Authors' response to referee comments #1 regarding 'An improved Bayesian inversion to estimate daily NOx emissions of Paris from TROPOMI NO2 observations between 2018-2023' by Mols et al. (2025).

The reviewer's comments are in black, the authors' replies in blue.

Reviewer #1

This article presents an new, improved method for estimating NOx emissions over urban areas based on TROPOMI or other high-resolution spaceborne NO2 data. The method builds on a previous method (Lorente et al. 2019) but introduces a well-thought Bayesian framework for the optimization of NOx emissions and lifetimes. In this way, the various uncertainties are taken into consideration, and overfitting is avoided. The advantages of the method are shown by tests (OSSE) using synthetic observations generated by a high-resolution model. Next, the method is applied to the estimation of NOx emissions over Paris using TROPOMI data. The results lead to several interesting insights on the emissions, including their trends, seasonal and weekly cycles, and variability due to covid-19 lockdowns. Overall, the manuscript is well-written, the methodology is clearly presented, with a few minor reservations (see below), and the results appear robust and useful to the top-down emission community. I see no reason why this method could be applied to many other cities and industrial centers worldwide. I recommend publication in this journal, provided that the authors address the following minor comments listed below.

We thank the reviewer for their encouraging words and suggestions for additions to the manuscript. Please see below for replies to the specific comments.

Minor comments

l. 11-12 and l. 321: The decrease is -27% based on the 2018 and 2023 totals, not 17.5 or 18%. Please clarify.

We are glad that this reviewer spotted this error. This value was indeed wrong, we changed it to -27%, also in the results and conclusions.

Abstract and Conclusions: Can this method be applied to other large cities or industrial centers? A bit of discussion would be welcome.

We agree that a discussion about the applicability of the method to other NO_x sources is a good and needed addition to our manuscript. We added the following paragraph at the last part of the conclusion:

"In the future, the superposition model can be applied to estimate NO_x emissions from other large cities or industrial centers, provided that emissions from a given source are clearly attributable to that source. This requires that the NO_2 plume signal exceeds the detection threshold, and that the origin of the NO_2 plume can be linked to a spatially distinct city or emission source. In cases where multiple plumes from different sources overlap, the current model is not applicable. However, future model developments may allow for the separation of overlapping emission signals from multiple sources. Also, with new, high resolution geostationary satellites, it will become easier to attribute NO_2 plumes to specific sources. For example, ESA's TANGO mission, scheduled for launch in 2027, will detect NO_2 at a spatial resolution of 300 × 300 m over Europe,

enabling much more detailed information on emission sources and their variability (Landgraf et al., 2020)."

l. 23 NO2+OH is not the only major sink, also formation of PAN (for example) might be important in VOC-rich areas. PAN and other compounds may play the role of NOx reservoirs, which might partly invalidate the assumptions of the superposition model. I think that this issue should be mentioned and possibly discussed.

The superposition model is designed to estimate effective NO_x emissions and lifetimes from TROPOMI NO_2 enhancements over urban areas. It is not intended to explicitly resolve all chemical pathways, but rather to capture the dominant processes controlling NO_x removal on spatial and temporal scales relevant to TROPOMI retrievals.

We note that (except in cold conditions) PAN formation is not a permanent sink for NO_x. PAN is a reversible NO_2 reservoir: CH_3O_2 + NO_2 + M <-> PAN + M (e. g. Fischer et al., 2014). Once formed, PAN decomposes rapidly in the warm urban air masses and releases NO_2 at the timescale of minutes to an hour. Moreover, the city centre of Paris is generally VOC-limited (e.g. Johnson et al., 2024), and the dominant sink for NO_2 in these conditions is oxidation to nitric acid.

