Reply to Reviewer 1

This manuscript show the capabilities of NO2 satellite retrievals from the TROPOspheric Monitoring Instrument from wildfire smoke plumes. An exponentially modified Gaussian (EMG) approach, NO2 TROPOMI retrievals, MODIS FRP, aerosol layer heights from TROPOMI, and reanalysis data are used to estimate the fire emissions of NO2 and its lifetime in the smoke plumes from >3000 fires globally. Fire locations and intensity are derived using MODIS Fire Radiative Power (FRP). The authors used GEOS-CF to modify the NO2 a-priori profile to correct the low bias of NO2 retrievals over fire plumes. The authors made a detailed comparison of their results with previous references regarding biomass burning emissions. Finally, the authors found that there is an anticorrelation between fire size and NO2 lifetime, possibly attributed to the higher emissions of HOx in larger fires. The manuscript has detailed methods, has an in-depth discussion of uncertainties, results are interesting and presented in a clear way, and is well written. Therefore, I suggest publication after minor revisions.

Reply: We would like to thank the reviewer for their constructive feedback and time spent reviewing this paper. Below is our response to reviewer's comments.

Specific comments.

1. L66: looks like a good place to introduce PAN and organic nitrates?

Reply: Great suggestion.We now revise the sentence as follows:

Satellite instruments observe fire NO_x plumes as a mixture of fresh and aged smoke. NO_x is a short-lived species, and its concentration will decay in the plume due to the formation of nitric acid (HNO_3), peroxyacetyl nitrate (PAN) and organic nitrates ($RONO_2$).

2. L83 and elsewhere: It would be good to specify the local time of TROPOMI overpass. I am guessing that this influenced the choice of the NOx/NO2 ratio. I would like a little more discussion about how this ratio can change as time of the day. Is there any variation of it as the plume ages?

Reply: The overpass time of TROPOMI is around 1:30 PM local time. We have revised the sentence as follows:

TROPOMI provides afternoon (~ 1:30 PM local time) global observations in the UV−visible−near infrared−shortwave spectra with a fine spatial resolution of 7 × 3.5 km^2 at nadir (increased to 5.5 × 3.5 km^2 since August 2019).

We use a constant NO_x/NO_2 ratio of 1.32, which is in between the measured mean NO_x/NO_2 ratio of 1.50 reported in Akagi et al. (2012) and 1.24 in Juncosa Clahorrano et al. (2021). Juncosa Clahorrano et al. (2021) show the ratio the median NO_x/NO_2 varies little from fire centre to plume edge. Juncosa Clahorrano et al. (2021) show the ratio peaks at noon, and our

chosen ratio is indeed at the upper bound of their reported ratio. We discuss the choice of NO_x/NO_2 in the revised manuscript as follows:

γ is assumed to be 1.32, which is in between measured mean NO_x/NO_2 ratio of 1.50 reported in Akagi et al. (2012) and 1.24 in Juncosa Clahorrano et al. (2021). We assume a constant γ because O_3 and the photolysis rate of NO_2 varies little in the plume, and the time scale for NO and NO_2 to reach steady state is of order 100s (Alvarado and Prinn, 2009). Juncosa Clahorrano et al. (2021) shows the NO_x/NO_2 ranges from 1.15 to 1.50 near the fire centre before 3PM LST, but the median NO_x/NO_2 varies little from centre to plume edge. Mebust et al. (2011) suggest the uncertainty of NO_x/NO_2 is ~20%.

3. L153. I had a little bit of trouble understanding if the calculated lifetime included dilution. Reading the manuscript a second time, it was clearer. Is there a way that you can separate dilution from chemistry (i.e., using a NO2 normalized excess mixing ratio with respect to CO or CO2?). This might help you to further constrain or interpret your idealized plume model.

Reply: We use a Gaussian function in Eq. (7) to represent the smoothing in line densities due to dilution. The calculated lifetime should be representative of chemical lifetime if the transport speed is uniform, the direction is constant and deposition is negligible (De Foy et al., 2014). We have clarified this:

The effective lifetime should represent chemical lifetime of NO_x if the transport speed is uniform, the direction is constant and deposition is negligible (De Foy et al., 2014).

