

CO emissions and NO_x/CO ratios from the extreme 2025 Iberian wildfires: TROPOMI-based estimates and comparison with inventories

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1.1 TROPOMI-derived uncertainties

1.1.1 Integrated mass enhancement and mole density ratio

TROPOMI uncertainties are computed using the propagation errors from Eq. (2) and read as follows

$$\Delta E = \left| \frac{IME}{L} \right| \Delta u + \left| \frac{u}{L} \right| \Delta IME + \left| \frac{u \cdot IME}{L^2} \right| \Delta L , \quad (S1)$$

where $IME = M_m \sum_i \Delta VCD_i A_i$ and ΔIME is its standard deviation. Δu is the wind speed standard deviation. As discussed in Sec. 4.1.3, the wind speed is obtained averaging within the hours of the time of the overpass and in altitude up to the **PBL**. The uncertainties are mainly driven by the wind speed standard deviation. Approximately, it is found that this factor corresponds to 80% of the error.

Uncertainties for NO₂/CO mole density ratios (MDRs) defined in Eq. (5) are computed using the vertical column density precision provided by L2 TROPOMI. Similarly to Eq. (5), MDR uncertainties are defined as follow

$$\Delta MDR = \frac{\overline{VCD}_{prec,NO_2}}{\overline{VCD}_{prec,CO}} \cdot 10^3 , \quad (S2)$$

where $\overline{VCD}_{prec,gas}$ is the TROPOMI precision variable of the specific gas averaged over the plume pixels.

1.1.2 Quality assurance pixel value

Following the work of Griffin et al., 2021, 2024, in this study we used a quality flag of TROPOMI data of $qa = 0.5$. This quantity corresponds to the quality assurance provided by L2 TROPOMI. In extreme wildfire scene we noted that pixels close to the hotspot or even the pixels containing the hotspot were discarded by this filter. Since wildfires could spread over several

square kilometres, some pixels could be discarded due to changes in the albedo coming from the burned area and/or the flames and the dense particles emitted by the fire. We tested the algorithm for $qa > 0$ to quantify this feature and the results are presented in Fig. S1. We find that the qa value does not seem to affect the emission rates retrieved. However, we still noted that some pixels were discarded even after relaxing the qa value. These pixels then are classified as errors by the L2 TROPOMI retrieval. **These errors could be result in data loss.**

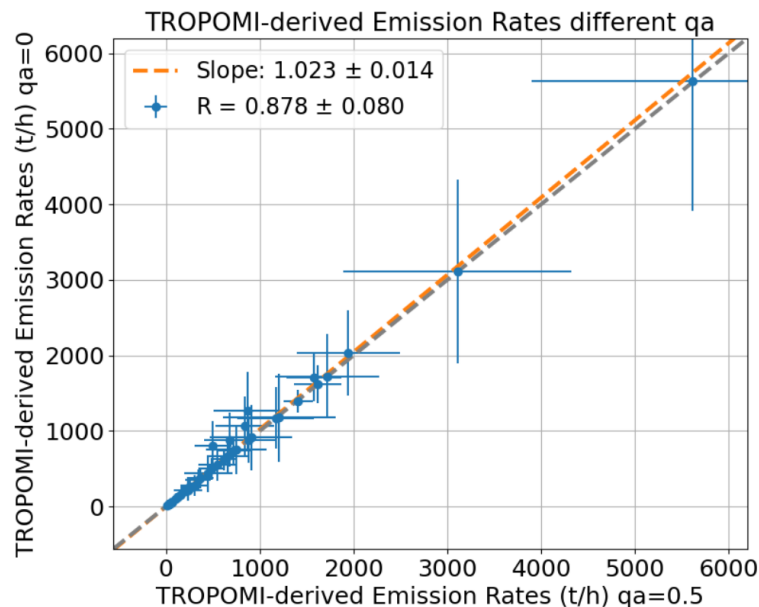


Figure S1: TROPOMI-derived emission rates for quality assurance flag values of $qa=0$ (y-axis) and $qa=0.5$ (x-axis). The grey dashed line shows the 1:1 correspondence, and the orange dashed line represents the linear trend.

1.1.3 Other background subtraction approaches

We also explored a different background subtraction method to test the performance of the chosen one (Sec. 4.1.1). In this case, the monthly average VCD CO was computed for the region of interest within the month before the fire season started.

