

General comments

Buyse et al present a manuscript showing BVOC fluxes measured in a rapeseed field in France. This is a crop that has seldom been studied for its ecosystem-scale emissions. Partly due to this lack of data, this work is a valuable dataset that deserves to be published. The manuscript mixes several analysis approaches (average diel cycles, measurement-model comparison, OH reactivity, and strange phenomena with high mixing ratios and deposition). However, there are some points that should be addressed before accepting the manuscript. The text would also benefit from some improvement of the structure and readability of the text.

Specific comments

-L275: Eq 9 has the Guenther light-independent temperature algorithm duplicated in the denominator.

Yes, indeed, thanks for spotting this typo which has now been corrected in the revised version of the manuscript.

-L282-291, Table 2, L440-468: I am not that familiar with the works of Gomez et al (2021) and Havermann et al (2022), and I have not read those in detail, but I am familiar with the MEGAN2.1 model. The comparison of measured fluxes with the MEGAN2.1 SEF and its derived fluxes is not as straightforward as the authors have made it seem. First of all, the SEF from MEGAN2.1 are canopy-scale emission factors. So, in principle, to compare them to the EC emissions measured in this work, it is not needed to transform the measurements into leaf-level emission factors. However, MEGAN2.1 relies on canopy models to derive the light and temperature conditions (to use with its "extended" version of the light and temperature Guenther algorithms) of a number of different levels inside the canopy. To make the MEGAN2.1 model work with such a layered canopy, the canopy-scale emission factors in the Guenther et al 2021 paper are standardized to correspond to a canopy with a LAI of 5. Thus, it is not that straightforward to simply use the simplest version of the leaf-level light and temperature Guenther algorithms, together with the MEGAN2.1 SEFs, and declare that this is a comparison with the MEGAN2.1 model results.

While it can be legitimate to use those leaf-level algorithms to compare with measurements, either by converting the measured emission factors to leaf-level (as done in this work) or by assuming that the canopy is a "big leaf" (and applying those algorithms to the canopy flux data), this needs to be conveniently and clearly explained in the manuscript to avoid confusion or claims of "comparison with MEGAN2.1".

We thank the reviewer for this important remark. We indeed assumed the canopy was a big leaf when comparing the canopy-scale measurement-derived SEF to the MEGAN2.1 SEF. We acknowledge that our derived SEF are not strictly comparable to

MEGAN2.1 SEF, as we did not use the MEGAN2.1 algorithms to derive them, but the equations from Guenther et al. (1993, 1995). The differences are small but may lead to differences in SEF that we need to characterise. Therefore, taking the reviewer's remark into account we have re-computed the SEF with the MEGAN2.1 algorithms (Guenther et al., 2012, "Megan 2.1" in Table 1), namely Equations 2-11, where γ is the emission factor defined as:

$$\gamma = C_{CE} LAI \gamma_P \gamma_T \gamma_A \gamma_{SM} \gamma_C \quad (\text{Eq1})$$

This equation was applied considering a few hypotheses:

- The product ($\gamma_A \gamma_{SM} \gamma_C$) was set to 1, assuming no aging, soil moisture and CO2 inhibition effects
- C_{CE} was set so that γ is equal to 1 under standard conditions, with the standard conditions defined as $T_{\text{ref}} = 297 \text{ K}$, $\text{PAR} = 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$. In practice, $LAI \gamma_P \gamma_T$ was computed from Guenther et al. (2012) eqns. 3-11 and divided by its means when $T_a = 20 \pm 2^\circ\text{C}$ and $\text{PAR} = 1000 \pm 20 \mu\text{mol m}^{-2} \text{ s}^{-1}$, in subperiods 1 and 2. This led to values of C_{CE} varying from 0.19 to 0.64 depending on LDF and the subperiod considered (Table 1). The subperiod had an effect on P24, P240, T24 and T240.