We agree that the issue deserves to be mentioned, and we do that now in section 2.1 right after introducing the rate constant of daytime chemical NO_x loss: "PAN formation is not explicitly considered in this framework, as it is a reversible NO_x reservoir rather than a permanent sink:(e.g., Fischer et al., 2014). In the warm, VOC-limited conditions typical of central Paris (e.g., Johnson et al., 2024), PAN decomposes rapidly and contributes little to net NO_x loss. The dominant NO_2 sink under these conditions is oxidation to HNO_3.

l. 24 Dry and wet deposition of HNO3 are about equally important sinks (see e.g. https://doi.org/10.1029/2018JD029133)

We have added dry deposition as well here: *"Due to its high water solubility, HNO_3 is efficiently removed from the atmosphere, primarily through precipitation and direct deposition onto surfaces (Seinfeld and Pandis, 2016)."*

l. 90 Why not adopt a temperature-dependent rate for NO2+OH? The rate is higher in cold conditions (~10% higher at 283K compared to 298K)

We calculate the reaction rate of the NO_2 + OH +M -> HNO_3 + M reaction using the rate constants from Burkholder et al., 2020 (page 434). We use the following equation to obtain the second-order rate constant for a certain temperature and pressure. We use a total gas concentration [M] at 1atm=$2.5*10^{19}$ molecules cm^{-3}.

$$k_f([M],T)=\left(\frac{k_o(T)[M]}{1+\frac{k_o(T)[M]}{k_\infty(T)}}\right)0.6^{\left\{1+\left[\log_{10}\left(\frac{k_o(T)[M]}{k_\infty(T)}\right)\right]^2\right\}^{-1}}$$

	k_0 [cm^3/molecule/s]	**K_∞ [cm^3/molecule/s]**	**K (1atm, T) [cm^3/molecule/s]**

270K	2.74×10^{-30}	2.5×10^{-11}	1.193×10^{-11}
288K	2.26×10^{-30}	2.5×10^{-11}	1.101×10^{-11}
298K	2.04×10^{-30}	2.5×10^{-11}	1.053×10^{-11}

In our model, we use k' = 1.1×10^{-11} cm^3/molecule/s, so the rate constant for 288K, a quite average yearly daily max temperature for Paris. Indeed, as the reviewer indicates, the rate constant is higher at colder conditions, around 8% higher for 270K, and it is lower for higher temperatures, 4.5% lower for 298K. This temperature dependence on the reaction rate constant is relatively small, and we only use it to calculate a prior estimate of the reaction rate, which we fit later together with the NO_x emissions using our inverse model. We assume that this small error is captured by the 30% uncertainty that we apply during the inversion.

l. 206-208 Based on Fig. 4, the prior is very close to the truth. Why is that? This might contribute to explain why the Bayesian inversion results are closer to the truth, due to the constraint from the first term of the cost function (Eq. 3). What would happen if the prior was more different from the truth?

The reviewer raises an important point here. Our primary goal with the OSSEs for Symcity was to assess whether the simple inversion method can reliably infer emissions and lifetimes when the prior is accurate. However, we acknowledge that in realistic scenarios, prior information is not known with a high degree of certainty. To investigate the sensitivity of our results to deviations in the prior, we conducted an additional test. Specifically, we repeated the OSSEs for both Symcity cases 50 times, introducing a ±20% deviation in either the prior lifetime or emissions. We then analyzed the performance of both the Bayesian and Least-Squares inversion methods.

In the first sensitivity test, we evaluated the accuracy of the inferred NO_x emissions and lifetimes when the prior emissions were biased by 20%. The resulting posterior emission and lifetime deviations (calculated as $\frac{posterior-true}{true} * 100\%$) for both inversion approaches are presented in Table 1 below. The results from the least-squares inversion are not dependent on the prior emission and thus remain unchanged from the case with a known prior. For the Bayesian inversion, we used the same uncertainty settings as described in Section 3.2 of the manuscript.

	Least-squares	**Bayesian**		
	Prior = True values	**Prior = True values**	**Prior E +20%**	**Prior E -20%**
Emissions case 1	14% ± 22%	-1% ± 7%	0.8% ± 6.3%	-6.7% ± 6.2%
Emissions case 2	26% ± 34%	-5% ± 11%	-4.6% ± 10%	-11% ± 6.8%
Lifetimes case 1	2% ± 46%	32% ± 31 %	-1.6% ± 8.2%	31% ± 24%
Lifetimes case 2	-19 ± 37%	13% ± 61%	2.5% ± 25%	22% ± 45%

*Table 1: Errors in the posterior NO_x emissions and lifetimes inferred using the 2 inversion methods, using prior emissions that deviate ±20% from the true emissions. Errors are (calculated as (posterior-true)/true*100%).*

We did the same sensitivity test for a bias in the prior NO_x lifetimes. The results for both inversion approaches are shown in Table 2 below.