We compute the average VCDs for the whole region, a value of VCDs = 0.027 mol/m² was found. Figure S2 shows the CO regional average evolution within the months of July and August of 2025. The region boundaries used are latitude = 38.0 °, 44.0° and longitude = -9.0 °, -3.0°.

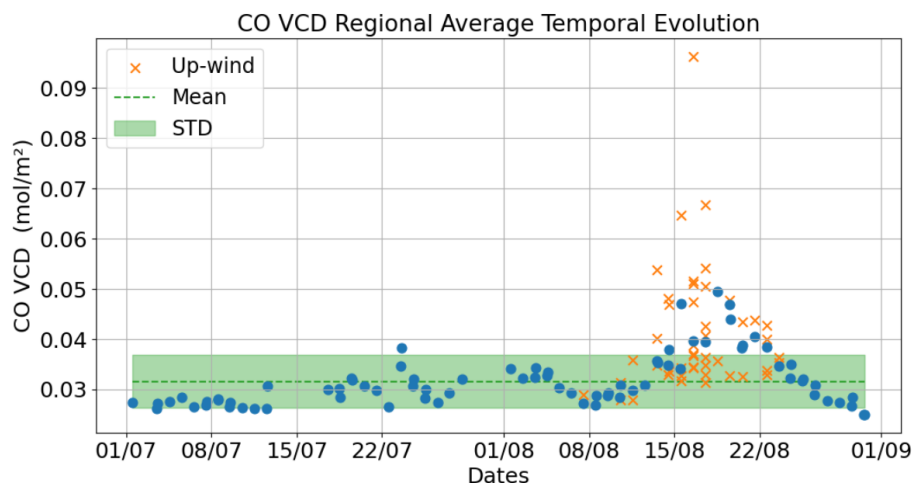


Figure S2: CO regional average temporal evolution in mol/m². Crosses correspond to up-wind background for each scene studied in this work. Green dashed line represents the average value within the months of July and August 2025 and green shadows represents its standard deviation.

On one hand, since the fire season was complex the entire background was modified increasing its normal value. We compare the emission rates computed with TROPOMI subtracting this constant value against the subtracting the up-wind background method used in this work (Sec. 4.1.1). The results found are shown in Fig. S3. We find an increase of around 38% in the emission rates estimated **with fixed** background, likely due to the CO double counting from near hotspot.

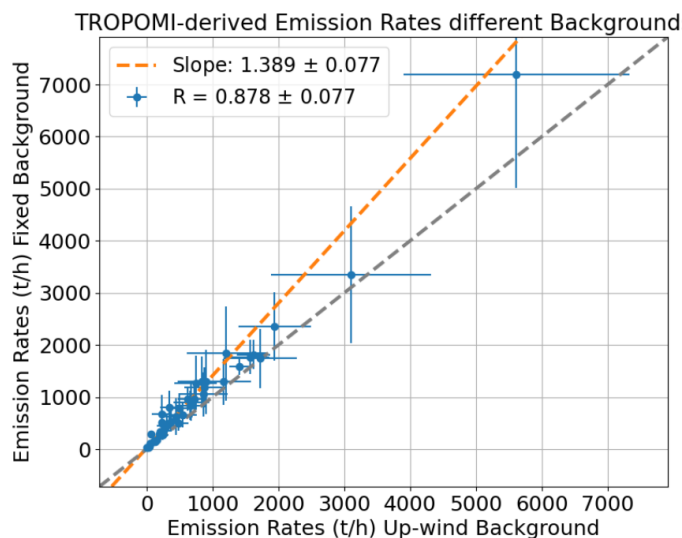


Figure S3: TROPOMI-derived emission rates for up-wind background (x-axis) and fixed background 0.027 mol/m² (y-axis). The grey dashed line shows the 1:1 correspondence, and the orange dashed line represents the linear trend.

1.1.4 Other sources of uncertainties

Here we describe qualitatively other possible sources of uncertainties in TROPOMI-based estimates.

Since wildfires can spread over several square kilometres, it can be complex to consider a specific hotspot. Moreover, due to the temporal evolution of a wildfire, this hotspot location could evolve as well. The evolution of the burned area, and therefore the consideration of the hotspot, could be taken into account in two different aspects. As discussed in Sec. 4.1.3, the IME method uses the plume pixels and the wind speed. On one hand, the distance of the plume pixels with the hotspot location could affect the plume area variable in Eq. (2). Although, given its lifetime, for CO we believe this uncertainty does not have an important effect. However, this consideration could be highlighted when NO₂ emission rates are computed when the distance from the hotspot is used as variable in Eq. (2) (Griffin et al., 2021). On the other hand, uncertainties on the hotspot location could result in uncertainties on the wind speed selection. As discussed in Sec. 3.3.1, we used the nearest wind field from ERA5 to the hotspot. Evolution on the burned area and hotspot location could change the ERA5 coordinate selection and therefore the wind speed used in Eq. (2). Since ERA5 has a spatial resolution of 0.25°, corresponding to roughly 25 km in this region, wind speed can vary substantially between adjacent ERA5 grid points due to e.g. orographic effects.