4. L175 Repeated comment but I would like to see more discussion about NOx/NO2 ratio as a function of the time of the day or distance from plume. References that might be helpful include Yokelson et al., 2009; Akagi et al 2011; Alvarado et al 2010; Juncosa Calahorrano 2021).

Reply: Please see our reply to Comment 2.

5. L195 Section 3.4 Did you used a plume specific NO2 background (i.e., for the background condition the day the plume was retrieved by TROPOMI)? For locations with fire seasons that last for months, background conditions can change because of the presence of dilute smoke in the area.

Reply: The background NO_2 is fire specific. We define background NO_2 as mean TROPOMI NO_2 columns 3 to 30 days before and after the fire. For locations with long fire season, the background NO_2 columns should be larger than non-fire season. We have clarified this definition of background as follows:

We then select fires where TROPOMI NO_2 tropospheric columns on the fire day are at least one standard deviation higher than the mean TROPOMI NO_2 columns 30 days before and after the fire day (excluding the nearest four days as fires may last for several days, defined as Ω_{NO2_B}).

We only use this threshold to select candidate fires, which will not influence on the calculation of emissions and lifetimes. For calculation of emissions and lifetime of fire plume, we fit the line density as Eq. (7), and parameter B here represents the background NO_2 line density, which is determined by NO_2 value over upwind regions.

6. L220. Please include more details on figure S1 e.g., rotation angle. Might be good to have a final figure after rotation as well.

Reply: We have added rotation angle to Figure S1 (now Figure S3). We'd like clarify the figure is indeed the final figure after rotation. We showed an example fire plume that does **not** meet our selection criteria, because the apparent direction does not align with the wind direction (*x* axis, i.e. rotation bias > 30˚). We have revised Figure S1 to show two plumes: one with small bias that satisfies the criterium, and the other with large bias that is not selected as candidate fire:

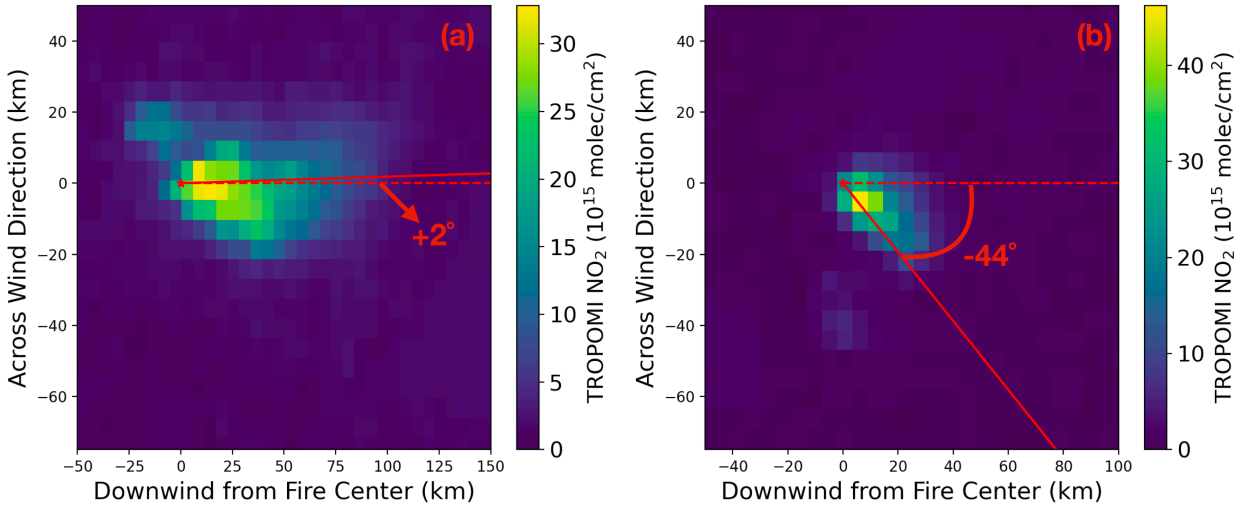

Figure S3 Illustration of two fire plumes with the absolute rotation biases (a) less and (b) greater than 30˚. We define the rotation biases as the angle of the two red lines. The right plume is not selected because it does not align with the wind direction (i.e., rotation bias = -44˚)

7. L221 Can you please explain how you differentiate between the fire center vs. the apparent fire center? Is the first based on the FRP and the latter based on visual inspection? Also, this line needs more detail. What do you mean by "give good fitting statistics"? What is the correlation that needs to satisfy R2>0.5?

