

Observation and tentative of interpretation of atypical events of large deposited fluxes during the measurement campaign.

1. BVOC mixing ratio profiles and BVOC fluxes computation with the aerodynamic resistance approach

A BVOC mixing ratio profile was installed in the rapeseed field, comprising 5 lines positioned at 0.05 m, 0.25 m, 0.80 m, 1.55 m and 3 m above the ground, the rapeseed vegetation being 1.55 m height surrounding the mast. The concentrations measured at 3m were used in comparison with those measured by the EC system to filter out some data during specific periods (periods 3 (9-10 May) and 4 (23-30 May), see section 2.4.1). Every 30 minutes, each height was sequentially scanned by the PTR-Qi-TOF-MS for 1 minute using an 8 port 1/4" VICI valve. The air was drawn from each of these lines (1/4" external diameter, 1/8" internal diameter; 30 m length) with a Busch SV1010 pump at 6 NL min⁻¹ in each line using a flow splitter. The BVOC mixing ratio at each level was determined as the average mixing ratio over the last 30 s of sampling at this level. BVOC mixing ratio were calculated in the same way as explained at section 2.2.

The profile mixing ratio was further used to compute the flux based on the aerodynamic resistance approach using the two uppermost sampling heights (1.55 and 3.0 m), to serve as a diagnostic for the EC flux. Indeed, according to the resistance analogy, the BVOC profile flux (*Profile_Flux_i*, nmol m⁻² s⁻¹) above the canopy is equal to the difference in mixing ratios divided by the aerodynamic resistance (Flechard et al. 2013). Acknowledging that the BVOC concentration is equal to the mixing ratio divided by the molar volume of air ($RT_a/\overline{p_a^d}$), we find:

$$Profile_Flux_i = -\frac{C_i(3\text{ m}) - C_i(1.55\text{ m})}{R_a(1.55\text{ m}, 3\text{ m})} \times \frac{\overline{p_a^d}}{RT_a} \quad (6)$$

Where $C_i(3\text{ m})$ and $C_i(1.55\text{ m})$ (ppb) are the BVOC mixing ratios measured at 3 m and 1.55 m height, and R_a (s m⁻¹) is the aerodynamic resistance which was approximated as $R_a(1.55\text{ m}, 3\text{ m}) \sim \frac{1}{\kappa u_*} \ln\left(\frac{3-d}{1.55-d}\right) \sim \frac{1.02}{\kappa u_*}$, with u_* being the friction velocity (m s⁻¹), d the displacement height (m), and κ the von Kármán constant (0.4), neglecting thermal stratification for simplification in this diagnostic approach. During the experiment the canopy height was 1.7 m height, the displacement height d and the roughness height z_0 were evaluated as 1.4 and 0.17 m respectively, where d was evaluated from Verhoef et al. (1997).

2. Fluxes by aerodynamic resistance approach during periods 1 and 2

Fluxes measured either by the eddy-covariance method (EC_Flux) or by the aerodynamic resistance approach (Profile_Flux) were generally in good agreement for emission behaviours, as for example for methanol and monoterpenes over the periods 11-22 May (Fig. 1 and Fig. S010b) and 9-30 June (Fig. 1 and Fig. S010d). Differences in magnitude were however observed for deposited compounds over the period 9-30 June (Fig. 1 and Fig. S010d), with Profile_Flux being larger e.g. for formic acid (m/z 47.013) and acetic acid (m/z 61.029). For some compounds (m/z 75.025, 115.078), the flux direction is even different between both estimations over the period from 9 to 30 June (Fig. S010d), with emission observed by the EC method and deposition observed with the aerodynamic resistance approach. Such differences were not observed during period 1 (Fig. S010b).