1.2 Plume masking methods

1.2.1 Threshold method

This standard plume masking method is based on selecting the plume as those pixels which represent an anomaly respect to a specific background (Finch et al., 2022; Lauvaux et al., 2022; Schuit et al., 2023). As discussed in Sec. 4.1.2, this method is used only for NO₂, with the intention of later applying it to CO to the synergy plume masking method. Aiming at assessing this synergy method, we applied threshold method to CO in simple scenes, shown in Sec. 1.3 of this Supplementary information.

We select the background by fixing the region around the point of interest within $\pm 1.5^\circ$ or roughly ± 150 km. An anomaly from the background is considered when the value of a TROPOMI pixel is larger than a fixed threshold value (t). This is computed according to

$$t = \Delta VCD_{mean} + n \cdot \Delta VCD_{std} , \quad (S3)$$

where ΔVCD_{mean} and ΔVCD_{std} correspond to the mean and standard deviation of the column of the background region once the background is subtracted (Eq. 1). For NO₂ the threshold plume masking the parameter n in Eq. (S3) is set in the range of $n = 3.5 - 5.5$, although larger values can be set for specific scenarios. Previous studies used lower values (Huang and Wang, 2026). We chose stricter values due to the complexity of the scenes investigated. A specific value within the range mentioned is selected for each case addressing the complexity and coherence of each plume.

Although this standard threshold method worked well for a few of the scenes analysed in this work, depending also on the wind conditions, its performance was limited in cases where several fires co-existed nearby within the same scene. In these cases, the plume assigned to a given hotspot by this standard method, could include mixed contributions from neighbouring fires. Thus, we suggest a stricter plume masking method called “synergy method”.

1.2.2 Assessment of synergy plume masking method

As mention in Sec. 4.1.2, in this study a two-step plume masking synergy method was introduced in order to facilitate the identification of individual plumes in our top-down approach. The CO emission rates retrieved with the synergy and with the standard threshold plume masking method defined above under simple scenes are quite similar in magnitude and variability as shown in Fig. S4.

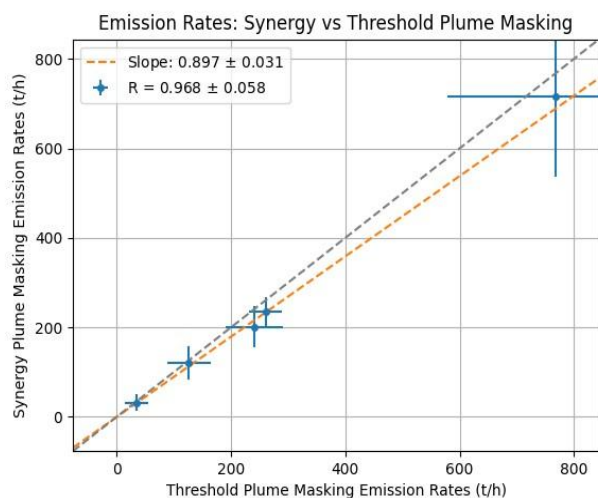


Figure S4: Correlation study of the CO TROPOMI-derived emission rates between both plume masking methods used in this work: synergy and threshold. In this plot, only clear and simple fire scenarios are considered. The overpasses used for this plot are shown in Fig. S7.

In such simple scenes, the wind and fire conditions make easy to isolate the plume investigated hotspot regardless the plume masking method. The simple scenes considered in Fig. S4 are shown in Fig. S7, with the two-step plume masking synergy method for the overpasses for point of interests #1, #5 and #9. This comparison suggests that, at least, for simple scenes, both methods provide similar results. The correlation found is consistent with a relevant $R \sim 0.97$, with the synergy method yielding lower CO emission rate values (10%).

