Referee Comments – A comprehensive assessment of emissions from prescribed fires in two Mediterranean shrublands: chemical and morphological analysis

(https://doi.org/10.5194/egusphere-2026-952)

General Overview:

The manuscript (egusphere-2026-952) presents results from prescribed fires in two Mediterranean shrublands in 2016. The analysis includes emission factor, chemical composition, and morphology. The topic of this study falls within the scope of the journal Atmospheric Chemistry and Physics (ACP). This manuscript is generally laid out well and shows its academic value. This manuscript is recommended to be published after addressing the concerns and comments below with minor revisions.

We thank the reviewer for the positive assessment of our manuscript and for recommending publication after minor revision. We appreciate the reviewer's recognition that the topic falls within the scope of Atmospheric Chemistry and Physics and that the manuscript is generally well structured and academically valuable. We have carefully addressed all the concerns and comments raised, as detailed below.

Major Concern:

- Tables 1, 2, and 3 are mentioned but not provided in the manuscript.

We apologize for this oversight. Due to an error during manuscript preparation, Tables 1–3 were not included in the submitted version. These tables have now been added and are available in the revised manuscript.

Minor Concerns:

- Figure 1: Please provide the Direction, Scale, and Legend.

Figure 1 has been revised to include a north arrow, scale bar, and legend.

- Equation 1: The 100 on the right-hand side of the equation is suggested to be replaced with 100%.

To make the notation clearer, we have revised the equation by expressing the result explicitly as MCE (%), while keeping the multiplication factor as 100.

"The MCE, expressed as a percentage, is calculated as (1):

$$\mathrm{MCE}\ (\%) = \frac{[\mathrm{CO_2}]}{[\mathrm{CO_2}]+[\mathrm{CO}]} \cdot 100 \qquad (1)"$$

- Lines 153 - 154: How are the numbers 53.3% and 53.2% obtained? Are they obtained from the chemical analysis described in Section 2.2? If so, please specify here for clarity.

The values 53.3 % and 53.2 % correspond to the carbon mass fraction of the dry fuel for *Calluna* and *Genista*, respectively, obtained from the elemental analysis described in Sect. 2.2 and reported in Table 2. This has now been clarified in the revised manuscript.

"The carbon mass fraction of the dry fuel used in Eq. (2) was obtained from the elemental analysis described in Sect. 2.2 and reported in Table 2. The $\%C_{fuel}$ values were 53.3 % for *Calluna* and 53.2 % for *Genista*."

- Line 161: How can the particle overlapping be avoided by estimating sampling periods? Please provide more detailed descriptions.

We agree that the original wording was not sufficiently clear. Particle overlapping was not completely avoided but minimized by limiting the SEM sampling duration in order to reduce filter loading and obtain a particle surface density suitable for single-particle observations. This approach is commonly used in individual-particle SEM/TEM analysis, where excessive filter loading can hinder the identification of particle morphology and composition. We have revised Sect. 2.4 to clarify this point.

"Sampling periods for SEM analysis were kept short and adjusted according to smoke-plume intensity to minimize filter overloading and particle overlap on the substrate, which is essential for reliable single-particle SEM/EDS analysis (Mamane et al., 2001)."

Mamane, Y., Willis, R., and Conner, T.: Evaluation of Computer-Controlled Scanning Electron Microscopy Applied to an Ambient Urban Aerosol Sample, Aerosol Science and Technology, 34, 97–107, https://doi.org/10.1080/02786820118842, 2001.

- Lines 184 - 185: How were the proportions 53.5% and 5936% obtained? Please provide detailed descriptions.

The values 53.5 % and 59.6 % correspond to the proportion of live biomass in the total fuel load for Genista and Calluna, respectively. These proportions were obtained from pre-fire fuel-load measurements, in which live and dead biomass fractions were separated and weighed. We have revised the manuscript to clarify how these values were obtained.

"The live/dead proportion in the fuel load was determined from pre-fire vegetation sampling by separating, drying, and weighing live and dead biomass fractions. The live fraction was calculated as the dry mass of live biomass divided by the total dry fuel mass. The resulting live biomass proportions were 53.5 % for *Genista* and 59.6 % for *Calluna*."

- Line 187: The numbers 90 and 90.6 are suggested to be replaced with 90% and 90.6%.

We have corrected these values and now report MCE consistently as a percentage throughout the manuscript, including the values 90 %, 90.6 %, and 70.8 %.