	Least-squares	**Bayesian**

	Prior known	Prior tau +20%	Prior tau -20%	Prior known	Prior tau +20%	Prior tau -20%
Emissions case 1	14% ± 22%	8.4% ± 17%	13% ± 20%	-1% ± 7%	-4.8 ± 7.6	2.1% ± 6.0%
Emissions case 2	26% ± 34%	7.4% ± 26%	29% ± 35%	-5% ± 11%	-9.6% ± 7.4	-0.5% ± 8.8%
Lifetimes case 1	2% ± 46%	4.5% ± 54%	-9.7 ± 34%	32% ± 31 %	28% ± 27%	-4.3% ± 18%
Lifetimes case 2	-19% ± 37%	2.9% ± 48%	-29% ± 30%	13% ± 61%	17% ± 14%	-7.5% ± 17%

*Table 2: Errors in the posterior NO_x emissions and lifetimes inferred using the 2 inversion methods, using prior lifetimes that deviate ±20% from the true lifetimes. Errors are (calculated as (posterior-true)/true*100%).*

These sensitivity tests show that increasing or decreasing the prior emissions by 20% results in a posterior bias of no more than 6% compared to the case with a known prior. This confirms that the Bayesian inversion method uses both the prior and the observations effectively. Even with deviating prior emissions, the Bayesian inversion method still outperforms the Least-Squares approach, producing smaller biases and a smaller standard deviation.
Also when the prior lifetime is varied (Table 2), the Bayesian inversion retrieves posterior emissions much closer to the true values than the Least-Squares inversion.
In practice, when applying the superposition model to real cases, one would typically also have some estimate of the prior uncertainty. These uncertainties can be reflected in the values of $\sigma_{a,E}$ and $\sigma_{a,k}$ to prevent the Bayesian inversion from relying too heavily on a potentially inaccurate prior.

Unlike the Least-Squares approach, which fits the line densities directly, the Bayesian method balances observational data with prior knowledge. Even if the prior is not perfectly accurate, it can still help guide the solution in the right direction, leading to more consistent and reliable estimates.

We appreciate that the reviewer raised this point, as it demonstrates the robustness of the Bayesian approach under more realistic conditions. We added this analysis to the supplementary material, and now refer to it in the manuscript at the end of section 3.2: *"To investigate the sensitivity of our results to deviations in the prior, we conducted an additional test. We repeated the OSSEs for both Symcity cases 50 times, introducing a ±20% deviation in either the prior lifetime or emissions. The results can be found in section 2 of the Supplementary Material. These sensitivity tests show that increasing or decreasing the prior emissions by 20% results in a posterior bias of no more than 6\% compared to the case with a known prior."* … *"The sensitivity tests show that also with deviating prior information, the Bayesian inversion method outperforms the Least-Squares approach, producing smaller biases and a smaller standard deviation."*

l. 247 Some more explanation (or maybe a reference) might be needed regarding the rotation and re-scaling step.

We agree, and added some more explanation on this step. We now added the following section on this to the manuscript:

"For the calculation of the line densities, the TROPOMI NO2 data is first rotated towards the effective wind direction (elaborated in the next section) and re-scaled into grid cells of 0.05x0.05°. Specifically, we do this by generating a target grid with a 0.05° × 0.05° resolution, aligned parallel to the wind direction at the time of the TROPOMI overpass. The TROPOMI NO2 data are then regridded onto this new grid, using weights based on the overlapping areas between the original and target grids."

l. 264 CAMS NOx data are used for the domain average NOx/NO2 ratio. At what altitude above ground?

We use the boundary layer mean NO and NO2 values for this. We added this to the manuscript.

l. 275 "The NO2 concentrations (...) never completely decreased to the original levels": I do not follow here. Do you mean "increased"?

The reviewer is correct, we changed this. Also, for more clarity we changed '*original*' to '*pre-Covid*' here.

l. 288 What altitude for CAMS OH? Or is it an average weighted by the NO2 profile?

We use the boundary layer mean OH values for this. We added this to the manuscript.

l. 319-320 The higher variability of posterior emissions is expected due to uncertainties in their derivation.