γ_P and γ_T were calculated respectively according to Equations 3-6, and Equations 7-10 in Guenther et al. (2012), which implies to take the LDF (light-dependent fraction) parameter into account, which we did not consider previously with Guenther et al. (1993, 1995). Therefore, we also re-calculated the emission factors based on the equations described in Guenther et al. (1993, 1995), this time including the LDF fraction ("G95-new" in Table 1). We furthermore harmonized the standard temperature to 297 K as in Guenther et al. (2012). It was indeed initially 303 K in Guenther et al. (1993, 1995). We further did the same standardisation of γ to 1 in standard conditions in Guenther et al. (1993, 1995) to be consistent between the two approaches. Finally, as an empirical approach we also computed the emission factors as simply equal to the mean measured flux when the temperature and PAR were equal to the standard conditions ($T_a = 20 \pm 2^\circ\text{C}$ and $\text{PAR} = 1000 \pm 20 \mu\text{mol m}^{-2} \text{ s}^{-1}$) ("Empirical" in Table 1 below).

The comparison of the SEF obtained with the four calculation methods (initially submitted version (G95 – initial, Table 1), re-calculated G95 version (G95 – new, Table 1) and that based on Guenther et al. (2012) (Megan 2.1, Table 1) is shown in Table 1 below.

Table 1 – Comparison of standard emission factors (SEF [$\mu\text{g m}^{-2}$ (leaf) h^{-1}]), and its standard error (se) calculated with three different versions of the MEGAN model and compared to an empirical data-based approach. The "G95-initial" contains the

values present in the initial version of the manuscript. The RMSE is also given, together with the LDF used for each compound (as in Gunther et al. 2012), and the C_{CE} parameter retrieved by forcing γ to 1 in standard conditions for each model.

	Tentative VOC identification		G95 (initial)		G95 new		Megan 2.1		Empirical		G95 new		Megan 2.1								
m/z	Ion formulas	VOC names	SEF ± se [μg m ⁻² (leaf) h ⁻¹]										RMSE [μg m ⁻² (leaf) h ⁻¹]				LDF	CCE Megan		CCE G95	
			P1	P2	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2		P1	P2		
Oxygenated and terpenes VOC																					
33.033	(CH4O)H+	methanol	485	641	130 ± 8	199 ± 13	123 ± 7	175 ± 11	89 ± 0	423 ± 126	104	305	103	304	0.8	0.42	0.34	0.21	0.18		
59.049	(C3H6O)H+	acetone	13.9	39.2	3.6 ± 0.1	12 ± 1	5.1 ± 0.2	17 ± 1	2.7 ± 0	12 ± 4	1.5	17.2	1.4	16.6	0.2	0.22	0.19	0.2	0.18		
69.07	(C5H8)H+	isoprene	13.1	6.5	3.4 ± 0.1	3.2 ± 0.2	2.5 ± 0.1	1.9 ± 0.1	1.7 ± 0	13 ± 4	1.7	3.5	1.9	3.8	1	0.64	0.51	0.21	0.18		
87.078	(C5H10O)H+	MBO	2	0.3	0.5 ± 0.02	0.1 ± 0.01	0.4 ± 0.01	0.1 ± 0.004	0.4 ± 0	0.3 ± 0.1	0.2	0.1	0.3	0.1	1	0.64	0.51	0.21	0.18		
137.129	(C10H16)H+	monoterpenes	40	7	10.2 ± 0.3	7.1 ± 0.2	13 ± 0.3	8 ± 0.3	8 ± 0	12 ± 3	4	5	3	4	0.5	0.27	0.23	0.21	0.18		
205.186	(C15H24)H+	sesquiterpenes	3	0.2	0.86 ± 0.05	0.12 ± 0.01	0.7 ± 0.05	0.06 ± 0.01	0.5 ± 0	0.3 ± 0.2	3.2	0.2	0.7	0.2	0.5	0.39	0.32	0.21	0.18		
Bi-directional VOC																					
31.018	(CH2O)H+	formaldehyde	na	102	na	45 ± 3	na	38 ± 2	na	11 ± 6	6	53	6	48	0.8	0.42	0.34	0.21	0.18		
45.033	(C2H4O)H+	acetaldehyde	8	6	2.6 ± 0.1	2.6 ± 0.2	2.5 ± 0.1	2 ± 0.1	0.3 ± 0	8 ± 3	1.5	3.7	1.5	4	0.8	0.42	0.34	0.21	0.18		
Stress VOC																					
118.078	(C8H7N)H+	indole	0.9	0.04	0.23 ± 0.01	0.029 ± 0.002	0.22 ± 0.01	0.02 ± 0.002	0.3 ± 0	0.02 ± 0.01	0.14	0.05	0.14	0.05	0.8	0.42	0.34	0.21	0.18		
Other VOC leaf surface compounds																					
49.014	(CH4S)H+	methanethiol	2.6	1.4	0.68 ± 0.03	1.2 ± 0.1	1 ± 0.04	1.5 ± 0.1	0.4 ± 0	2.5 ± 1	0.4	2.2	0.4	2.2	0.2	0.22	0.19	0.2	0.18		
101.059	(C5H8O2)H+	4-oxopentanal (4-OPA)	2.4	2.8	0.65 ± 0.02	0.5 ± 0.02	0.9 ± 0.03	0.6 ± 0.02	1.1 ± 0	0.9 ± 0.4	0.3	0.4	0.3	0.4	0.2	0.22	0.19	0.2	0.18		