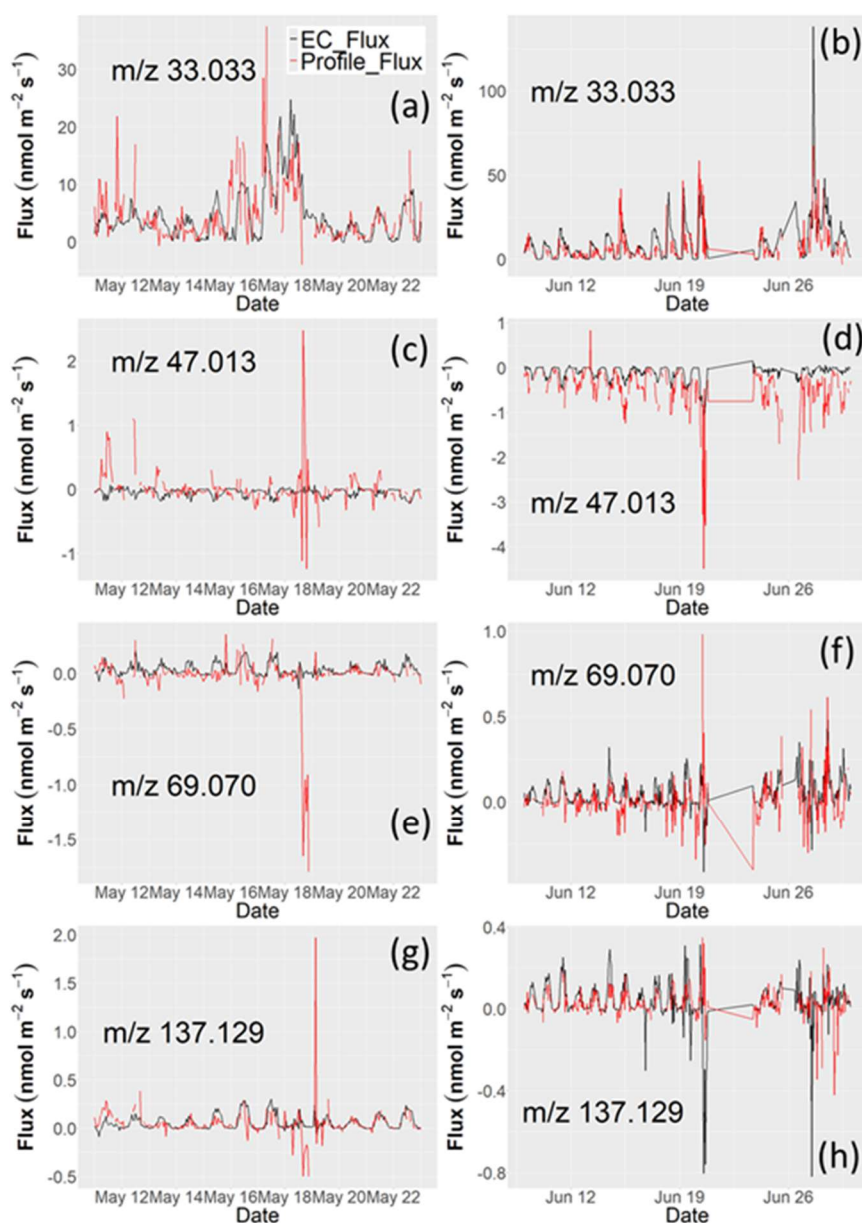


Figure 1: Comparison of BVOC fluxes measured by eddy-covariance (black lines) or with the aerodynamic resistance approach (red lines) for four BVOCs during both flowering (period 1) and senescence (period 2) vegetation stages. a and b: methanol (m/z 33.033). c and d: formic acid (m/z 47.013). e and f: isoprene (m/z 69.070). g and h: monoterpenes (m/z 137.129).

3. Identification of potential fast gas-phase chemical reactions for BVOCs at the site

We observed that, most of the time, mixing ratios were in good agreement between EC and profile measurement systems sampling at the same height of 3 m, for the majority of compounds during the whole measurement campaign (Fig. S010a-d). However, during periods 3 (9-10 May), and 4 (23-30 May), the mixing ratios were up to 15 times higher in the EC line, indicating a very strong gas-phase reaction occurring for some BVOCs, and in particular terpenes and siloxanes during these periods, combined with high mixing ratios of these compounds (Fig. S010a and S010c).

