Characterization of volatile organic compound exchanges at a mixed forest site in the Belgian Ardennes

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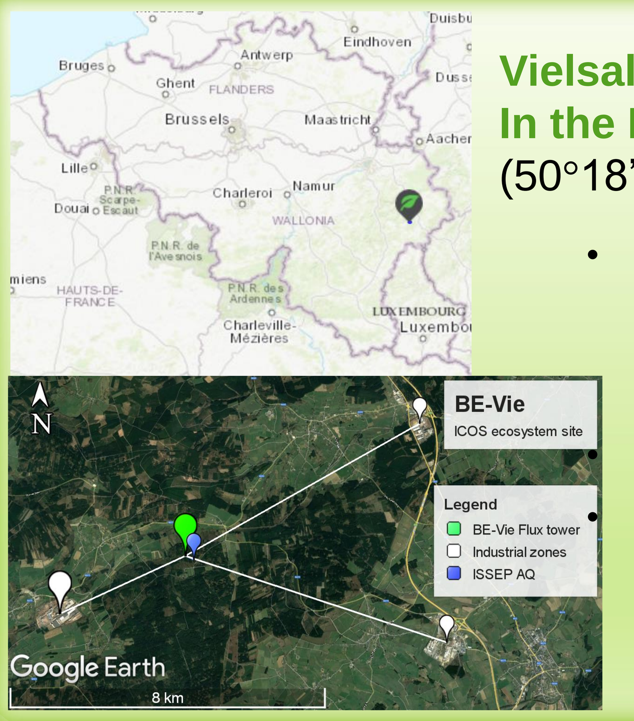
1. Background

- Forests are a major source of biogenic VOCs, which are precursors of air quality and climate related substances (O_3, SOA)
- Forest/atmosphere (O)VOC exchange is often bidirectional and above canopy fluxes result from a variety of processes occurring along the soil/canopy/atmosphere gradient.
- A good understanding of those processes and their seasonality is needed for improved BVOC emission, air quality and climate modelling and for better constraining (O)VOC budgets.

3. Site description

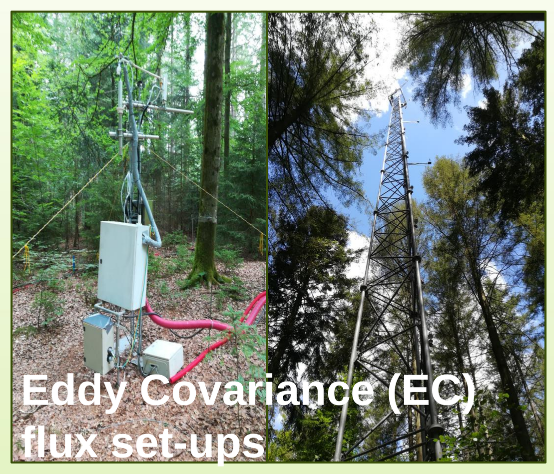


Vielsalm ICOS ecosystem station (BE-VIE) In the Belgian Ardennes

(50°18'18.2"N, 5°59'53.0"E, 450 m.a.s.l.)

- Mixture of coniferous (mainly Douglas fir, Norway spruce and Silver fir) and deciduous (mainly European beech) species
- Temperate maritime climate
- Some anthropogenic influence from a nearby sawmill (data filtered by setting a threshold on the variance of monoterpene concentrations)

2. Objectives & Methodology



Overall research objective: extensive characterisation of (O)VOC exchange at the Vielsalm mixed forest site

