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ELECTRON IMPACT IONIZATION TECHNIQUE ON THE STUDY OF TERPENES AND RELATED SPECIES IN FRENCH GUIANA TROPICAL FOREST

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ABSTRACT

The electron impact ionization is, originally, a mass spectrometry ionization method and still the most widely used of all ionization methods. In this technique, a beam of electrons passes through the gas phase sample. An electron that collides with a neutral analyte molecule can knock off another electron, resulting in a positively charged ion. The fragmentation process dependents upon many qualities including primary structure, electron energy and ion source temperature. This paper presents a study on the seasonal variation of isoprene and some other significant biogenic volatile organic compounds (BVOC) such as α-pinene, β-pinene, limonene, e-β ocimene and longifolene, measured at the Guyaflux Tower located in a wet tropical forest in French Guiana using the Relaxed Eddy Accumulation technique and analyzed by a mass spectrometer coupled to a gas chromatographer, a thermo desorption unit and a flame ionization detector (TD-GC-MS-FID). The results showed that isoprene was by far the biogenic volatile organic compound with the highest concentration and flux, followed by alpha-pinene. Previous limited studies in Amazonia and the Congo suggested that a higher concentration and flux rate of isoprene and alpha-pinene should be expected during the dry season with lower emissions during the wet season, which is in relative agreement with what was observed at this tropical forest site in French Guiana. The exceptions were observed in a long wet period in which the concentration of isoprene and alpha-pinene increased more than it was expected to, for this time of the year.

1. INTRODUCTION

The Earth System is a complex system in which not only biosphere-atmosphere processes are coupled, but the biology of the biosphere interacts strongly with the chemistry and physics of the atmosphere.

Due to these interacting processes, a top research priority is to study the important feedbacks that control Earth System, especially in tropical ecosystems. For instance, aerosol particles influences strongly the radiation balance that is closed linked to biogenic volatile organic compounds (VOC) emissions, atmospheric chemistry and cloud formation processes.

The atmosphere of tropical forests is closely linked to the biosphere, with active mechanisms linking emission and deposition of gaseous compounds as well as aerosol particles. Terrestrial vegetation has been widely studied in order to understand this prominent part of the atmosphere-biosphere interaction, in particular emissions of VOCs comprising thousands of different compounds of alkanes, alkenes, alcohols, esters, organic acids and carbonyl compounds, among others[1].

The most prominent VOCs are isoprene, monoterpenes and sesquiterpenes, the latter being the most reactive trace gases within these groups. All these compounds have a significant influence on atmospheric chemistry and physics [2].

In addition, these natural VOC emissions serve important biological functions including attracting pollinators and repelling herbivores. Some biological organisms use the ambient air as a communication and transport medium, and oxidation of these compounds brings about the concentration gradients sensed by insects [3].

Isoprene is the predominant biogenic volatile organic compound (BVOC) emitted by vegetation and the tropical forests are the dominant global source. This compound is very reactive in the atmosphere and contributes to the reactions that control tropospheric oxidant concentrations and thus the concentrations and lifetimes of longer-lived species.

The aim of this research is to present a study of isoprene and some other significant BVOCs such as α-pinene, β-pinene, limonene, e-β ocimene and longifolene, measured at the Guyaflux Tower located in a wet tropical forest in Cayenne, French Guiana, during the year of 2011, using the relaxed eddy accumulation (REA) technique at 30 meters high approximately above the canopy.

2. EXPERIMENTAL PROCEDURE

2.1. Biogenic Volatile Organic Compounds Measurements

The sampling procedure was performed using an REA system set up on top of the GuyaFlux tower (Figure 1) and samples were periodically collected in cartridges (Figure 2) containing tenax TA and carbograph 5TD absorbents for a period of ten months in 2011.

The compact system was developed by the Biosphere-Atmosphere Interactions (BAI) group from the National Center for Atmospheric Research (NCAR) and consists of a sampling system designed to segregate air based on the direction of the instantaneous vertical wind velocity measured by a sonic anemometer.

Air samples were accumulated in two set of storage reservoirs (cartridges), one for upward moving air and one for downward moving air. The sampler operated automatically for three periods of 30 minutes each over a period of one hour and a half after which the sampling cartridges needed to be replaced manually.

Figure 1: REA system coupled to the sonic anemometer device on the top of the tower.

Figure 2: Stainless cartridges for BVOCs collection.