The reason for these differences may be due to chemical reactions in the gas-phase occurring during the transport in the tubes. Indeed, given the difference in inlet lines length and flow rates in those lines, the transport time was $t_{EC} = 3.6$ s in the EC set-up and $t_{profile} = 11.3$ s in the profile set-up. This led to BVOCs being either consumed or produced in differing amounts in the two tubing systems. Assuming a first-order reaction with a non-limiting reactant mixing ratio, the reaction constant of a compound i in the atmosphere k_{atm_i} (s^{-1}) could be computed as $k_{atm_i} = \ln(C_{EC} / C_{profile}) / (t_{profile} - t_{EC})$, with $t_{profile} - t_{EC} = 7.7$ s.

We find reaction rates varying up to $0.04\ s^{-1}$, $0.12\ s^{-1}$ and $0.25\ s^{-1}$ during the periods 3 and 4 for isoprene, monoterpenes and D3-siloxane, respectively (see Fig. S11 for reaction rates for all compounds during the experiment).

We also observed during these periods 3 and 4, that some BVOCs, and in particular, monoterpenes, isoprene, siloxanes, exhibited large eddy-covariance deposition fluxes that followed a diel pattern (Fig. 2, S10a and S10c).

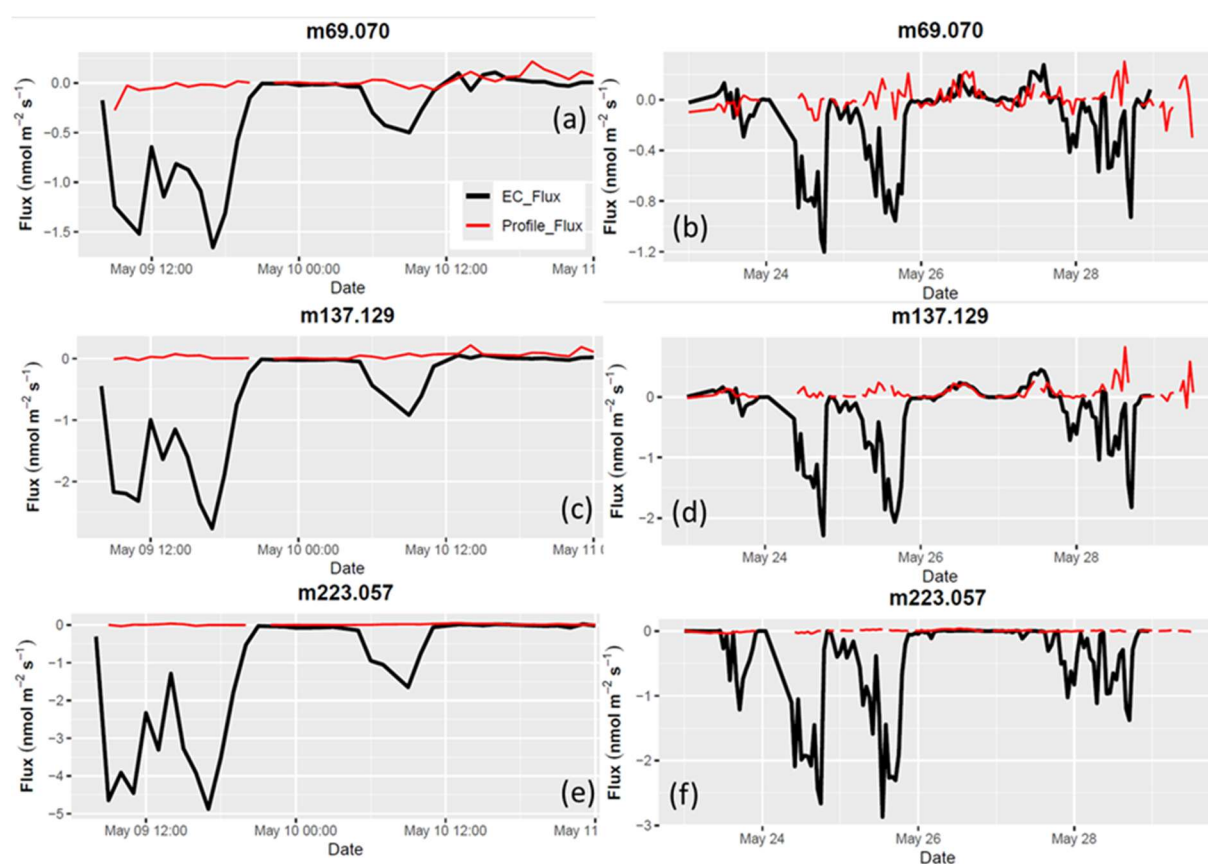


Figure 2: Fluxes of isoprene (m/z 69.070, a), monoterpenes (m/z 137.129) and D3-siloxanes (m/z 223.057) measured with the eddy-covariance (black curves) and the aerodynamic resistance approach (red curves) during periods 3 (a, c, e) and 4 (b, d, f).

For monoterpenes, these deposition fluxes reached about 10 times the magnitude of emitted fluxes for the same compounds during periods 1 and 2, and deposition velocities (V_d , $m\ s^{-1}$) were far above the maximum exchange deposition velocity (V_{max} , $m\ s^{-1}$) indicating clearly a gas phase reaction mechanism