we provide the first evidence that at high temperatures, isoprene biosynthesis increasingly utilizes 'old carbon' sources to maintain high emission rates.
- This supports previous findings of an important functional role for isoprene in protecting against abiotic stress.
- Isoprene estimates for the Amazon Basin, as predicted by MEGAN-CLM, also show strong correlations between PPFD and leaf temperature, but no decoupling at high temperatures.
- Model estimates of mean annual emissions (~6,000 – 10,000 ug C $m^{-2}$ $h^{-1}$), are higher than the few observed values ranging from ~2,000 – 5,000 ug C $m^{-2}$ $h^{-1}$.
- Need to improve model parameters describing light and leaf temperature responses of BVOC emissions for various plant functional types, ages, and height within canopies.

## REFERENCES


Barkley M.P. *et al.* (2008) Net ecosystem fluxes of isoprene over tropical South America inferred from Global Ozone Monitoring Experiment (GOME) observations of HCHO columns. *Journal of Geophysical Research-Atmospheres*, 113.
Guenther A. *et al.* (1995) A Global-Model of Natural Volatile Organic-Compound Emissions. *Journal of Geophysical Research-Atmospheres*, 100, 8873-8892.
Kulmala M. *et al.* (2004) A new feedback mechanism linking forests, aerosols, and climate. *Atmospheric Chemistry and Physics*, 4, 557-562.




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