"iii) Combustion efficiency was evaluated by calculating the MCE (Sect. 2.3). In the prescribed fires on the *Calluna* plots, the MCE was higher than 90 % (90.6 %), indicating that more than 50 % of the emissions were produced by flaming combustion. On the other hand, in the *Genista* plots, the MCE was lower than 90 % (70.8 %)"

- Lines 191 - 192: Is there a way to quantitatively estimate the amount and effect of litter and mulch? If so, please provide relevant descriptions. If not, how can this statement be convincing with academic rigor? Please make revisions accordingly.

We agree that the effect of litter and mulch cannot be quantitatively assessed because their loads were not measured separately during the field campaign. Therefore, we have revised the statement to avoid overinterpretation. In the revised manuscript, litter and mulch are mentioned only as a possible qualitative factor that may have contributed to the lower MCE observed for *Genista*, together with fuel structure and combustion conditions.

“Differences in combustion efficiency may be related to variations in fuel humidity and fuel packing, given that it has been argued that MCE increases with decreasing biofuel packing (Soares Neto et al., 2009). The lower MCE observed for *Genista* may also be partly associated with the presence of litter and mulch beneath the shrub layer, which may favour smouldering combustion. However, because litter and mulch loads were not quantified separately, this interpretation should be considered qualitative.”

- Lines 192 - 196: How can the residence time and the rate of spread be both higher at the same time?

We agree that the original wording could be clearer. Rate of spread and residence time describe different aspects of fire behaviour: the rate of spread refers to the horizontal advance of the fire front, whereas residence time refers to the duration for which temperatures remained above 300 °C at a given location. Therefore, both parameters can be higher simultaneously when combustion is more intense and the heated zone associated with the fire front is broader or persists longer. We have revised the manuscript to clarify this point.

“Fires on the *Genista* plots were characterised by a rate of spread of 0.40 m min^{-1}, a mean maximum temperature of 454 °C at ground level and a residence time of 23.7 s, defined as the period where temperatures exceeded 300 °C (Wotton et al., 2012). *Calluna* burning was the most intense, presenting higher values of mean rate of spread (4.23 m min^{-1}), mean maximum temperature (809 °C) and residence time (103.3 s). Rate of spread and residence time describe different aspects of fire behaviour: the former represents the horizontal advance of the fire front, whereas the latter represents the duration of heating above 300 °C at the measurement point. Thus, a faster-spreading fire may also show a longer residence time when the flaming zone is broader or combustion is more intense”

- Line 207: Is the “subtracted from” meant to be “subtracted by” or not? Please double check.

The intended meaning was that background concentrations were subtracted from the concentrations measured in the smoke plume. To avoid ambiguity, we have revised the sentence accordingly.

“Net concentrations (concentrations measured in the smoke plume minus the corresponding background concentration) of gases obtained through high-resolution Fourier transform infrared (FTIR) analysis of combustion products collected from *Calluna* and *Genista* burnings are shown in Table 3.”

- Lines 287 - 289: Does this statement mean that 0.104 is higher than 3.4, and that 0.241 is higher than 4.2? If not, please revise the statement to improve clarity and readability. Make sure to provide descriptions on how to determine if the K+/EC values are considered high or not.

The original statement did not intend to compare K^+/EC directly with Cl^-/EC. To improve clarity and avoid an unsupported interpretation of the K^+/EC values as “high”, we have revised the sentence. In the revised version, we simply state the Cl^-/EC and K^+/EC ratios separately and interpret the presence of K^+ relative to EC as evidence of biomass-burning influence, since water-soluble potassium is widely used as a biomass-burning tracer.

“The Cl^-/EC ratios were 3.4 ± 2.0 for *Genista* and 4.2 ± 2.1 for *Calluna*, while the K^+/EC ratios were 0.104 ± 0.071 and 0.241 ± 0.045, respectively. The presence of K^+ relative to EC supports the influence of biomass combustion, as water-soluble potassium is widely used as a tracer of biomass-burning aerosol (Andreae, 2019; Yu et al., 2018). Together with the observed Cl^- levels, this suggests the possible presence of potassium-containing salts such as KCl internally mixed with carbonaceous particles. These species may act as cloud condensation nuclei (CCN), contributing to regional indirect radiative forcing in Mediterranean regions (Alves et

al., 2010a; Petters et al., 2009)."

- Line 346: The 90.6 and 70.8 are suggested to be replaced with 90.6% and 70.8%.

We have corrected these values and now express MCE consistently as a percentage throughout the manuscript, including the values 90.6 % and 70.8 %.

- Line 365: The word "though" seems to be a typographical error of "through".

The word "though" has been corrected to "through" in the revised manuscript.