to explain the observed apparent deposition velocity (Fig. S12a for isoprene and Fig. S12b for monoterpenes). During these episodes, we further observed that the compounds exhibiting large EC deposition fluxes showed a mixing ratio much larger (and variable) in the EC setup than in the profile setup at the same sampling height of 3 m. This was in particular true for siloxane compounds (D3-siloxane, m/z 223.057 and isotopes, and D4-siloxane, m/z 297.071 and isotopes

+ fragments), and terpenes for all four periods. Furthermore, during these periods, the fluxes computed with the aerodynamic resistance approach for these compounds showed no or slight deposition when compared to the large EC deposition fluxes, even for BVOCs that are usually seen to be deposited like formic acid or acetic acid (Fig. 2, and S10a).

To investigate the origin of these atypical fluxes, meteorological conditions during periods 3 and 4 were looked into details. While no atypical events were observed for rain, air humidity or air temperature (Fig. 2), wind direction was always in the North-East sector (0 – 100 deg/N, Fig. S05). Polar plots of BVOC mixing ratios measured in the eddy-covariance line (Conc_EC) over the whole measurement campaign, showed that those BVOCs characterized by atypically large deposition in periods 3 and 4, exhibited peaking mixing ratios with wind from the north-east sector, which strongly suggests a local source of these compounds in that direction (Fig. 3 and S13). We further see in Fig. 3 that for monoterpenes (m/z 137.129) and D3-siloxane (m/z 223.057) the concentration increases for wind speeds above a certain threshold ($\sim 1 \text{ m s}^{-1}$ for D3-siloxane), indicating advection from a local source of a highly reacting compound.