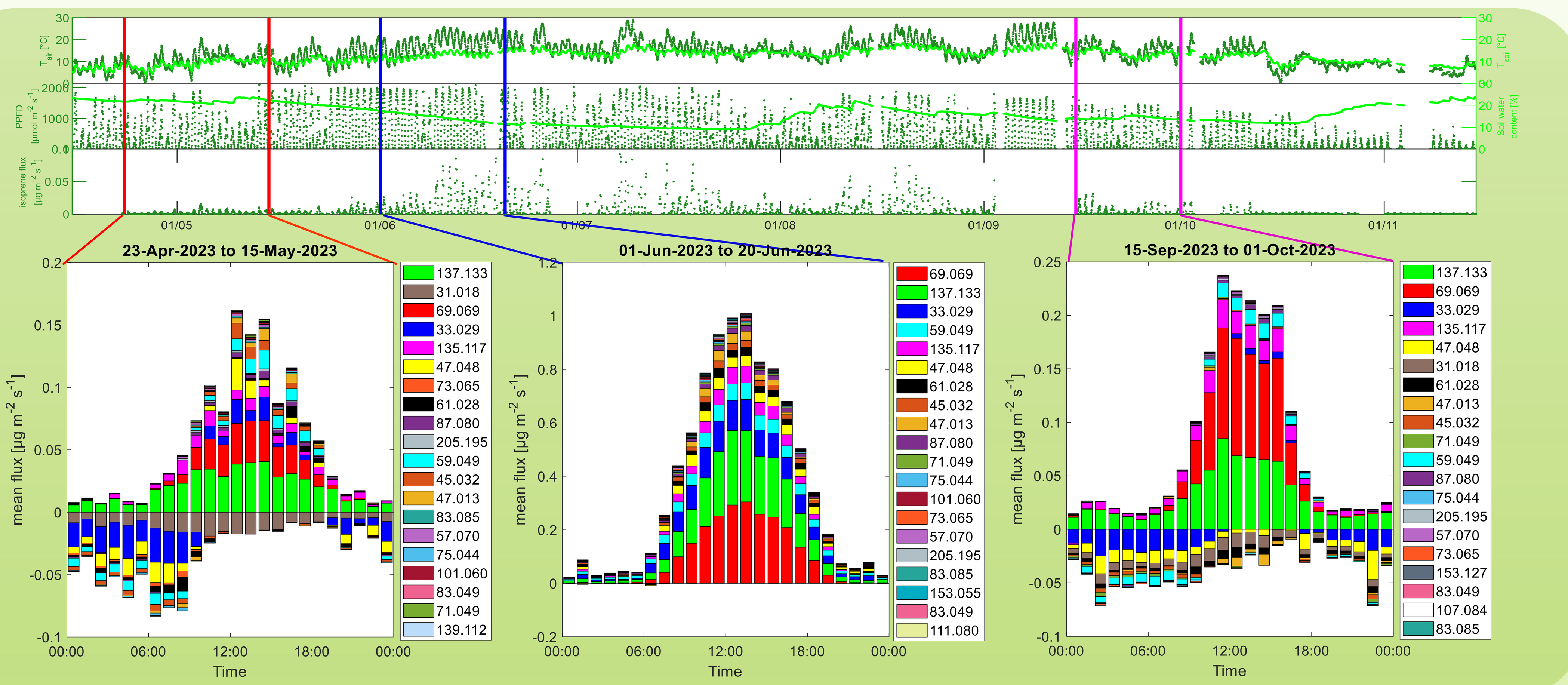
- Identify the exchanged (O)VOCs and the drivers of the exchanges
- Identify (O)VOC sources and sinks and their location along the soil/canopy/atmosphere continuum
- Investigate the role of in-canopy chemistry on (O)VOC exchanges
- Quantify the contribution of the exchanged (O)VOCs on the OH reactivity at the site

How ?

- **Two dedicated measurement campaigns** (21 April - 27 October 2022 and 20 April – 06 December 2023)
- Alternated measurements of:
  - ***Above-canopy*** (51 m a.g.l.) EC (O)VOC fluxes
  - ***Below-canopy*** (3 m a.g.l.) EC (O)VOC fluxes (only in 2023)
  - ***Vertical (O)VOC concentration profiles***
- (O)VOC measurements with a PTR-TOF-4000 analyser (Ionicon GmbH, Austria)
- Regular zero (every 4.5 hours) and calibration measurements (every 3 to 4 days, using an Apel-Riemer (O)VOC standard)
- Peak area quantification using IDA software (v2.0.1.2)
- VOC quantification and further analysis with matlab-based software

- Flux computation and quality control using GEddySoft (in Python) based on the InnFlux open-source code (in matlab) [1]

4. Some preliminary results (from 2023) & discussion



m/z selection:

- 223 m/z values were selected by applying the DBSCAN clustering algorithm for quantifying m/z stability between different IDA analyses, and considered for further analysis
- Significant fluxes were obtained for 69 of those 223 m/z values

Fig. 1: Mass flux diurnal pattern of the 20 most exchanged (O)VOCs during three specific periods. The m/z values in the corresponding legends are ordered from most to least exchanged compounds.