Blanco-Alegre et al. reported particulate and gaseous emissions from prescribed fires in two Mediterranean shrubland ecosystems. Through chemical and morphological analyses, they established a link between the fuel characteristics and the emissions. The emission factors of various organic and inorganic species reported will be useful for future assessment of the air quality impacts of prescribed fires in the Mediterranean region. However, in its current form, I feel the manuscript's novelty is mainly about reporting emission factors from these two fuels. It appears better suited for publication as a measurement report rather than a full research article. The authors should try to highlight the novelty of this work beyond reporting emission factors. I also recommend more analysis and discussion on its implication on air quality/fire management policy.

We thank the reviewer for this helpful comment. We have revised the manuscript to better highlight the novelty of the work beyond simply reporting emission factors. We now emphasize the link between fuel characteristics, combustion conditions, and the chemical and morphological properties of the emissions.

We have also expanded the discussion on the implications of our results for air quality assessment, emission inventories, and prescribed-fire management in Mediterranean ecosystems.

Another critical issue is, the authors refer to several tables in the text, including Tables 1-3, but I am not able to find these tables in the submitted manuscript. They should be provided.

We apologize for this oversight. Due to an error during manuscript preparation, Tables 1–3 were not included in the submitted version. These tables have now been added and are available in the revised manuscript.

Specific comments:

Line 101-106: The description about sampling is too brief. More details should be included. For example, what is the sampling duration and flow rate for each filter sample? Where were the filter/bag collection instruments placed? Do they belong to the airborne instruments mentioned at Line 105?

We have revised Sect. 2.1 to include additional details on the sampling duration, flow rate, and positioning of the filter and gas-sampling systems.

"i) a low volume TECORA ECHOPM sampler operated at a flow rate of 38.3 L min^{-1} to collect $PM_{2.5}$ onto quartz filters; *ii*) TEDLAR bags to sample smoke for further analysis; iii) CO and CO_2 Combo IAQ Meter; and iv) a weather station Geos N11 to record meteorological variables at 1.85 m above the ground, at 10 s intervals; *v*) an infrared camera type Flir Systems to obtain the characteristics of the fires (mean rate of spread, mean temperatures and residence time). The sampling duration for each $PM_{2.5}$ filter was adjusted to the duration of the smoke plume generated by each prescribed fire and ranged from 6 to 15 min. Four $PM_{2.5}$ filter samples were collected during *Genista* burning and two during *Calluna* burning. Smoke samples for gaseous analysis were collected in TEDLAR bags during the active combustion period, avoiding the entrainment of background air as far as possible. The $PM_{2.5}$ sampler, TEDLAR bag sampling system, CO/CO_2 monitor, meteorological station, and infrared camera were positioned at ground level approximately 10 m downwind of the fire front."

Line 130-131: Gas phase emissions were sampled into Tedlar bags for analyses. Although the analyses were made a few hours after sampling, I am still concerned whether a substantial amount of NH3 and methanol could have been adsorbed by the surface of the bags. Please check literature or perform QA/QC experiments to provide more quantitative description. Also, this paper talks about the emissions of HF and HCHO, but the measurement methods are not provided.

We have revised Sect. 2.2 to clarify that HF and HCHO were measured using the same Gasmet™ DX-4000 FTIR multicomponent analyser as the other gas-phase species. We have also expanded the discussion of potential storage losses in TEDLAR bags. Specifically, we now state that adsorption onto the bag walls, diffusion through the polymer film, or chemical transformation during storage may affect reactive, soluble, or polar compounds such as NH_3 and methanol. Since no compound-specific storage-stability QA/QC experiment was performed during the campaign, the concentrations

of NH_3, methanol, and other highly reactive or polar compounds are now explicitly interpreted as conservative lower-limit estimates. References on sampling-bag stability have also been added.

"iv) Major gaseous components in the smoke samples were obtained from samples collected in TEDLAR bags, previously flushed with N_2. To avoid secondary reactions, the samples were protected from UV radiation and analysed within a few hours after sampling. Gas-phase species were quantified using a Gasmet™ DX-4000 multicomponent analyser equipped with a high-resolution Fourier transform infrared (FTIR) spectrometer. The FTIR method identifies and quantifies gases from their compound-specific infrared absorption spectra, allowing simultaneous multi-compound analysis. The analysed species included CO_2, CO, N_2O, NO, NO_2, SO_2, NH_3, CH_4, ethane (C_2H_6), propene (C_3H_6), acetylene (C_2H_2) and methanol (CH_3OH), hydrogen chloride (HCl), hydrogen fluoride (HF), and formaldehyde (CH_2O). A detailed description of the preparation of the TEDLAR bags before and after sampling and of the instrumentation procedure can be found in Alves et al. (2010b).