Another source of uncertainty relates to the chemical differences of NO₂ and CO within a fire plume. Due to the different chemical lifetimes of CO (weeks to months; Novelli et al., 1998) and NO₂ (4-8h; Beirle et al., 2011), the NO₂ plume and the

CO plume might not be identical. NO₂ it **is expected closer** to the hotspot and CO could be transported further from the source as shown in Figs. 3 and 4. Also, since NO₂ is a reactive tracer (Krol et al., 2024), its plume may **have different** shape than CO's plume. Thus, with this masking method we might be missing pixels older or more smoldering parts of the plume for the CO emission estimations. In order to assess the effects of this limitation, we investigated the effect on CO emission rates depending on the chosen distance from the source fire (i.e., selected plume area). We applied the threshold plume masking method to CO with a distance threshold. We slightly modified the threshold plume masking method to be limited up to a specific distance from the source and studied the emission rates as a function of this distance variable. ~~Similar procedure has been done in~~ Griffin et al., 2024 finding similar results. We chose a simple scenario located at #1, where the synergy and threshold approach provided similar emission rates (Fig. S4). The results found are shown in Fig. S5, where it is found that the emission estimates retrieved using the threshold approach seems to reach a plateau **once we get far away of the source**.. In Fig. S5 the estimated emission (and uncertainty) using the synergy approach is shown as a grey block, indicating that the synergy method is consistent with the threshold approach if the plume masked is large enough.

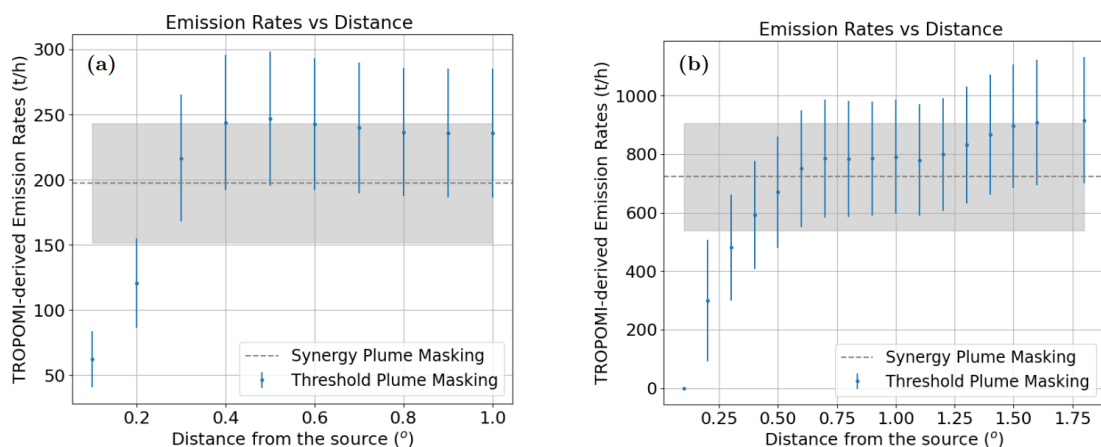


Figure S5: Threshold plume masking method applied to compute emission rates (t/h) as a function of the distance from the source at #1 (a) day 16th, (b) day 17th. In both panels the synergy plume masking method is also shown as a grey block.

As discussed previously, the synergy plume **might provide slightly smaller** than the threshold plume. As Fig. S5 proved, this fact does not seem to influence the emission estimates as long as the synergy plume reaches a distance similar where the threshold reaches the stability. In the investigated cases, this stability is reached around a distance between 0.4 - 0.6°. For this region, this distance corresponds approximately to 60km away from the hotspot, a similar ~~value is found~~ **in** Griffin et al., 2024. In Fig. S9 we show the threshold plume masking as a function of distance applied at #1 on 17th August 2025 used to compute Fig. S5b.

Furthermore, due to the differences of the chemical lifetimes, for complex scenarios, with varying wind fields and final stages

of the fire (when it is expected the NO_2 to be emitted in less quantity), the NO_2 density is spread over an extended area causing the synergy method to break down. Only one example was found in this work and is shown in Fig. S6

