Study of biogenic volatile organic compound emissions and depositions over a mixed temperate forest by PTR-TOF-MS and eddy covariance

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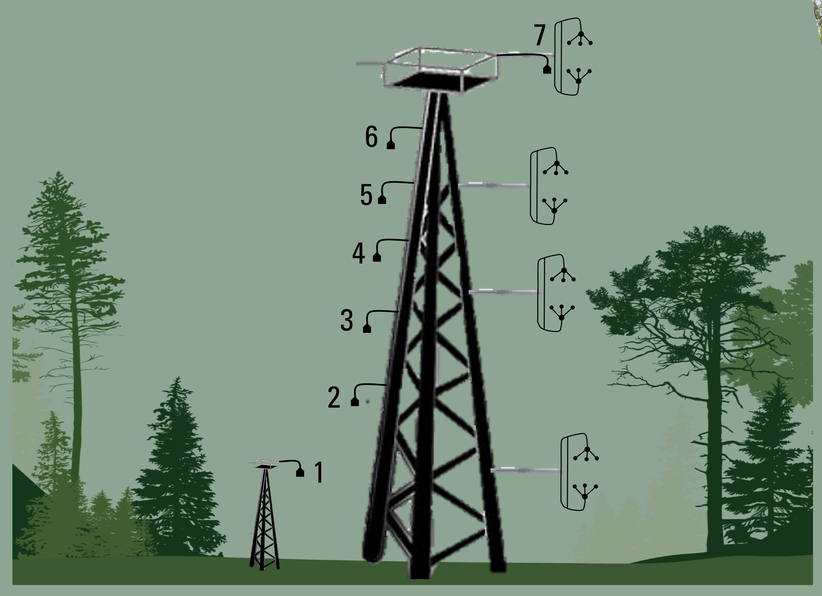
OBJECTIVES

Due to technical limitations, BVOC measurements were traditionally limited to a few dominant BVOC species, mostly emitted by vegetation. This study aims at providing a more detailed and complete overview of BVOC bidirectional exchanges over a temperate mixed forest site, even for less emitted/deposited compounds which can play a key role in atmospheric chemistry due to their high reactivity.

EXPERIMENTAL SITE AND MEASUREMENTS

- Vielsalm station, Belgium (BE-Vie): mixed temperate forest equipped with a flux tower (part of the ICOS network)
- Measurement campaign from May until October 2022
- 1 sampling point at 51 m for BVOC + O_3 flux measurements and 6 additional points for BVOC + O_3 profile measurements
- 4 sonic anemometers at 6, 24, 36 and 51 m above ground level
- Ancillary measurements (meteorological + phenological variables)



DATA PROCESSING

PTR-TOF-MS → (1) 10 Hz mass spectra → (2) 10 Hz ncps for each mz → (3) 10 Hz ncps for clustered mz → (4) 30 min uncal. flux for clustered mz → (5) 30 min uncal. flux for significant mz → (6) 30 min uncal. flux for significant compounds → (7) 30 min cal. flux for significant compounds

1 PTR-TOF-MS measurements

- PTR-TOF-4000, Ionicon Analytik GmbH
- 10 Hz measurements with E/N = 136 Td
- Background meas. every 4 hours
- Calibration meas. ± every 5 days

2 Peak detection & peak area quantification

- Carried out with IDA (Ionicon Data Analyser) software
- Runs on mass spectra acquired in the course of a day
- Provides the detected mass to charge ratios (m/z) and their peak areas (in normalized counts per second, ncps)
- Up to 820 m/z detected per day

3 m/z peaks clustering

- m/z values can slightly shift between IDA runs → need to unify the detected m/z correlated to the same signal
- Density Based Clustering in Application with Noise (DBSCAN) algorithm to identify m/z clusters
- Optimization of the trade-off between fraction of m/z values not assigned to a cluster, and fraction of clusters containing multiple m/z peaks for a single IDA analysis
- Clusters considered for further analysis based on constraints on the cluster width and the fraction of data above the limit of detection for 20s aggregates
- 224 m/z selected after clustering

4 Fluxes computation: critical steps

- Tool based on InnFlux (Striednig et al., 2020), transcripted in Python
- Lag time determined for isoprene (m/z 69.069) and applied to other m/z
- Spectral correction factors determined from the comparison on sensible heat and isoprene cospectra, then applied to other m/z. Yields a half-power cut-off frequency of 0.14 Hz and a flux correction factor of about 1.10 for the mean wind speed.
- Flux limits of detection (LODs) computed at the 99% confidence level:
  $$LOD = 3 \cdot random\ error$$
- Stationarity tests not considered relevant for this dataset

5 Detection of significant exchanges

- Methodology:

A. Consider half-hour (HH) significant if: $|flux| > |LOD|$

B. Consider the day significant if the ratio of significant HH to the number of available HH during daytime (8 to 20h) is superior to 0.125 (i.e. at least 3 of the 24 HH during daytime are significant).