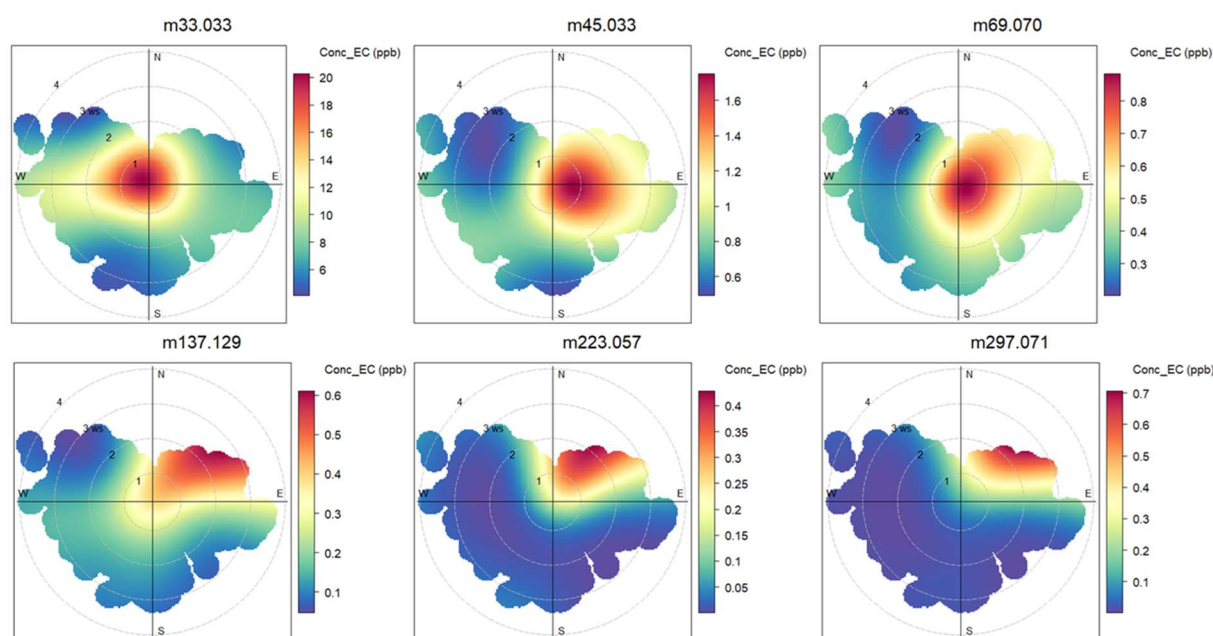


Figure 3: Polar plots of the mixing ratios of six selected BVOCs, as measured by the eddy-covariance set-up over the whole measurement campaign (9 May – 30 June). The radius variable is the wind speed. The first row shows compounds that do not exhibit atypical fluxes in subperiods 3 and 4 (m/z 33.033, m/z 45.033 and to a lesser extent m/z 69.070) while the second row shows such compounds (m/z 137.129, m/z 223.057 and m/z 297.071). The complete set of polar plots for all significant BVOCs in this study is displayed in Fig. S13 in the Supplementary Material.

4. Hypothesis to explain the observed uncommon large deposition fluxes of isoprenoids and siloxanes

We found overall good agreement in both magnitude and temporal dynamics between the mixing ratios measured with the EC and profile setups at the same sampling height of 3.0 m (Fig. S10a–d) for most compounds. Moreover, isoprene mixing ratios were consistent in dynamics, and even if they were twice larger compared to those from a permanent AIRPARIF air quality station in Paris (Fig. 4), which can be explained by the fact that this air quality station is in an urban area, that is, less influenced by biogenic emission. These reasonably good agreements

strengthen confidence in the accuracy of BVOC quantification during the campaign, and in turn in the observed high deposition fluxes during periods 3 and 4 for compounds typically considered as emitted species (Fig. 2).