Table 1 shows that the new computation provides lower emission factors than initially submitted, which is mostly due to the standardisation of the γ to 1 in standard conditions. Megan 2.1 gives slightly smaller values than G95, except for acetone, monoterpenes and methanethiol.

In the revised manuscript we propose:

- To replace the initial SEF values (recall: obtained using the equations from Guenther et al. (1993, 1995) without LDF consideration) by those obtained using the Guenther et al. (2012) Megan 2.1 model, keeping in mind that this is still not strictly the MEGAN2.1 version, considering the above-mentioned hypotheses about the product ($\gamma_{AY_{SM}\gamma_C}$). We would likely need a longer time series to fully answer the question.
- To advise the reader by stating more precisely that the model version we used is not strictly the MEGAN2.1 model and how it differs from the actual MEGAN2.1 model.
- To include as well the SEF values obtained using the “G95 – new” model version (recall: obtained using the equations from Guenther et al. (1993, 1995) with LDF consideration), as it will allow us to keep comparing the SEF values we obtained with Gonzaga-Gomez et al (2019) and Havermann et al. (2022), who both used algorithms derived from Guenther et al. (1993, 1995). We will carefully advise the reader that the models are slightly different from one paper to another.
- Not to show the “Empirical” results, which are just there for a simple comparison between modelled SEF and data-derived SEF estimations.
- As we did previously, to provide the scripts that we used to calculate the SEF.

Importantly, in the revised version of our paper, the comparison between the SEF values reported in the three studies will show that (Table 2):

- For most studied BVOCs our SEF values are lower than what is reported in Guenther et al. (2012), sometimes up to about 100 times (indole, methanethiol, acetaldehyde, m/z 101.059).
- Our methanol SEF values were lowered and are now more in the range of what was determined by Havermann et al. (2022), and about 6 times lower than what is reported in Guenther et al. (2012).
- Our isoprene SEF values are now comparable to what is reported in Guenther et al. (2012) but 10 times lower than what was shown in Gonzaga-Gomez et al (2019) and Havermann et al (2022) (when comparing with “G95 – new” results instead of “Megan 2.1”).
- For monoterpenes our study agrees pretty well with values reported in Gonzaga-Gomez et al (2019) (when comparing with “G95 – new” results instead of “Megan 2.1”) and Havermann et al (2022), and provides slightly (up to twice) larger numbers than what is shown in Guenther et al. (2012).
- To re-calculate and provide the OH reactivity fluxes based on our revised SEF values.

Table 2 – Comparison of the Standard Emission Factors (SEF [$\mu\text{g m}^{-2}$ (leaf) h^{-1}]) calculated in the revised form of this study (“This study”) with those reported in Guenther et al. (2012) (“MEGAN2.1”), Gonzaga-Gomez et al. (2019) (“G2019”) and Havermann et al. (2022) (“H2022”).