Reply: Fire center is defined as where $x = 0$, and the apparent fire center is obtained from EMG function as μ_x. The first is based on FRP, and the latter is based on EMG function (Equation 7). Good fitting statistics refer to the three criteria listed after that: 1) $R^2 > 0.5$; 2) $\sigma_x < x_0$; 3) $|\mu_x| < 50$ km. R^2 is the Pearson correlation coefficient between fitted and the observed NO_2 line density.

8. Figure 1. I would have expected more tropical fires detected by TROPOMI. Did one of the criteria to remove plumes excluded those? Why? Also, it looks that there are not many fires in

the equatorial line in South America and Africa, which is odd. Can you explain please? Perhaps this is an issue with the satellite retrievals?

Reply: We have implemented strict criteria to select candidate fires suitable for EMG approach. The EMG approach works best for isolated point source with clear plume patterns. In tropical regions, fires often expand over a wide region, which is better considered as area source rather than point source. Satellite retrieval may also be affected by cloud and smoke. We only select satellite retrievals with good quality and low cloud fraction (Sect. 3.4).

9. L235 How did you identify Ag fires?

Reply: We classify the fire episodes based on the fuel classification in the Global Fire Emission Database (GFED), which is estimated using the MODIS land cover type product. Agricultural fires refer to fires occur over cropland.

10. L247 and Figure 1 Very nice section. I was just wondering why you didn't remove the small fire towards the upper left side of the bigger fire. I assumed your criteria will remove it because it is clearly overlapping with the bigger one. Please explain.

Reply: Our filtering algorithm can filter out fire plumes **not** overlapping with the center plume. The small fire shown in the figure overlaps with the center plume, so they are considered as a single plume. A supplementary figure is added to help explain the grouping procedure:

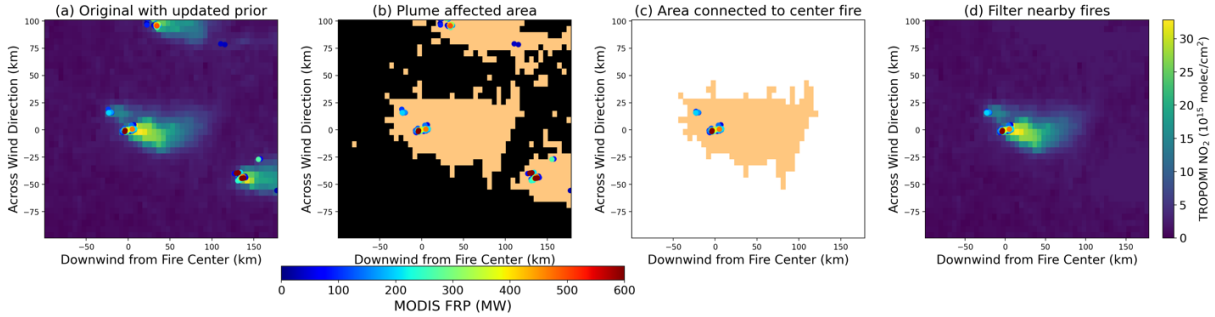

Figure S2 Illustration of the processes that identify and filter out nearby plumes.

11. L267 This sentence is confusing. I would remove the first part (before the comma) from this sentence.

Reply: We have revised the sentence as follows:

MODIS FRP, which represents the radiant energy released by fires, has been used to approximate the biomass burned consumption in top-down emission inventories such as Global Fire Assimilation System (GFAS; Kaiser et al., 2012). We define the emission coefficient (EC) as the mass of pollutant emitted per unit of radiative energy (i.e., Emissions/FRP), which has been used to derive the emissions of chemical species from fires (Ichoku and Kaufman, 2005; Mebust et al., 2011; Mebust and Cohen, 2014).

12. L284 I am a little concerned about the conclusion that emissions and Fire Radiative Power correlate. In past field campaign, its being shown that reduced vs. oxidized emissions of nitrogen correlate very well with the Modify Combustion Efficiency (MCE) (i.e., smoldering vs. flaming) but it has been difficult to correlate them directly to FRP. The fire condition can also impact the chemistry in PECANS. If the fire has lower MCEs, there will be a lot of reduced nitrogen (e.g., NH3) compared to oxidized nitrogen (e.g., HONO that produces OH, NOx, etc). I know that getting MCE from many different fires is challenging, but I am not convinced that using FRP is the right approach. At the very least, there should be more discussion about how MCE affects emissions in the manuscript.