It should be noted that the measured concentrations may be underestimates of atmospheric concentrations, since adsorption onto the bag walls, diffusion through the polymer film, or chemical transformation during storage may have occurred. These effects are particularly relevant for reactive, soluble, or polar compounds such as NH_3 and oxygenated VOCs such as methanol, whose stability in polymer sampling bags can be affected by storage time, humidity, concentration, and bag material (Szyłak-Szydłowski, 2015). In addition, some compounds such as SO_2, NH_3, and CH_4 may have been trapped in the air sampling system. Therefore, the concentrations of NH_3, methanol, and other highly reactive or polar compounds reported here should be interpreted as conservative lower-limit estimates."

Szyłak-Szydłowski, M.: Odour Samples Degradation During Detention in Tedlar® Bags, Water Air Soil Pollut., 226, 227, https://doi.org/10.1007/s11270-015-2495-2, 2015.

Line 265 (Figure 2): Since the manuscript focuses on emissions from prescribed fires, it would be helpful to include emission factors from wildfires in the same or closely related Mediterranean shrubland ecosystems. The author should also clarify whether the reference emission factors for savannas/grasslands and temperate forests in Figure 2 are derived from prescribed fires, wildfires, laboratory burns, or a mixture of fire types.

We have revised Figure 2 to include emission factors from Mediterranean shrubland wildfires reported by García-Hurtado et al. (2013), which provide a more regionally relevant comparison for the prescribed fires analysed in this study. We have also expanded the discussion to compare our measured values with those reported by them. In addition, the caption of Figure 2 has been revised to clarify that the savanna/grassland and temperate forest values from Andreae (2019) are literature-average emission factors compiled from multiple biomass-burning studies and therefore represent a mixture of fire types and measurement conditions, including field and laboratory burns.

"A more regionally specific comparison is provided by the experimental Mediterranean shrubland wildfires reported by Garcia-Hurtado et al. (2013), who obtained emission factors of 1257 ± 40 g kg^{-1} for CO_2, 453 ± 28 g kg^{-1} for CO, 46 ± 12 g kg^{-1} for CH_4, 3.4 ± 1.39 g kg^{-1} for $PM_{2.5}$, 1.4 ± 0.34 g kg^{-1} for OC, and 0.051 ± 0.028 g kg^{-1} for EC. Compared with those values, $EFCO_2$ in the present study was higher for Calluna (1700 g kg^{-1}) and lower for Genista (592 g kg^{-1}), which is consistent with the different combustion efficiencies observed for the two fuels. In contrast, EFCO and $EFCH_4$ were substantially lower in both prescribed fires than in Garcia-Hurtado et al. (2013), consistent with the strong smouldering contribution reported in their experiments. Conversely, $EFPM_{2.5}$, EFOC, and EFEC were markedly higher in the present study, particularly for $PM_{2.5}$ and EC. These differences highlight the influence of fuel type, combustion phase, fire behaviour, and sampling strategy on emission factors, even within Mediterranean shrubland ecosystems.

Garcia-Hurtado, E., Pey, J., Baeza, M. J., Carrara, A., Llovet, J., Querol, X., Alastuey, A., and Vallejo, V. R.: Carbon emissions in Mediterranean shrubland wildfires: An experimental approach, Atmos. Environ., 69, 86–93, https://doi.org/10.1016/j.atmosenv.2012.11.063, 2013.