			This study		MEGAN2.1	G2019	H2022
m/z	Ion formulas	VOC names	P1	P2			
Oxygenated and terpenes VOC							
33.033	(CH4O)H+	methanol	123 ± 7	175 ± 11	900		149.7
59.049	(C3H6O)H+	acetone	5.1 ± 0.2	17 ± 1	80		11.2
69.07	(C5H8)H+	isoprene	2.5 ± 0.1	1.9 ± 0.1	1	12-18	11.5
87.078	(C5H10O)H+	MBO	0.4 ± 0.01	0.1 ± 0.004	0.01		
137.129	(C10H16)H+	monoterpenes	13 ± 0.3	8 ± 0.3	0.3 - 5	9-23	14.2
205.186	(C15H24)H+	sesquiterpenes	0.7 ± 0.05	0.06 ± 0.01	2 - 4		
Bi-directional VOC							
31.018	(CH2O)H+	formaldehyde	na	38 ± 2	80		
45.033	(C2H4O)H+	acetaldehyde	2.5 ± 0.1	2 ± 0.1	80		5.5
Stress VOC							
118.078	(C8H7N)H+	indole	0.22 ± 0.01	0.02 ± 0.002	300		
Other VOC leaf surface compounds							
49.014	(CH4S)H+	methanethiol	1 ± 0.04	1.5 ± 0.1	140		
101.059	(C5H8O2)H+	4-oxopentanal (4-OPA)	0.9 ± 0.03	0.6 ± 0.02	140		

Finally, we do not see in the referee’s comment which is the paper behind the reference “Guenther et al, 2021” but we guess it is a typo, and that we should read “Guenther et al., 2012”.

-L720: An air quality station in Paris, which is 40 km apart and, without more information in the text, probably affected by a substantial urban influence, may not be the best comparison possible for the dynamics and magnitude of isoprene mixing ratios measured in a crop field.

We fully agree with the reviewer comment. However, this was the only measurement that could be used to check the isoprene concentration in the region. The comparison

shows a reasonable agreement in terms of daily variability and the expected divergences with a larger isoprene mixing ratio measured above the field which is a source of isoprene and also which is also placed in a rural environment with forests around contributing to the biospheric sources. An updated version of the figure is displayed below and will be added to the revised version of the manuscript as supplementary material.