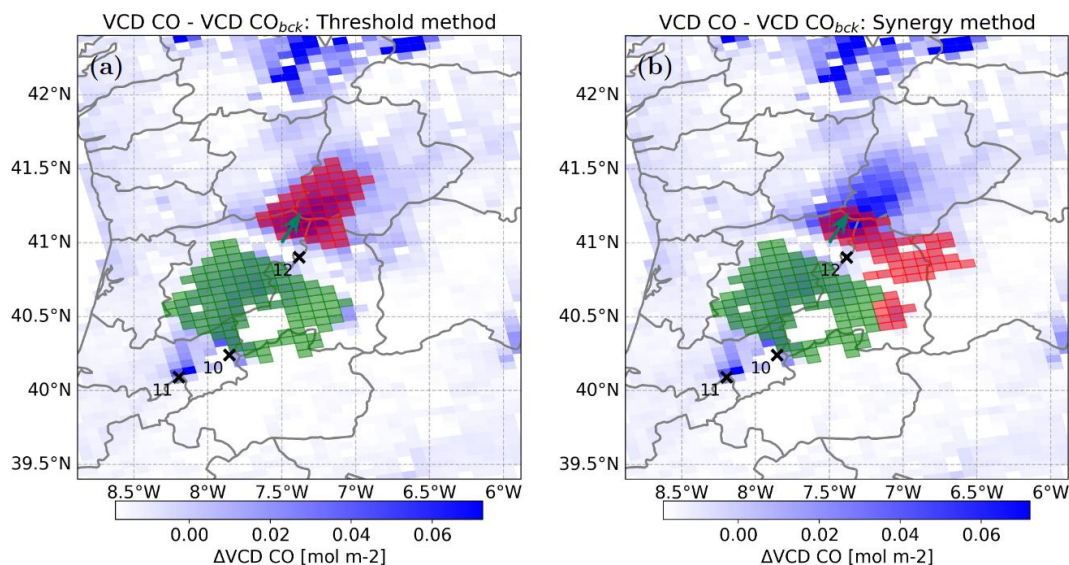


Figure S6: Representative failure of the synergy method. CO TROPOMI background corrected overpasses on 16th August 2025. (a) CO Threshold plume masking method applied at point of interest #12. (b) CO synergy plume masking method applied at point of interest #12.

