Changes in chiral monoterpenes during drought in a rainforest reveal distinct source mechanisms

Joseph Byron\textsuperscript{1}, Christiane Werner\textsuperscript{2}, Nemiah Ladd\textsuperscript{2}, Laura Meredith\textsuperscript{3}, Gemma Purser\textsuperscript{4}, and Jonathan Williams\textsuperscript{1}

\textsuperscript{1}Max Planck Institute for Chemistry, Mainz, Germany
\textsuperscript{2}Institute of Ecosystem Physiology, University Freiburg, Freiburg, Germany
\textsuperscript{3}School of Natural Resources and the Environment, University of Arizona, Tucson, USA
\textsuperscript{4}UK Centre for Ecology & Hydrology, Edinburgh, United Kingdom

Monoterpenes are used by plants as antioxidants in the defense against reactive oxygen species and are also contributors to the formation of secondary organic aerosol and cloud condensation nuclei. Understanding how the emissions of monoterpenes from biogenic sources change due to different stresses such as drought is of importance as more frequent drought events are expected to occur in the future due to climate change. Monoterpenes such as alpha pinene and limonene exist as optical isomers in mirror image forms, (+) and (-). Studies on the effect of different stresses on plant emissions commonly measure the sum of enantiomers rather than conducting separate measurements for the individual enantiomers [1]. Recent measurements of chiral monoterpenes have highlighted the importance of independently measuring the individual enantiomers of a chiral pair, due to differences such as environmental drivers [2] and local measurement source [3]. Despite the enantiomers of the same monoterpene having the same chemical properties, they can interact differently with biologically active chiral molecules such as those that exist as olfactory receptors within insect antennae [4].

The atmospheric dynamics of chiral monoterpenes from beneath the canopy of the tropical rainforest biome at Biosphere 2, Arizona, USA, were measured during pre-drought, drought and rewetting using an online GC-MS during the B2 Water, Atmosphere and Life Dynamics campaign (B2WALD). Furthermore, sorbent tube samples were obtained from different forest compartments, to investigate the compartment specific chiral VOC emission. Drought was found to be a driver of a change in the enantiomeric excess of specific monoterpenes. (-) alpha pinene was the dominant monoterpene present in agreement with results from the Amazonian rainforest despite there being no atmospheric chemistry in the Biosphere greenhouse. Interestingly, during the pre-drought phase, due to the conditions in the greenhouse, (-) alpha pinene showed an average daily maximum at 11:00 while (+) alpha pinene peaked at 15:00, coincident with peak light and temperature respectively. By the rewet phase, the average daily maximum for (-) alpha pinene shifted to 13:00, coincident with peak isoprene, whilst it remained at 15:00 for (+) alpha pinene. The average maximum daily mixing ratios of (+) and (-) alpha pinene, during the drought phase, increased by a factor of 4 and 2 respectively, when compared to the pre-drought values. These
results reveal distinct source mechanisms for individual enantiomers and the differing impact drought has on the individual enantiomers in a rainforest ecosystem.