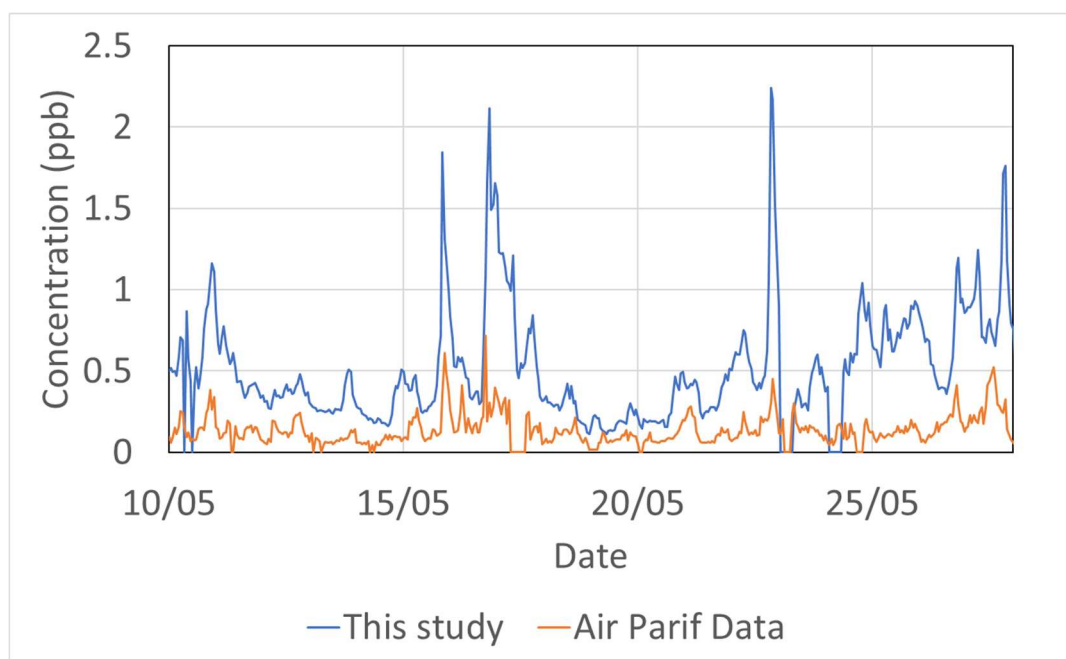


Figure 1 – Isoprene (m/z 69.070) concentrations (ppb) measured at our site (This study, blue line) and at the air quality station located inside Paris city (Air Parif data, orange line) during our measurement period. The measurement site of our study is located about 40km west of the Air Parif station, in a much more rural environment, explaining the large concentrations observed at that site compared to those measured in Paris city.

-Sections 3.4 and 4.9 (high deposition fluxes): Those particular episodes seem interesting and obviously something was happening at the field site. But what is the distance of this nearby field from the EC tower? Because the difference in mixing ratios between the 2 inlet lines due to a 8s longer residence time in the profile tube must mean that the emissions were very close to the measurement point (¿?). Moreover, was that field inside the footprint of the EC measurements during all those hours of high deposition fluxes? If not, I am not convinced that the mixing ratios would show such a strong correlation with the vertical wind speed (so no EC fluxes would be computed). Did the authors check the contribution of different eddy frequencies to the total measured flux during those periods, to see if the distribution differed from the other "normal" periods?

In a similar way, reviewer #2 underlined that these manuscript sections were underdeveloped and insufficiently justified. We have therefore produced a more detailed analysis of these events considering plausibility criteria (see the supplementary section at the end of the answer to reviewer #2). This led us to conclude that the derived chemical reaction rates for siloxanes are rather implausible,

with the current understanding of the situation. These episodes would therefore need further investigation to fully understand the observations. We therefore followed the two recommendations of reviewer #2 to filter out these episodes and focus the paper on the standard emission factors. This will also answer the comments from both reviewers to revise the manuscript structure in order to ease the readability.

-L557: Maybe I misunderstood something, but why would the share of methanol from soil be larger than that of vegetation if those studies showed at least 56% of the contribution from plants?

From reviewer's comment it appears that this paragraph was not clear enough. We actually did not discuss there the share of BVOC emissions from the soil and from the plants, which we cannot partition based on our experiment design. What we meant is that "the ratio of methanol to the total BVOC emissions from soil must necessarily be larger than the ratio of methanol to the total BVOC emissions from the plants". Indeed, since:

1. methanol represented 90% of total (ecosystem-scale = soil + plants) BVOC emissions (on a molar basis),
2. methanol represents 56% to 77% of BVOC emissions when measured at the plant scale (Gonzaga-Gomez et al., 2019),
3. we can hypothesize that total BVOC emissions from the soil, and total BVOC emissions from the plants are of similar magnitude,

We can conclude that methanol must necessarily represent a larger fraction of the total BVOC emissions from the soil.

-Fig 4: are the fluxes of m/z 31.01 (formaldehyde) shown in panels B1 and C1? Maybe I can see them in panel C2, but not in panel C1.

Formaldehyde is indeed not represented in panels B1 and C1, because for the sake of clarity, we decided to display only the 4 most emitted and the 2 most deposited BVOC for each sub-period. But we agree this can be confusing. We corrected the legend of the figure according to this in the revised version of the manuscript. Formaldehyde is actually the 4th most deposited BVOC in sub-period 1 after formic acid, m/z 297.071 and m/z 223.057.

Technical corrections

These comments will be addressed directly in the revised version of the manuscript.

-L16: quadrupole, not quadripole

-Table 1: the name of D4-siloxane in English does not have written accents.

-Fig. 3: I suggest alerting the reader that the Y axis ranges of the graphs on each side of the figure are different.

-L395: there seem to be too many parentheses in this paragraph.

-L635: A period is missing after the word "active".

-L660: was or was not observed in the present study?

-L733: the parenthesis with Silwet inside is probably not needed in this paragraph.