Fluxes of biogenic Volatile Organic Compounds in a holm oak forest

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Introduction

Context :
- Volatile Organic Compounds (VOCs) are precursors of ozone and secondary organic aerosols; 80% of VOCs stem from biological source (= BVOCs).
- In Europe: 55% forests, 27% croplands, 18% grasslands (Karl et al., 2009)
- Within the ANAEE framework: development of a service for measuring VOCs by proton transfer mass spectrometry in various ecosystem compartments (soil, plant and micro-organisms) in order to study biodiversity and biogeochemical cycles.

Objectives of this study:
This study is part of the COV3ER (CORTEA-ADEME) project and aims at developing a complete methodology to acquire and analyse BVOC flux data, based on joined Eddy-Covariance and PTR-Qi-TOF-MS techniques.

Research questions:
- Which BVOCs are exchanged at a mixed holm oak forest site? What are the dynamics and quantities of exchanged BVOC fluxes?
- How do these fluxes relate to climatic variables?
- Previous studies at this site showed that Quercus ilex is a strong Monoterpene emitter, and that the emission process is light-dependent (e.g. Staudt and Bertin, 1998; Kesselmeier and Staudt, 1999; Staudt et al., 1991)

Material and Methods

http://puechabon.cefe.cnrs.fr/

Site description:
- Mediterranean forest: FR-Pue ICOS site, South of France
- 80% holm oak (Quercus ilex), height 5.5m, LAI 2.5 m²/m²
- Main understorey species: *Buxus sempervirens*, *Phyllirea latifolia*, *Pistacia terebinthus* and *Juniperus oxycedrus*
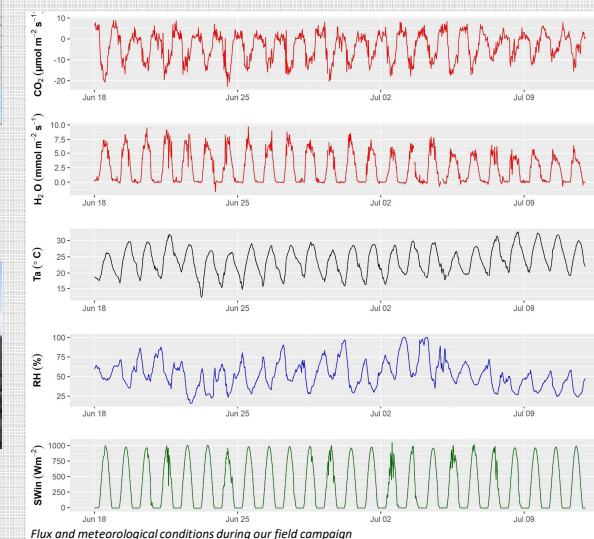
Eddy-covariance (EC) measurements:
- Sonic anemometer & VOC sampling inlet: 10.35 m height
- Acquisition rate: 10 Hz
- Li-COR 7500 for CO_2 and H_2O fluxes
- PTR-Qi-TOF-MS:
  - H_3O^+ soft ionization (E/N: 132 Td)
  - > 500 compounds can be detected
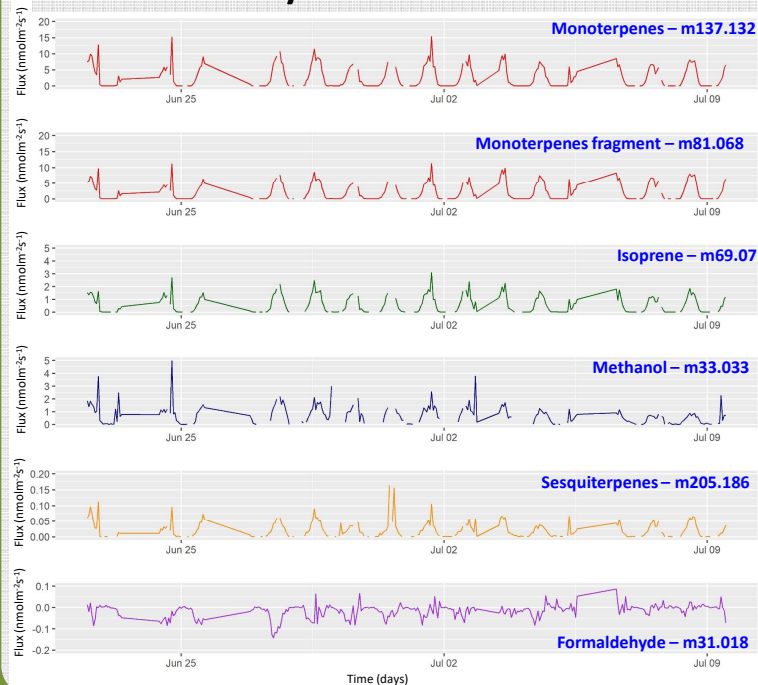 - On-line peak integration
- Campaign: 20 June – 10 July 2018

