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

Clément **Dumont**[1*], Bert **Verreyken**[1,2], Niels **Schoon**[2], Crist **Amelynck**[2,3] and Bernard **Heinesch**[1]

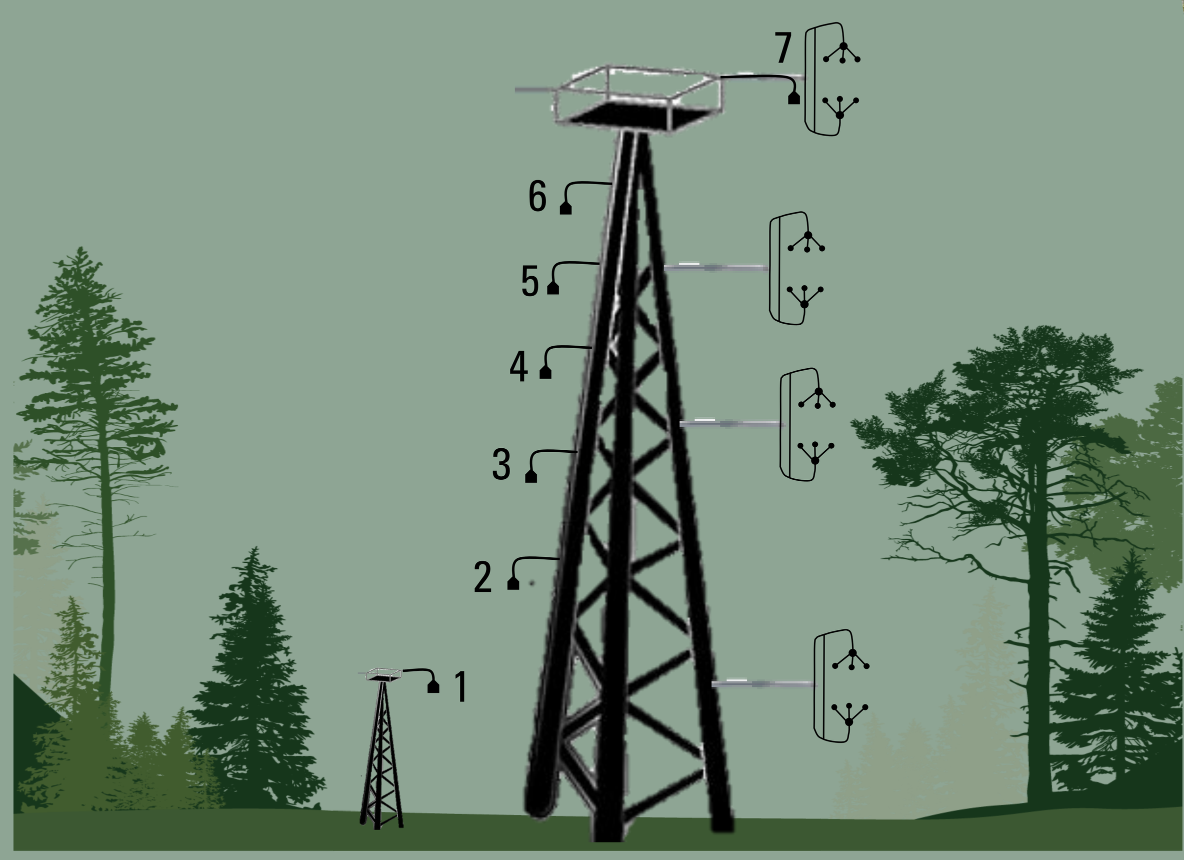
[1]Gembloux Agro-Bio Tech, University of Liège, Belgium [2]Belgian Institute for Space Aeronomy, Belgium [3]Department of Chemistry, Ghent University, Belgium
*Contact: clement.dumont@uliege.be

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 mixed temperate 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 m/z → (3) → 10 Hz ncps for clustered m/z → (4) → 30 min uncal. flux for clustered m/z → (5) → 30 min uncal. flux for significant m/z → (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 of 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.

