Chiral BVOCs composition over the Amazon and Atlantic Rainforest by TD-GCxGC-TOF/MS

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Introduction: Many BVOCs are chiral, meaning they exist in two non-superimposable mirror image forms termed enantiomers. Enantiomers have identical physical properties, such as boiling point, density, and reactivity to atmospheric oxidants; however, they differ in their specific biological activity. Since most monoterpene measurements do not distinguish enantiomers, relatively little is known about the natural abundance and behavior of the chiral speciated molecules. Previous studies have reported regiospecific patterns across Tropical and Boreal ecosystems for α-pinene [1] and have used them as tracers of secondary processes in air and soil [2][3], highlighting the potential use of chiral compounds in air to decipher processes linking the biosphere with the atmosphere. To better understand the sources, dynamics and sinks of BVOC in the forest environment we have investigated chiral BVOC in the pristine Amazonian rainforest environment at Amazon Tall Tower Observatory (ATTO) is located 150 km from Manaus/BR and in Atlantic Forest located in the Ecological Immigrant Park (PEI) at São Paulo/BR in 2019.

Methods: Samples collected in 2019, were thermally desorbed, separated and analyzed through a Bench-TOF select (TD-GCxGC-TOF/MS tandem ionization-14eV and -70eV) from Markes International, UK. First, all samples through to Thermo-Desorption, that one we separated in two desorption: Primary one we use at the cartridges during 10 min in 250°C and in the second one is for trap during 10 min with 250°C. In the GC the column is Dimethyl TBS Cyclodextrin based so the oven was settled in 5 min at 40°C and 1.5°C/min during the temperature increase from 40°C until 150°C and then 30°C/min from 150°C until 200°C.

Results: The VOCs and their chirals analyzed are: (-/+) α- Pinene, (-/+) Camphene, (-/+) β-Pinene, (-/+) Limonene, these chiral are of extreme importance because the fact of obtaining the same chemical composition, but different geometries the (-) and (+) differ in nature in their function/aroma, for example the (-) α- Pinene is found in pine and (+) α- Pinene is found in *eucalyptus*, such as (-) Limonene emitted by orange and (+) Limonene emitted by lemon. The separation method was specifically designed for the separation of chiral monoterpenes (C H) and sesquiterpenes (C H). A chiral column is therefore needed to separate the two enantiomers, standard columns for GC-MS, comparing to an online PTR-MS would not allow enantiomeric separation.

Conclusions: It was concluded that the ratio between the pairs of enantiomeric concentrations show a temporal and spatial variability. In forests not disturbed by humans, was found a significant amount of (-) α-Pinene, and due to human interference located in the metropolitan region of São Paulo, (+) Limonene was the BVOC with the highest concentration.

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