C. Consider the m/z value significantly exchanged if it shows at least 3 consecutive significant days over the campaign (consistent exchange).

- Allows for the detection of episodes of short exchanges
- This methodology detects 69 m/z with significant exchanges consistent in time

6 Compound attribution

- Analysis of the fluxes intercorrelations to detect pure fragments, (water) clusters and isotopes
- Attribution of a chemical formula and a compound name to parent ions
- Based on Pagonis et al. (2019) and Yáñez-Serrano et al. (2021, GLOVOCS) databases

7 Flux calibration

- For compounds not contained inside the calibration bottle, calibration factors either found in Koss et al. (2018) or taken from previous measurements with a PTR-Quad-MS in similar working conditions.

RESULTS

An 'ideal period' (in terms of measurement and meteorological conditions) was chosen between 2022-07-15 and 2022-08-01 for results presentation.

Figure 1 shows that all species are on average emitted for that period, except from formaldehyde and m/z 49.027 (uncertain compound attribution so far). The BVOC budget is dominated by monoterpenes, isoprene and methanol with respective percentages of the net flux for that period of 51%, 28% and 7%.

Figure 2 illustrates the clear dependence of BVOC emissions on air temperature. Moreover, methanol and ethanol show some deposition as relative humidity rises, probably linked to adsorption/desorption of these compounds in water films.

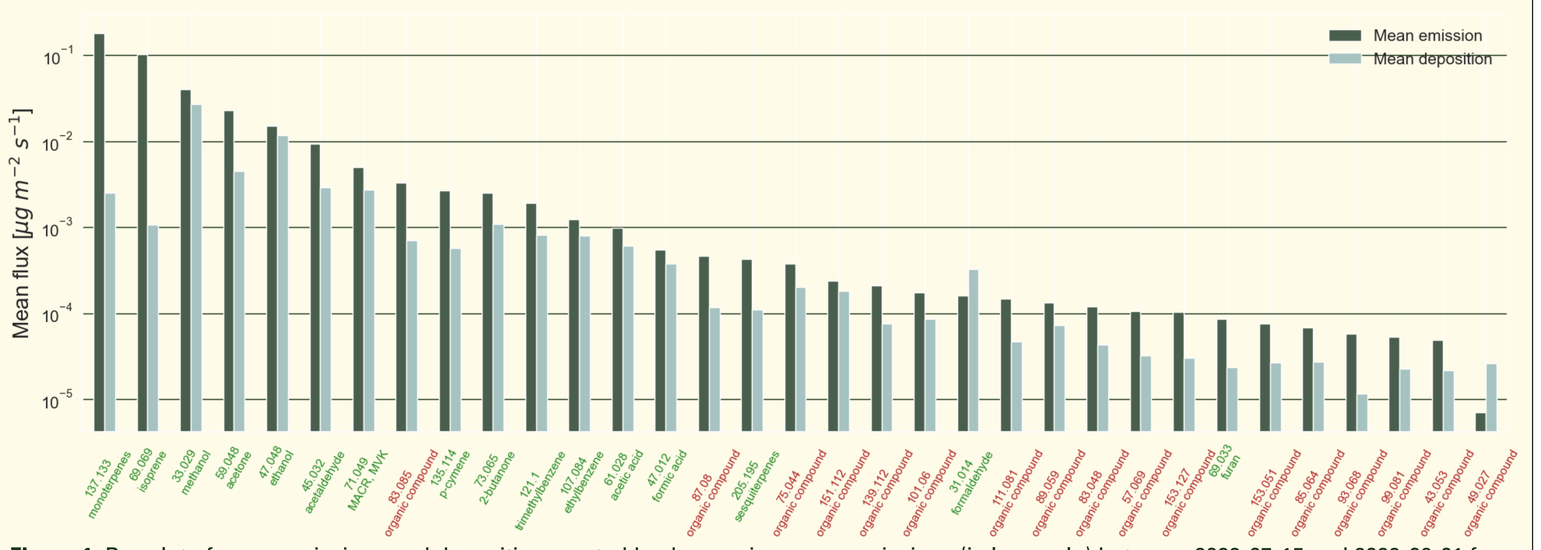


Figure 1. Bar plot of mean emissions and depositions sorted by decreasing mean emissions (in log scale) between 2022-07-15 and 2022-08-01 for calibrated compounds. Compounds with uncertain attribution are labelled as 'organic compound' in dark red.