Reply: We did not force correlation between FRP and NO_x emissions. Our data show reasonably good correlation between FRP and satellite-derived NO_x emissions for a large ensemble of fires, suggesting variation in fire NO_x emissions is largely driven by variation in FRP rather than other factors such as MCE. FRP has been used as a 'top-down' approach in biomass burning emission inventories (e.g. GFAS, FEER), which assumes an empirical linear relationship between emission rate and the amount of heat released by fires (FRP), and it does not need information on the MCE (Ichoku and Ellison, 2014). The validity of the relationship has been verified in laboratory (Wooster et al., 2005; Freeborn et al., 2008), field experiments (Wiggins et al., 2020) and satellite observations (Ichoku and Kaufman, 2005). We have added the following discussions on FRP:

Here we assume linear relationship between emission rate and FRP. While the validity of the relationship has been verified in laboratory (Wooster et al., 2005; Freeborn et al., 2008), field experiments (Wiggins et al., 2020) and satellite observations (Ichoku and Kaufman, 2005), the choice of the mass-to-energy conversion factor (K_r) slightly differ in Wooster et al. (2005, 0.368 g/MJ) and in Freeborn et al. (2008, 0.453g/MJ), suggesting an uncertainty of order 10% for the value of K_r.

13. L333 Here is where I realized that the lifetime included dilution. Please include a few sentences somewhere earlier in the manuscript identifying all the loss processes that the estimated NO2 lifetime includes.

Reply: The calculated lifetime should be representative of chemical lifetime if the transport speed is uniform, the direction is constant and deposition is negligible (De Foy et al., 2014). We have revised the sentence as follows:

Here we use the EMG approach to derive an effective NO_x lifetime of the entire fire plume. Chemical nonlinearities can result in an effective chemical lifetime that is averaged over the plume where at each point in the plume evolution a different chemical lifetime occurs. Besides, the effective lifetime in practice will be confounded by the mixing such as those plume movement in different directions that reduces the line density.

14. L465 I think you should discuss the thermal dependency of PAN. If the plume is injected high enough, PAN can be stable and thus its transportation can be very efficient (e.g., not a source of NOx close to the plume, at least in the time scales this relevant to this manuscript).

Reply: That's a good point. We've added the following discussions:

In the lower troposphere, PAN is generally considered as a sink of NO_x near the fire, but a source of NO_x over downwind region, which deepens the gradient of NO_2 near the source but flattens the gradient downwind (Valin et al., 2013). For those large biomass burning events that inject PAN into upper troposphere, PAN acts as a stable reservoir of NO_x, leading to long-range transport of NO_x (Tereszchuk et al., 2013).

15. L468 We know well that PAN forms rapidly in fire smoke plumes and that its production plateaus after ~4 after of plume aging (Yokelson et al., 2009, Akagi et al., 2011, Alvarado et al., 2010, Juncosa Calahorrao 2021). It might be helpful to look at how the ratio of PAN/NOx changes as the plume ages and have some discussion about it.

Reply: Thanks for the suggestion. We have added some discussions on PAN formation:

In the presence of PAN formation, we find the EMG approach tends to overestimate NO_x lifetime at low NO_x emission (< 5000 g/s), in which the flattening effect of PAN is more evident, while underestimating NO_x lifetime at high NO_x emissions and low $P(HO_x)$, in which the deepening effect takes over.
In-situ measurements show rapid formation of PAN in young smoke within 4 hours of aging, and PAN contributes about 25% of the total reactive nitrogen (Alvarado et al., 2010; Juncosa Calahorrano et al., 2021), suggesting a non-negligible sink of PAN for NO_x near fire source.

16. L470 can you find another word for "estimate" so it is not right before "overestimate"

Reply: We have revised the sentence as follows:

Overall, we assess that the overestimate at low NO_x emissions (< 5000 g/s) cause around 33% negative biases to the derived emissions, while 18% positive biases at high NO_x emissions (> 5000 g/s).

References:

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