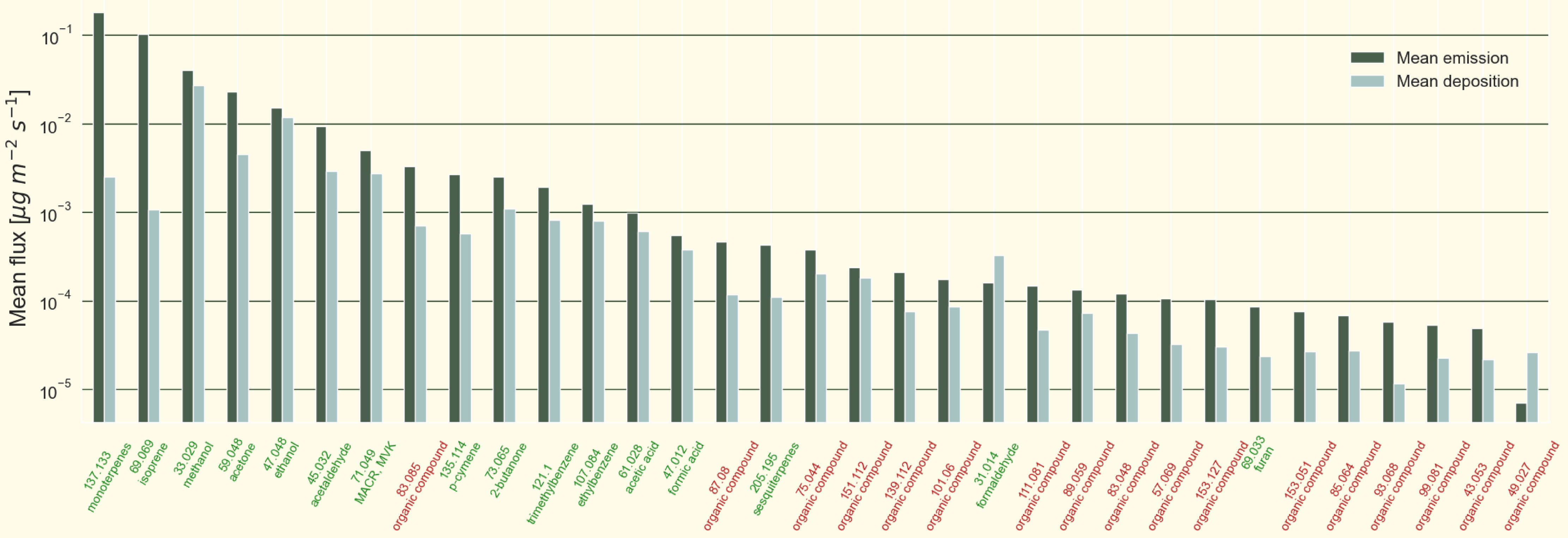


Figure 1. Bar plot of mean emissions and depositions sorted by decreasing mean emissions (in log scale) between 2022-07-15 and 2022-08-01 for calibrated compounds. Compounds with uncertain attribution are labelled as 'organic compound' in dark red.

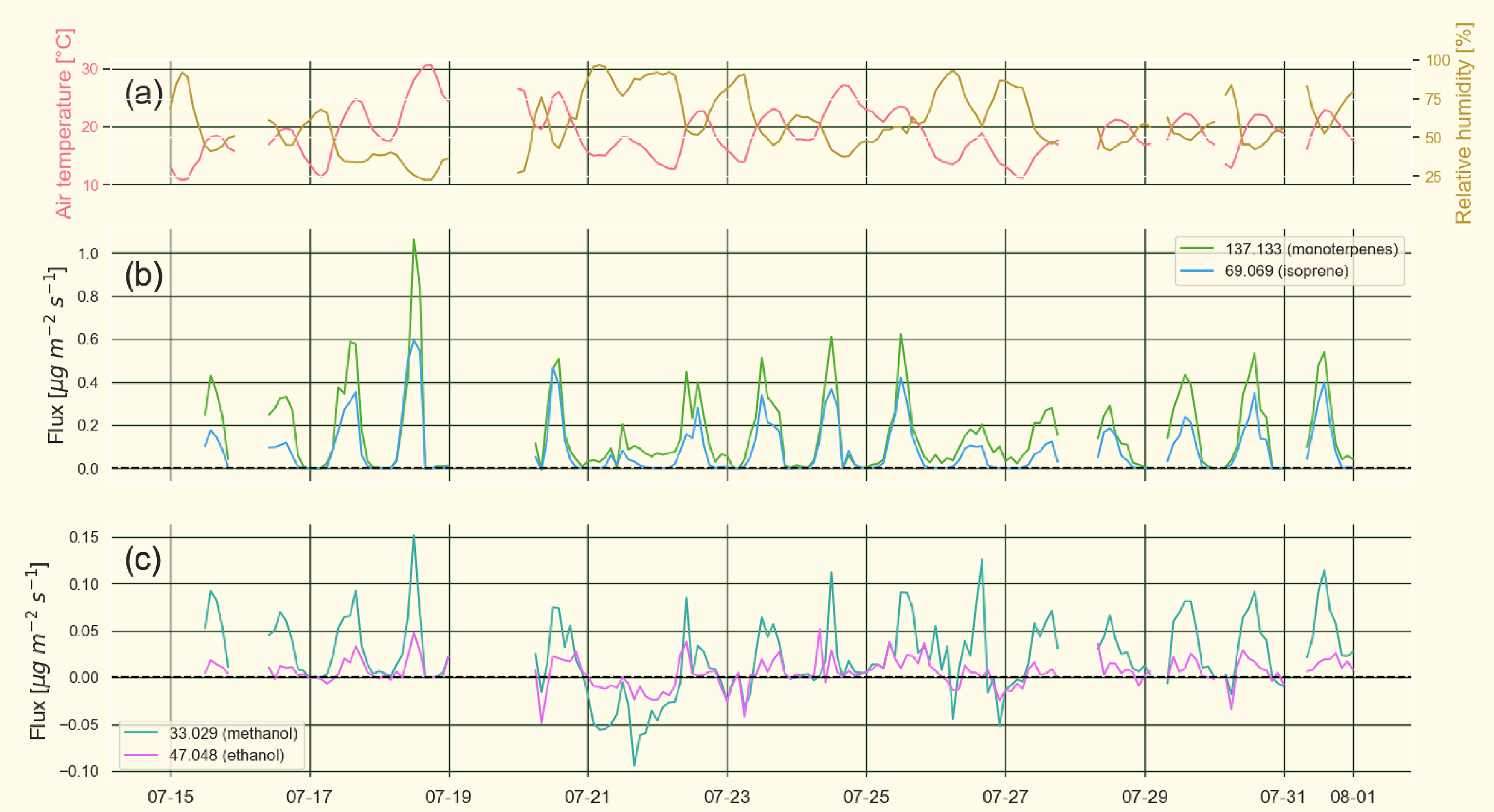


Figure 2. Times series of 2h-mean measured variables between 2022-07-15 and 2022-08-01.
(a) Air temperature and relative humidity. **(b)** Two compounds with highest emissions. **(c)** Two compounds with clear bidirectional exchanges.

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 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.

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Supplement of

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Correspondance to : Clément Dumont (clement.dumont@uliege.be)

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