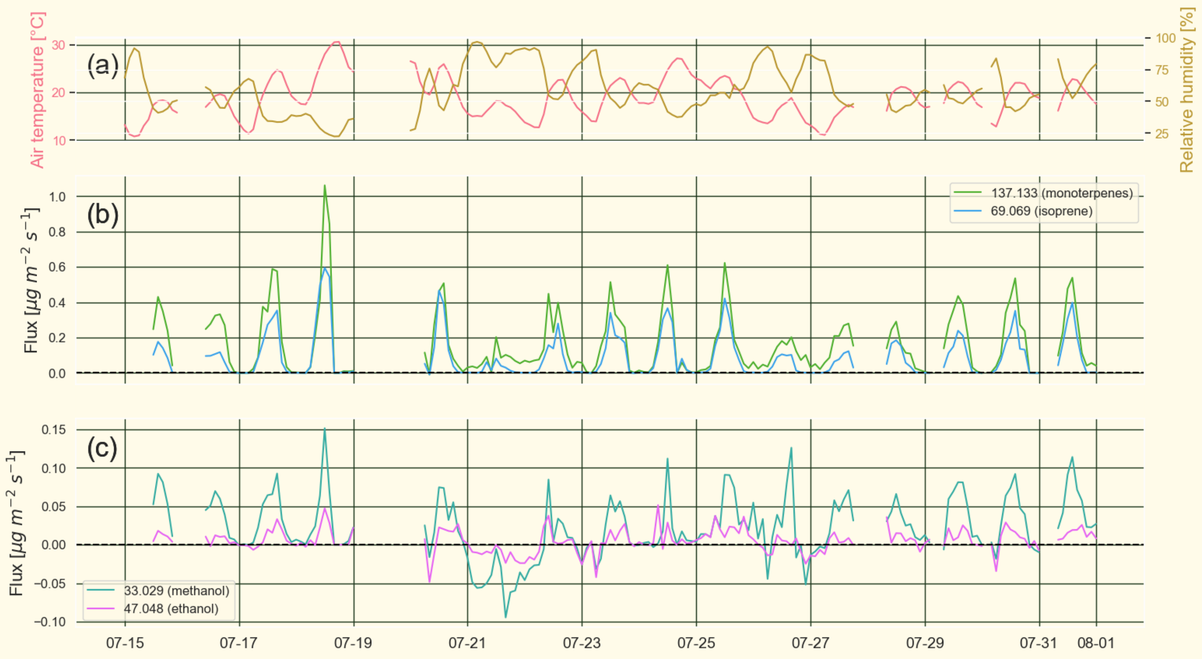


Figure 2. Times series of 2h-mean measured variables between 2022-07-15 and 2022-08-01.
(a) Air temperature and relative humidity. **(b)** Two compounds with highest emissions. **(c)** Two compounds with clear bidirectional exchanges.

PERSPECTIVES

- This poster presents the preliminary results of the 2022 measurement campaign. With the extensive dataset acquired, BVOC flux dynamics will be studied as well as their relationship with O_3 fluxes, meteorological and phenological variables.
- This BVOC + O_3 concentration and flux dataset will be used to to test and possibly improve existing mechanistic models simulating the vertical surface-atmosphere exchanges of trace gases. Measures of NO_x concentrations should also be carried out to complete this approach.
- The acquired BVOC and sonic anemometer profiles will be used in a Lagrangian inverse modelling approach to infer sources and sinks of BVOCs within the soil-plant continuum. Such information will increase our understanding of the mechanisms controlling BVOC exchanges.

The authors wish to acknowledge the Belgian Federal Science Policy Office for their support to the ACTRIS-BE project (FSIRI/00/AC1) and the BIRA/ULiège FEDtWIN project BERTRAC (Prf-2021-034_BERTRAC#2) as well as the Public Service of Wallonia for their support to the ICOS-Wallonia project (1217769)