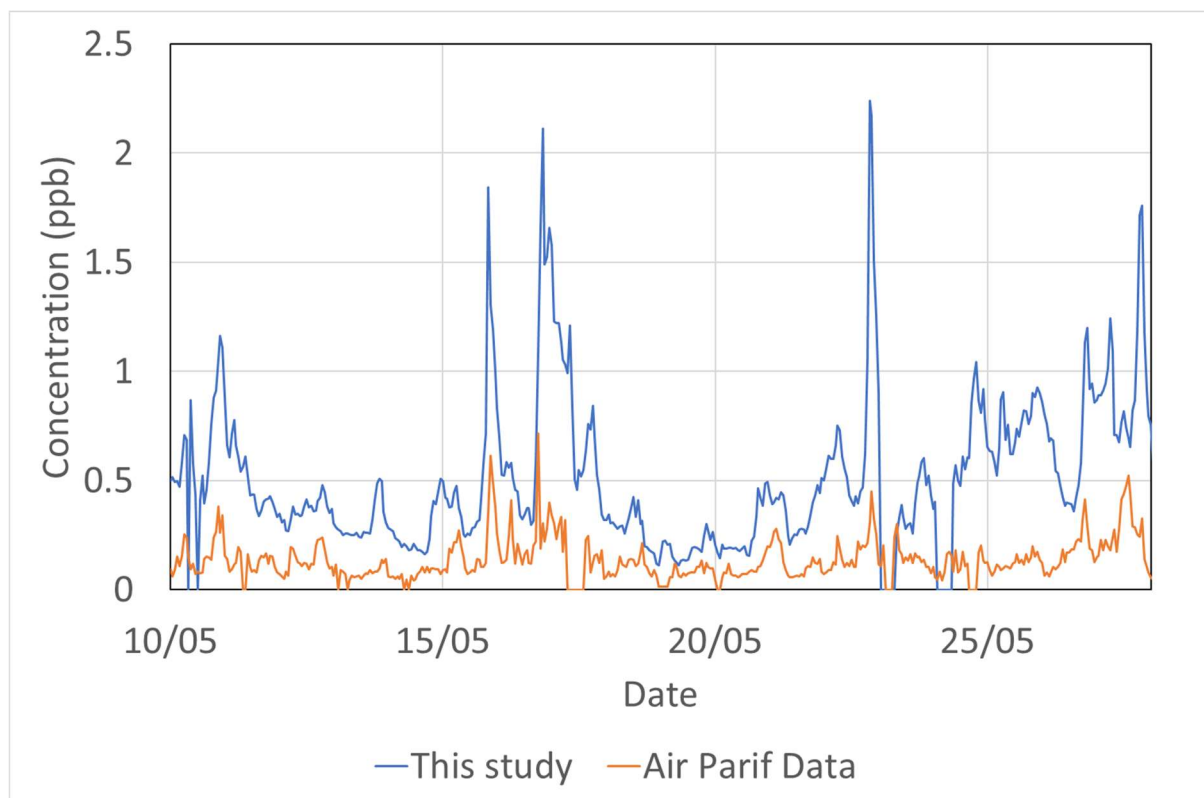


Figure 4: Comparison between isoprene concentrations (ppb) measured in this study (blue line) and at an AIRPARIF air quality station located in Paris during the measurement period.

The hypothesis of a regional pollution event from Paris seems unlikely, given the high reactivity of the compounds involved (e.g., monoterpenes, isoprene; Table 2 in the manuscript). A more plausible explanation is the local advection of a plume enriched in siloxanes and terpenes (Fig. 3). Such a plume would also contain other highly reactive species, to explain the strong chemical sinks of these compounds observed in the profile tubes. To explore this possibility, we gathered information on agricultural operations (e.g., pesticide applications, fertilizer use) in adjacent fields, and found that maize was planted in a nearby field located north-east of the site during the campaign. This suggests that herbicides may have been applied, as this is a common practice in the region. Herbicide formulations contain adjuvants and solvents, sometimes including organo-silicone compounds such as siloxanes (e.g. Li et al., 2019; Chen et al., 2022) like the commercial product Silwet® (EPHY, 2025) which we know was occasionally applied at the farm scale. In addition, herbicide application damages or destroys plants, which can trigger large pulses of terpenoid emissions, similar to those observed after herbivory (Piesik et al., 2011; Kammer et al., 2019) or extreme meteorological events (Bamberger et al., 2011). Based on this evidence, we hypothesise that herbicide application in adjacent fields may have generated a plume containing siloxanes and terpenes, leading to the observed concentration peaks and deposition fluxes at our site. While plausible, this explanation remains speculative and would require further targeted experiments to be confirmed.

References

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