The samples were transported to a laboratory and gases trapped in the cartridges during the collection procedure were released by a thermal desorption unit and then analyzed on GC-MS-FID system by a mass spectrometry ionization technique. The ionization technique used in the mass spectrometry was the electro impact with 70 eV of energy.

2.2. Concentration and Flux Determination

The REA sampler segregates the sample flow according to the vertical wind velocity measured by the sonic anemometer over some flux averaging period. The basic equation (Eq. 1) to derive fluxes of a given species (F_i) from the REA system over this period is:

$$F_i = \sigma_w b\left(C_{up} - C_{down}\right) \quad (1)$$

where σ_w is the standard deviation of the vertical wind velocity, *b* is an empirical coefficient calculated from the sonic temperature and heat flux and C_{up} and C_{down} are the concentrations (densities) of the species of interest in the up and down reservoirs, respectively.
The concentrations (up and down) were calculated based on the chromatograms results from the mass spectrometry ionization system (GS-MS-FID).

3. RESULTS

The results show a lower concentration of isoprene during the month of February and March which correspond to the wet season with an average of 0.545 μg/m^3 and 0.341 μg/m^3, respectively with a slight increase in middle April which is a period of transition between wet and dry and a higher concentration later in mid-June which corresponds to the transition from wet to dry season (Figure 3).

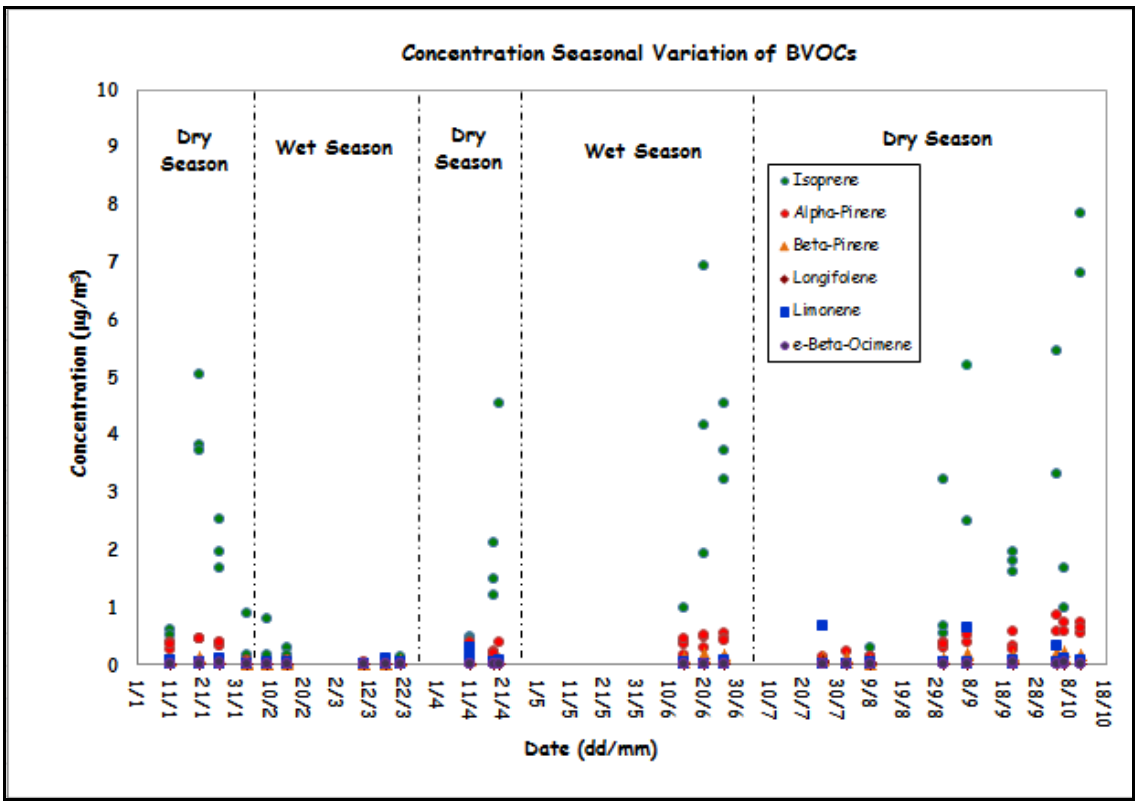

Figure 3: BVOCs concentrations for the wet and dry seasons.

The same behavior was observed for α-pinene with higher concentrations for the same periods as isoprene however with a smaller increase. All the other compounds had concentrations below 1 μg/m^3 during the whole year.