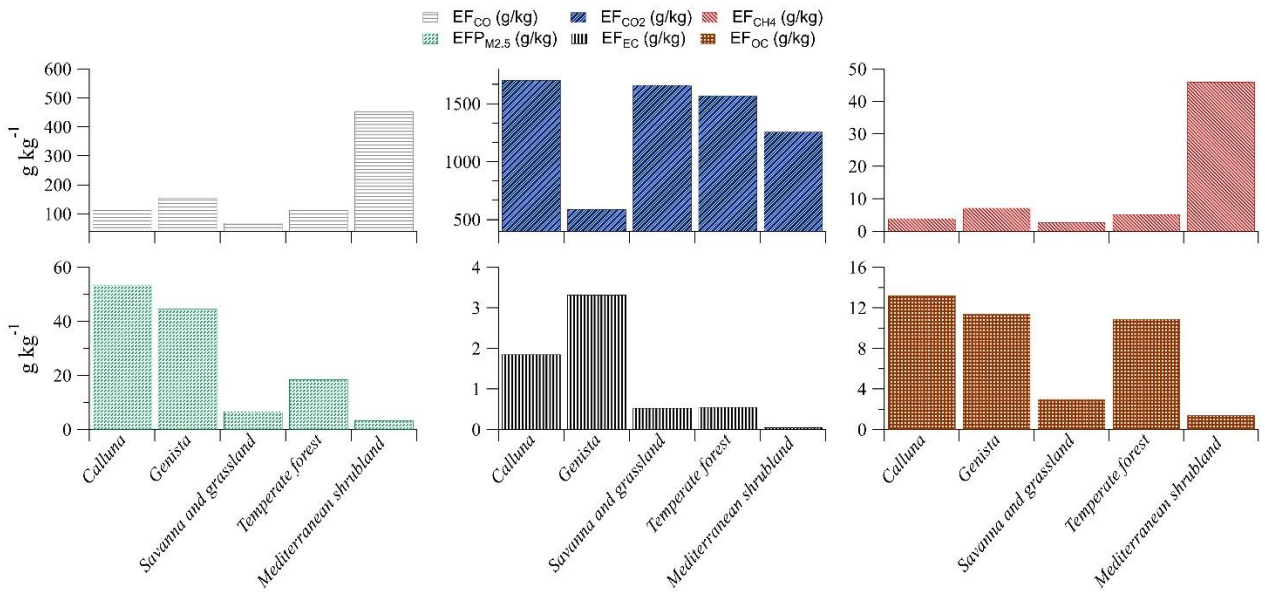

Figure 2. Comparison of emission factors (EF) for CO, CO_2, CH_4, $PM_{2.5}$, organic carbon (OC) and elemental carbon (EC) during Calluna and *Genista* prescribed fires with Mediterranean shrubland wildfire values from Garcia-Hurtado et al. (2013) and literature-average values for savannas/grasslands and temperate forests from (Andreae, 2019). The Andreae (2019) values are compiled averages from multiple biomass-burning studies and represent a mixture of fire types and measurement conditions, including field and laboratory burns."

Minor comments:

Line 18 and Lines 141-145: Please use consistent units for MCE throughout the manuscript. In some places, MCE is reported as a percentage, whereas in others it is reported as a dimensionless value. Please standardize the format.

We have corrected the MCE notation throughout the manuscript so that it is consistently expressed as a percentage.

- Line 53-55: Please give a citation for this statement. Organic Carbon, especially biomass burning OC also contains BrC which can absorb solar radiation as well. Are there papers about the net radiative effect of OC?

We agree that the original statement was oversimplified. Organic carbon generally contributes to light scattering, but biomass-burning organic aerosol may contain brown carbon (BrC), which absorbs solar radiation, particularly at near-UV and short visible wavelengths. We have revised the sentence accordingly and added references addressing the radiative effects of light-absorbing organic carbon and the net direct radiative effect of carbonaceous aerosols from biomass burning.

"Combustion produces large amounts of carbonaceous material in the atmosphere, especially elemental carbon (EC) and organic carbon (OC), which alter the Earth's radiative balance (Bond et al., 2013). EC is an important absorber of solar radiation, playing an important role in climate change, while OC primarily scatters solar radiation opposing the heating effect of EC. However, biomass-burning OC can contain light-absorbing brown carbon (BrC), which absorbs radiation mainly at near-UV and short visible wavelengths and can partly offset the cooling effect of scattering organic aerosol (Saleh et al., 2015)."

Saleh, R., Marks, M., Heo, J., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions, Journal of Geophysical Research: Atmospheres, 120, https://doi.org/10.1002/2015JD023697, 2015.

- Line 78-79: This sentence is hard to understand. What does “heatlands” mean?

The term “heatlands” was a typographical error and has been corrected to “heathlands”. We have also revised the sentence to improve clarity.

“European heathlands dominated by the ericaceous shrub Calluna vulgaris are ecosystems of high ecological, cultural, and carbon-storage value (Fagúndez, 2013), but they are also affected by both wildfires and prescribed fires (Grau-Andrés et al., 2019; McMorrow, 2011)”

- Line 154: Are these fuel carbon fraction values measured or from literature?

These fuel carbon fraction values were measured, not taken from the literature. They correspond to the carbon mass fraction of the dry fuel for *Calluna* and *Genista*, respectively, obtained from the elemental analysis described in Sect. 2.2 and reported in Table 2. This has now been clarified in the revised manuscript.

“The carbon mass fraction of the dry fuel used in Eq. (2) was obtained from the elemental analysis described in Sect. 2.2 and reported in Table 2. The $\%C_{fuel}$values were 53.3 % for *Calluna* and 53.2 % for *Genista*.”

- Line 300 (Figure 3): Subscript for nitrate ion

The ion labels in Figure 3 have been corrected to include the appropriate subscripts and superscripts, including NO_3^-.