- Equally large contributions from isoprene and monoterpene fluxes
- No net depositions during the warm and dry period of high photochemical activity from 01-June-2023 to 20-June-2023.
- Important net depositions during the other two considered periods
  - Mainly of methanol, ethanol, formaldehyde, formic & acetic acid, acetone
  - Mainly before 11h00 UTC+1 and after 19h00 UTC+1

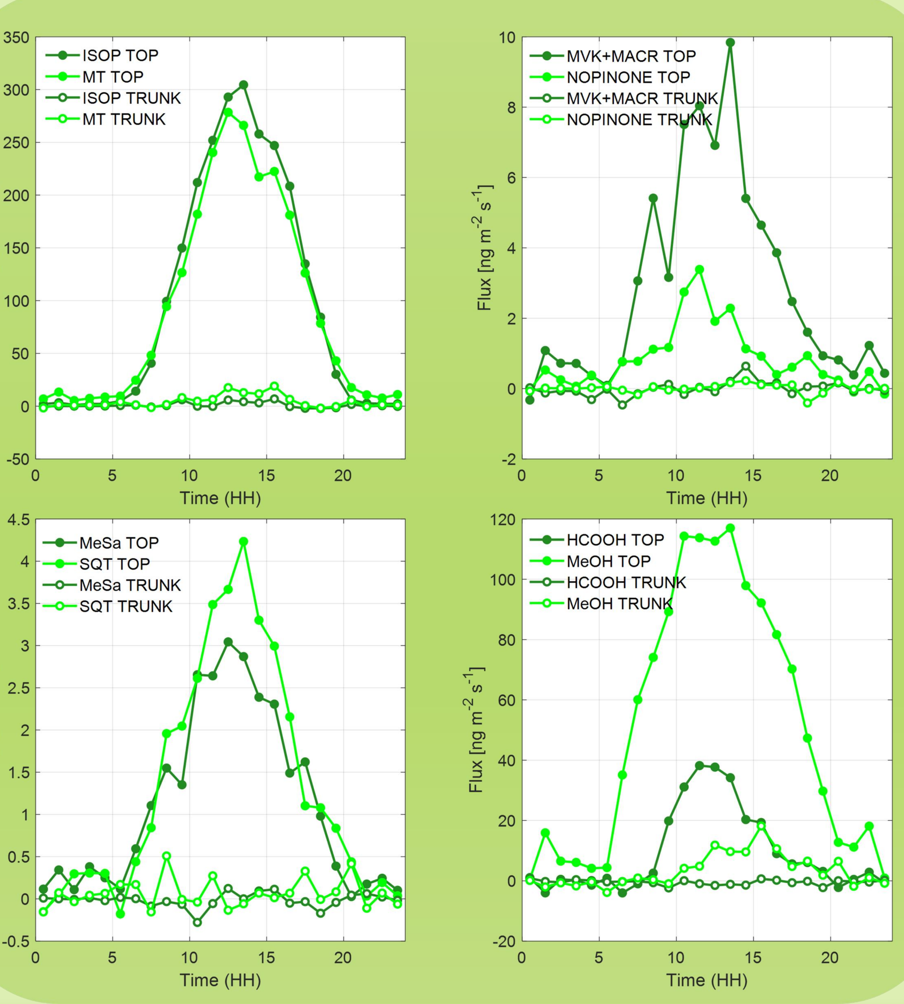
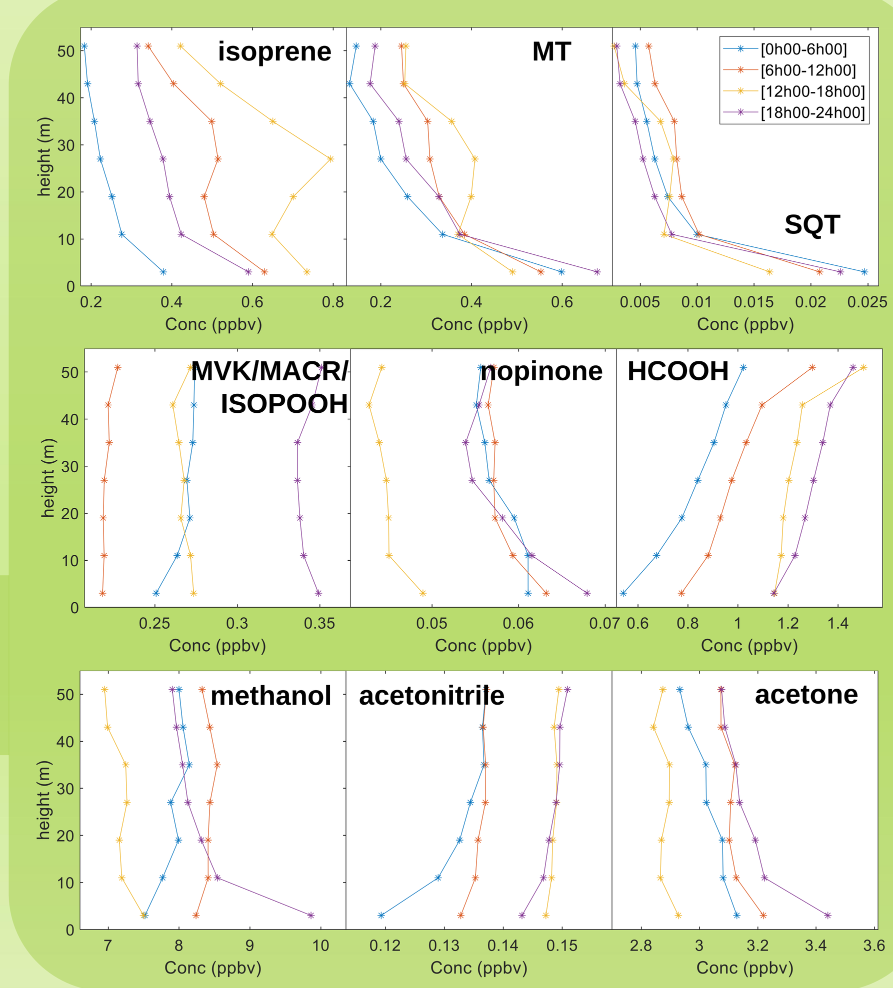