The monoterpene, e-β ocimene, was observed and is known as a stress compound but the vegetation at the site did not face any known severe stress condition such as excessive drought or flooding.

Concerning the fluxes, the results showed that just a small amount of BVOCs were deposited and the majority of them were released in the atmosphere. Isoprene was by far the biogenic volatile organic compound with the highest concentration and flux followed by alpha-pinene (Figure 4).

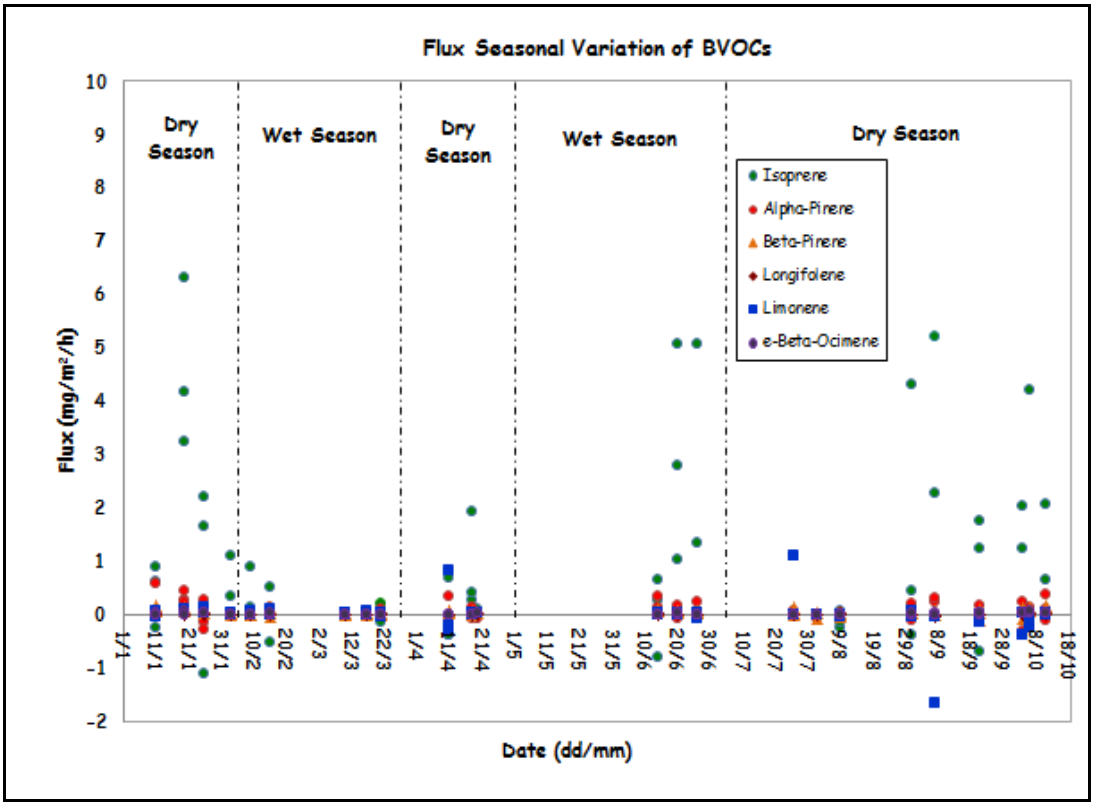

Figure 4: BVOCs fluxes for the wet and dry seasons.

The lowest concentration and flux rate for all the studied compounds was observed during the months of March and late July and beginning of August indicating a lower production of those BVOCs by vegetation during those periods.

Previous limited studies in Amazonia and the Congo suggested a higher concentration and flux rate of isoprene and alpha-pinene should be expected during the dry season with lower emissions during the wet season, which is in general agreement with what was observed at this tropical forest site in French Guiana. The exception was observed in June which corresponds to a wet season period in which the concentration of isoprene and alpha-pinene increased more than it was expected for this time of the year.

Further investigation is needed to better understand what caused a high emission of some BVOCs during the wet season under regular conditions for photosynthetically active radiation, precipitation and temperature.

4. CONCLUSIONS

The measurements so far, showed as expected, that the concentration and flux of isoprene and monoterpenes are higher in dry season than in the wet season, however the high concentration and flux in June which is a wet season cannot be well explained yet. It was expected a lower concentration for the referred month as well as lower flux due to the clouds and deposition process.

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