VOCs, their role in mapping ecosystem changes under high CO2; Identifying VOCs using data collected, with the Proton Transfer Reactor Mass Spectrometer (PTR_MS) & Interpreting patterns from early data samples, processed using R-Programing packages.

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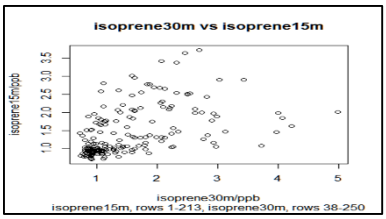
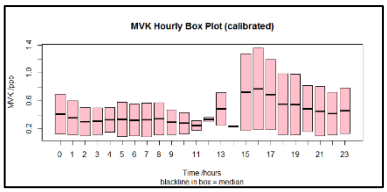
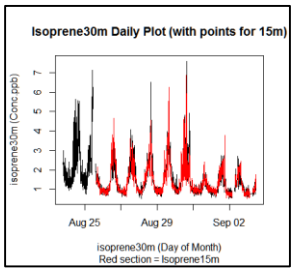
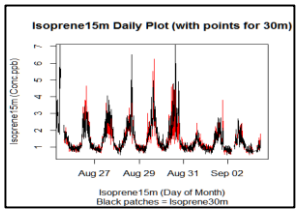
1. Introduction

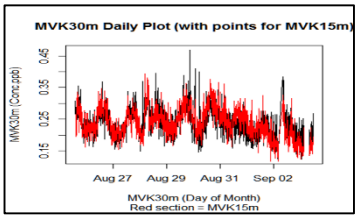
Biogenic volatile organic compounds (BVOC) such as Isoprene, and several others emitted in open forests like Mill Haft Oakland are known to be dependent on temperature and light intensity amongst others. They also rapidly produce other secondary organic compounds in the atmosphere (within and around the forest) through various reactions especially oxidation products. Hence effectively monitoring how they are changing can give a reasonable indication of how the ecosystem physiology is being affected by the factors under consideration. The need was therefore apparent, to take initial baseline measurements of VOC concentrations before switching on the CO2 enrichment system. This was done through experiments, carried out in 2015 and 2016. So that concentration values and emission patterns can be monitored and compared with those prior to the switch over. Some of the initial data gathered at those early stages, are now being analyzed as part of this work. Isoprene and some of its oxidation products like Methyl Vinyl Ketone (MVK) and Methacrolein (MACR) have already been identified and characterized as having a diurnal cycle. Results are still in the very elementary stages but a good starting point while experiments are now being set up for the high CO2 conditions.











2. Data Collection

The PTR_MS

VOCs go through and get differentiated and finger printed in a mass spectrometer system using the differences in their mass to charge ratio (m/z); z being the charge of a proton ion generated from water. Hence m/z effectively becomes a measure of the atomic mass of each VOC. The differences in mass results in varied counts per seconds for each specie as they travel through the PTR / MS system at different velocities. The most common MS systems used are the quadrupole or Time of flight (TOF). Some of the reasons why the PTR_MS is considered the most suitable for VOC measurements in BIFoR include-

Fast and reliable- VOC spend fractions of a second before their concentrations start to change due to secondary reactions especially oxidation. So, it is suitable for capturing the primary VOC and its oxidation products in this dynamic process over time

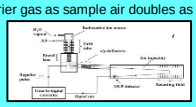
Measurements at different Heights- Can be set to take readings, at different heights to capture VOC concentrations at canopy level and other levels of the Forest.

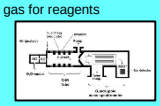
Reasonably portable - for onsite measurements and no need for initial preparation and pre-treatment of atmospheric samples before analysis. Enables the continuous monitoring of sample air online in real time

High sensitivity levels of up to 10 pptv for PTR_TOF_MS systems and eliminates the need for carrier gas as sample air doubles as a carrier gas for reagents

Relatively easy to set up compared to alternative systems

Repeatability- Easy to reset and repeat processes with negligible compromise to accuracy





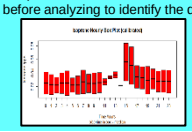
3. Data Processing

R programming packages – are Most suited for this specialized research in BIFoR due to the following advantages it offers;

Tailor made packages of R programs; written to meet specified data processing needs related to the highly sensitive and specialized data from the PTR_MS. An example is the normalization and calibration of initial data collected from the forest to present it at a universally comparable scale, before analyzing to identify the different possible VOCs involved (see table 1)

Fast rate of processing; enabling large volumes of data to be processed in a short time.

Standard presentation quality outputs; usable in a wide range of formats and software packages



4. Results

The plots show different patterns of various VOCs that are currently being characterized and identified as part of the data analysis process. One of the traits immediately obvious in plots (3,4 & 5), is the diurnal character of Isoprene and its oxidation products like MVK and MACR. Some of the plots (eg 1,3 & 4) are also comparing patterns at different heights, (isoprene30m / 15m and MVK30m / 15m, for heights of 30 / 15 meters), to differentiate canopy level reactions from other types of atmospheric and BVOC reactions in the forest.

Table 1, below is a typical sample from a 600 row, output of processed data from a typical R package, for a normalized and calibrated isoprene and MVK data. The initial PTR_MS data (source) table was 900 rows and about 20,000 columns; containing data for different VOCs.

	Datetime	H3O+ (m/z+ 21) (cps)	Isoprene (cps)	MVK (cps)	H3O+ (m/z+ 19) (cps)	Normalized isoprene (cps)	Normalized MVK (cps)	Normalized isoprene (ppb)	Normalized MVK (ppb)	Isoprene concentration (ppb) calibrated	MVK concentration (ppb) calibrated	
1	19/08/2015 10:10	8379	17	24	4189630	16.23105	22.91463	0.270518	0.381907	0.082915	1.14634	
2	19/08/2015 10:25	8303	22	23	4151630	21.19716	22.16004	0.353286	0.369334	0.108278	1.107944	
3	19/08/2015 10:30	8413	23	27	4054030	22.67605	26.62399	0.377934	0.443732	0.11641	1.330713	

5. Future Direction

The process of data analysis using R packages will be used to identify and characterize other VOCs besides Isoprene and its oxidation products

6. References

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