1.3 Supplementary figures

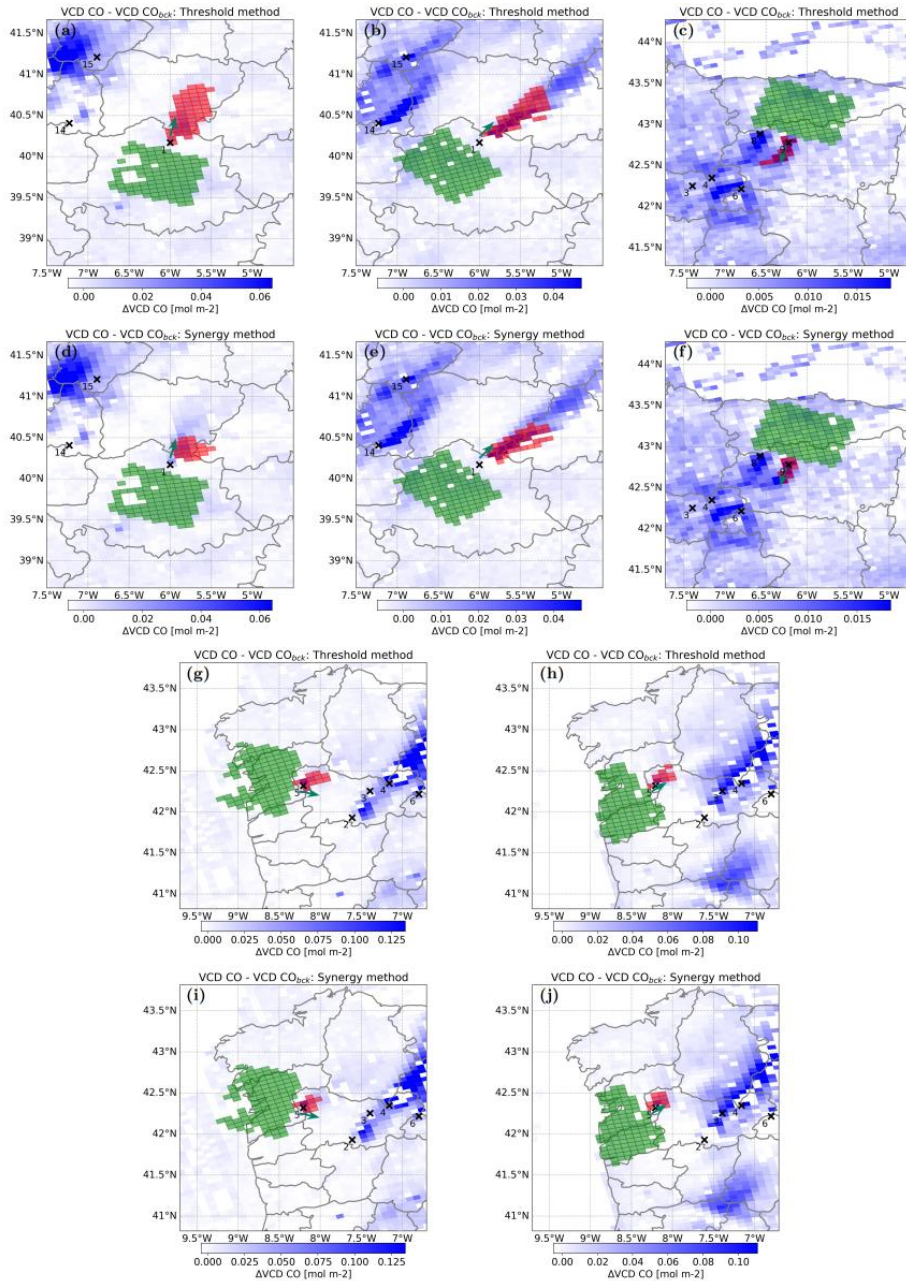


Figure S7: Threshold vs synergy plume masking for easy scenes. (a) and (b) threshold approach and (d) and (e) synergy approach applied at #1 on 16th and 17th respectively. (c) threshold approach and (f) synergy approach applied at #9 on 22th. (g) and (h) threshold approach and (i) and (j) synergy approach applied at #5 on 16th and 17th respectively.