Fig. 2: Average diurnal above-canopy (TOP) and trunk-space (TRUNK) EC flux patterns for some typical (O)VOCs during 1-20 June 2023

- Trunk space fluxes are very small compared to above-canopy fluxes, except for m/z 143.143 and m/z 83.085 fluxes (not shown)
- Significant above-canopy HCOOH fluxes, in line with the literature [2]
- Well-developed diurnal flux patterns for less abundant compounds (e.g. sesquiterpenes and methyl salicylate)

Fig. 3: Average vertical concentration profiles for some typical (O)VOCs during 1-20 June 2023

- Clear maxima around 27 m for the directly emitted pure hydrocarbons between 12h00 and 18h00 UTC+1
- Diurnal variability and height dependence of the oxidation products less pronounced than for their precursors
- The vertical concentration profiles, in combination with turbulence characteristics (from 3 sonic anemometers along the profile) will be used to infer the vertical distribution of (O)VOC sources and sinks [3]



5. Conclusions & prospects

- Two years of continuous flux measurements resulted in a rich dataset of (O)VOC fluxes, complemented by a large dataset of meteorological parameters and greenhouse gas fluxes characteristic for an ICOS ecosystem station
- Future exploitation of this dataset will focus on the drivers of (bidirectional) exchanges and their seasonality, on comparison with existing emission/deposition models
- (O)VOC sources and sinks along the soil/canopy/atmosphere continuum will be further investigated using
  - inverse Lagrangian dispersion modelling applied to VOC canopy concentration profile measurements
  - a site-specific multi-layer 1D canopy exchange model

6. References & Acknowledgements

[1] M. Striednig et al., AMT 13, 1447-1465, 2020.
[2] S. Fulgham et al., ACS Earth Space Chem. 3, 2017−2032, 2019.
[3] R. Peterson et al., ACP 23, 7839-7858, 2023.

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