Complementary measurements:
Concentration profile, dynamic chamber measurements, monoterpene speciation with Fast-GC; ozone fluxes, aerosols.
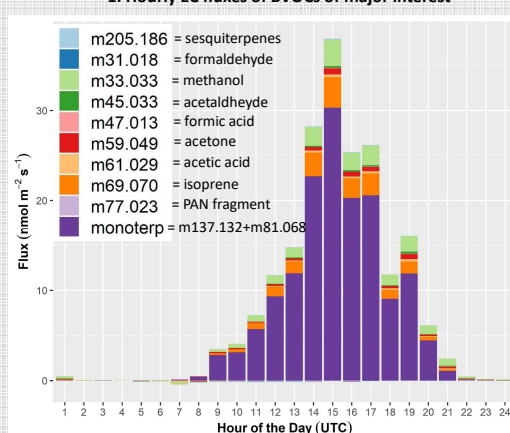
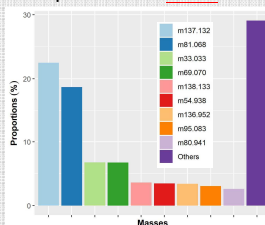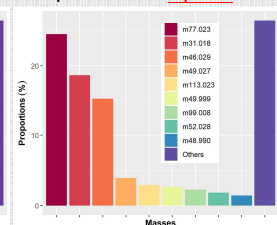*View on the eddy-covariance measurement system*

Flux and meteorological conditions during our field campaign

Preliminary results

Monoterpenes – m137.132

Monoterpenes fragment – m81.068

Isoprene – m69.07

Methanol – m33.033

Sesquiterpenes – m205.186

Formaldehyde – m31.018

Time (days)

Averages over the whole measurement campaign:
1. Hourly EC fluxes of BVOCs of major interest

- m205.186 = sesquiterpenes
- m31.018 = formaldehyde
- m33.033 = methanol
- m45.033 = acetaldheyde
- m47.013 = formic acid
- m59.049 = acetone
- m61.029 = acetic acid
- m69.070 = isoprene
- m77.023 = PAN fragment
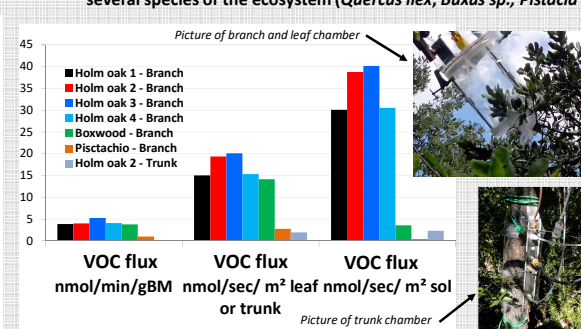- monoterp = m137.132+m81.068

Hour of the Day (UTC)

2. Proportions of main emitted BVOCs
3. Proportions of main deposited BVOCs

Masses

Complementary measurements by chambers on soil, branches + leaves, and trunks for several species of the ecosystem (*Quercus ilex*, *Buxus sp.*, *Pistacia sp.*) (from Lafouge et al.)

Picture of branch and leaf chamber

- Holm oak 1 - Branch
- Holm oak 2 - Branch
- Holm oak 3 - Branch
- Holm oak 4 - Branch
- Boxwood - Branch
- Pisctachio - Branch
- Holm oak 2 - Trunk

VOC flux nmol/min/gBM
VOC flux nmol/sec/ m² leaf or trunk
VOC flux nmol/sec/ m² sol

Picture of trunk chamber

The complementary chamber measurements revealed that:
✓ Holm oaks are the main VOC emitters
✓ Additional analyses revealed that monoterpenes are mainly emitted by holm oak branches, while methanol is mainly emitted by holm oak trunks and isoprene mainly by boxwood
✓ Emission profiles vary among individual oaks and Pistacia sp.(monoterpene speciation confirmed by fast GC, Bsaibes et al.)

Conclusion and perspectives

Conclusion:
✓ This mixed evergreen oak forest is a large source of BVOCs. Main emitted compounds: monoterpenes (m/z 137.132 + m/z 81.068), isoprene (m/z 69.070) and methanol (m/z 33.033).
✓ Compared to previous studies by gas chromatography (e.g. works by Staudt et al.), the use of a PTR-Qi-TOF-MS allowed to detect and quantify emissions of a large variety of compounds.
✓ Light and temperature are the main drivers of the observed emissions.
✓ Complementary measurements using chambers revealed very useful information to better understand the precise sources of the different emitted VOCs.

Perspectives:
✓ These results require to be consolidated (calibration, fragmentation, compound identification …)
✓ Ongoing data analysis of the concentration profile will provide additionnal information to understand sources and drivers of BVOC exchanges in this Mediterranean forest ecosystem.