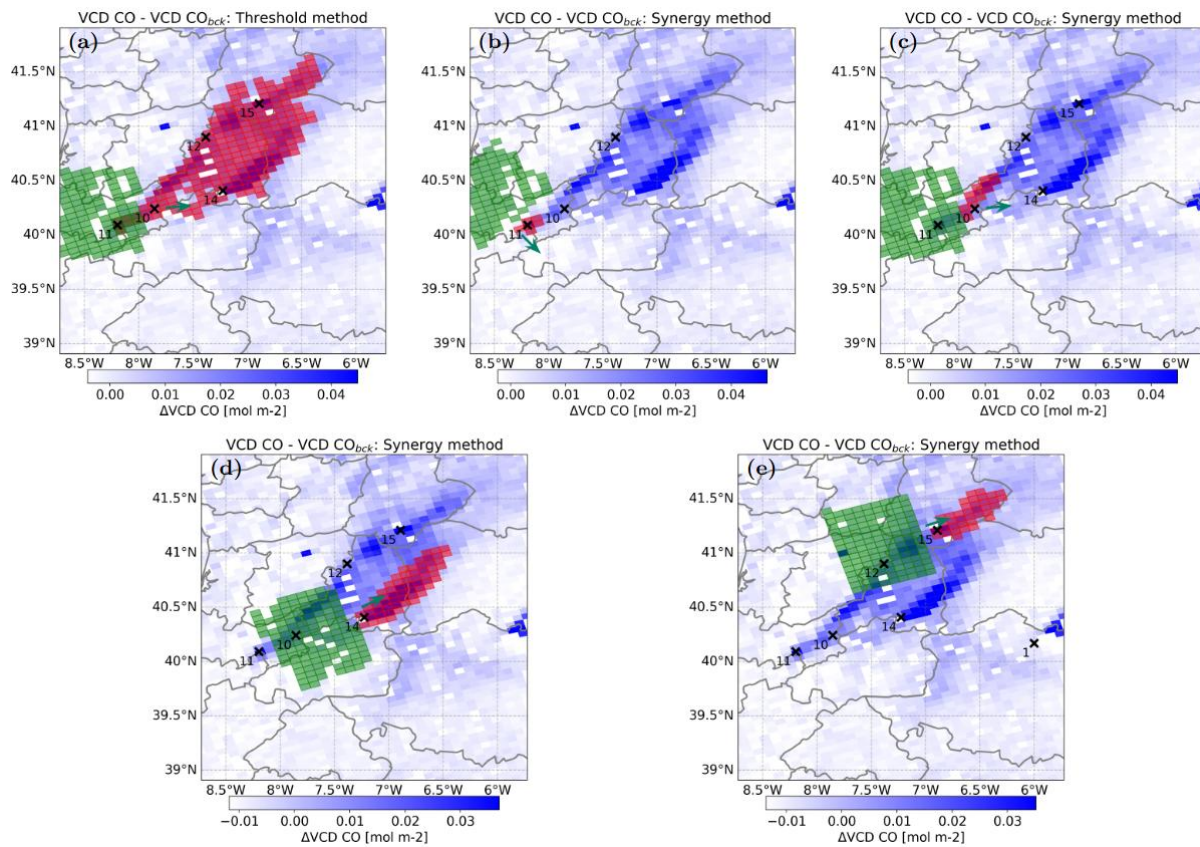


Figure S8: Representative CO TROPOMI background corrected overpasses on 17th August 2025. (a) CO Threshold plume masking method applied at point of interest #10. The rest of the panels correspond with synergy plume masking applied at the point of interest (b) #11. (c) #10. (d) #14. (e) #15.

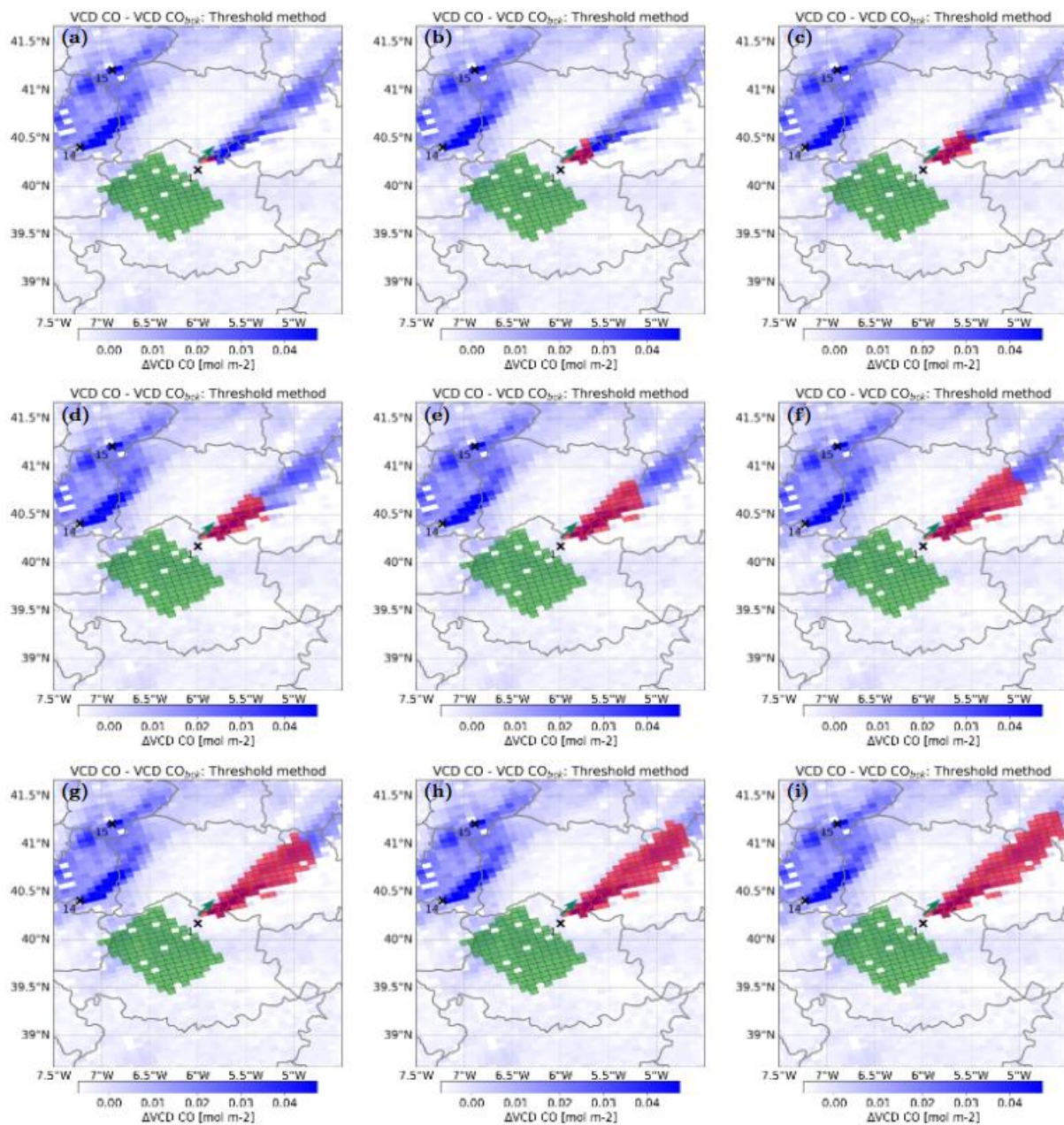


Figure S9: Threshold plume masking method applied at #1 on 17th with different distance threshold (a) 0.2° (b) 0.4° (c) 0.6° (d) 0.8° (e) 1.0° (f) 1.2° (g) 1.4° (h) 1.6° (i) 1.8°.

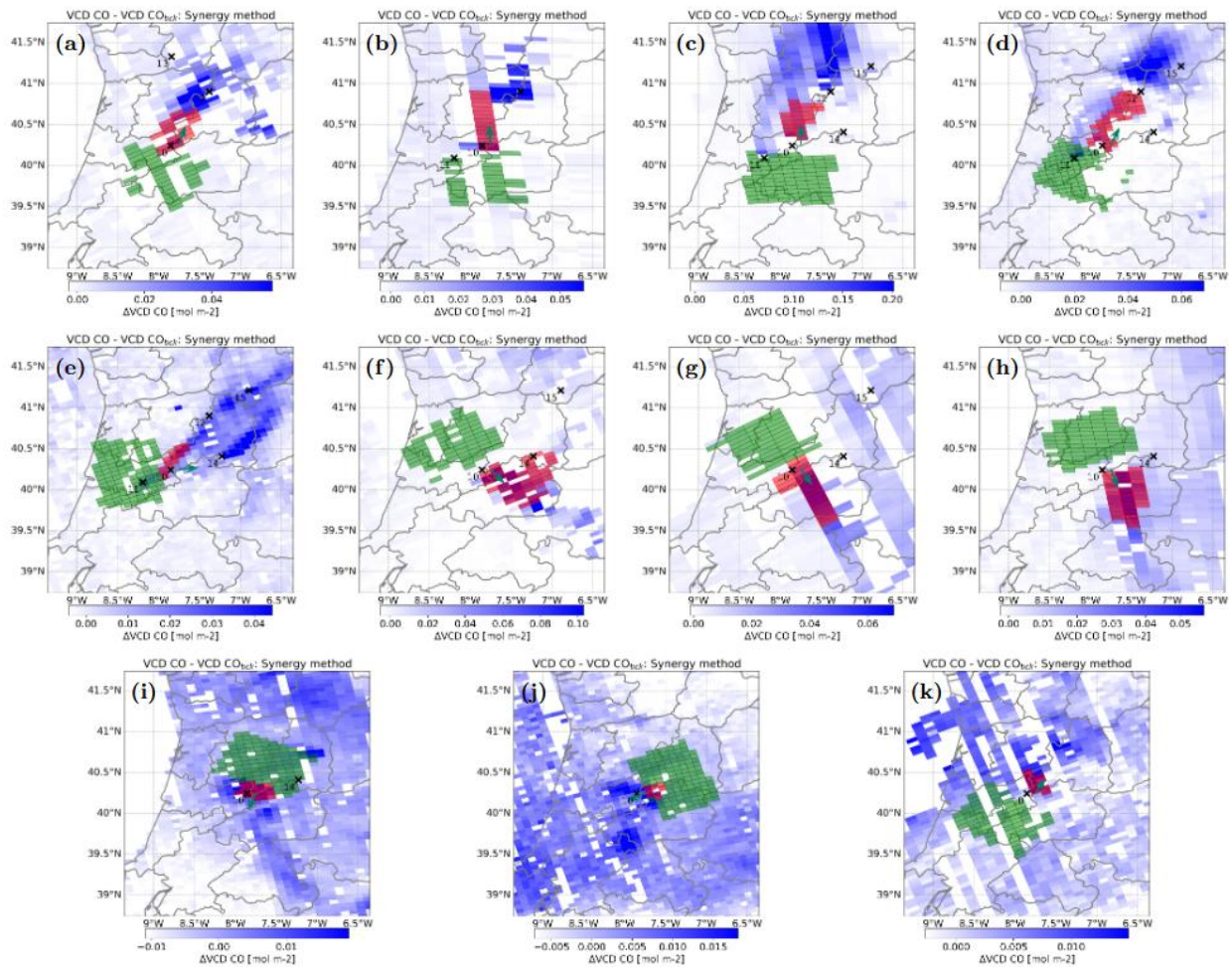


Figure S10: Synergy plume evolution associated to #10 wildfire. Each panel correspond with 1 day from 13th (a) to 23th (k) August 2025.

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