We agree with this, but argue that the higher variability is expected because of 1) uncertainties (as the reviewer points out), but also 2) because posterior emissions reflect real day-to-day and even diurnal variability, whereas prior is inherently less variable because it represents climatological emissions. We therefore added the following lines to the manuscript:

"The monthly average posterior NO_x emissions exhibit more variability than the prior. Higher variability of posterior emissions is expected because of uncertainties in their derivation. Additionally, posterior emissions reflect real day-to-day and diurnal fluctuations, while prior emissions are based on climatological averages and are therefore inherently less variable. This difference between prior and posterior NO_x emissions indicates that factors beyond the month and day of the week influence the emissions."

l. 345 and elsewhere in this paragraph: are the weekend reduction calculated relative to the weekly (7-day) average, or relative to Mon-Fri average?

We agree that this is not completely clear in the text and thank the reviewer for pointing this out. The weekend reduction is calculated as the weekend average relative to the Mon-Fri average. We added this clarification to this line.

l. 350-351 I don't see how the higher cold start emissions in winter would reduce the weekend effect. It would be the other way around since traffic emissions are (expected to be) more strongly reduced during weekends. Therefore, only residential heating would have to explain the much weaker weekly cycle in winter compared to summer. Is this reasonable? What are the relative shares of the different sectors in the Paris area?

We thank the reviewer for this comment, and we agree that this section indeed calls for some further discussion. The statement about the colds starts that we give now does not explain the reduced weekend effect in winter. And indeed, in the Paris area, traffic has a share of ~50%, and residential heating ~15% (AirParif, 2021: https://www.airparif.fr/surveiller-la-pollution/les-emissions). This is a year-round average, so the traffic share and residential heating share are closer together in winter, but still residential heating alone can probably not explain the much weaker weekly cycle in winter compared to summer.

We looked further into the cold starts and argue that cold starts in winter dampen the weekend effect because the diurnal cycle of emissions is different on weekend days than on weekdays (see Figure 1 below of the CAMS-TEMPO scaling factors from Guevara et al., 2021). On weekdays, people start their car in the early morning, whereas on weekend days the cars are started on average later in the morning, closer to the TROPOMI overpass time, and therefore this shows up as apparently higher weekend day emissions than otherwise.

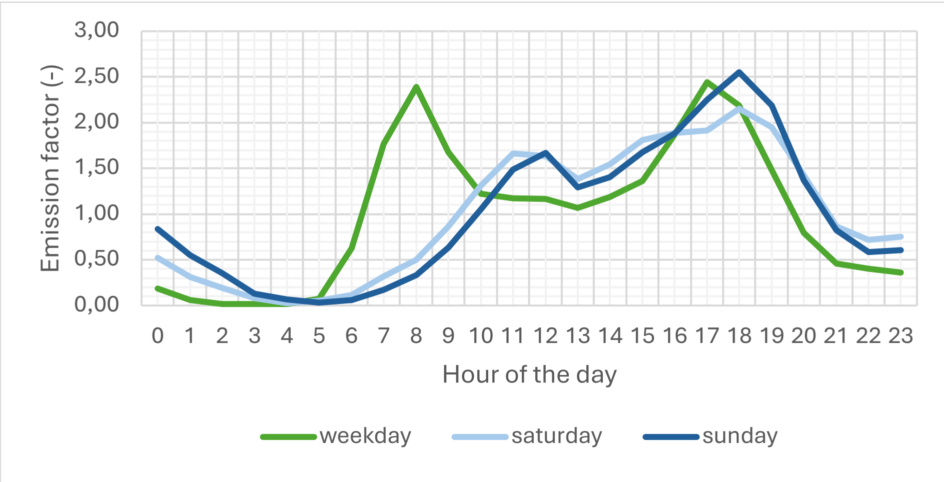

Figure 1: CAMS tempo diurnal scaling factors for weekdays and weekend days

We added this paragraph to the manuscript:

"In Summer, the decrease in NO_x emissions in the weekend is much larger 39% than in Winter 11%. This is likely because of a higher contribution of traffic emissions to the total emissions in the Summer months. In Winter the share of traffic emissions is smaller because of local residential heating and power generation. In Winter, our posterior weekend reduction is lower than in the prior inventory. This, again, points to an underestimation of residential heating emissions in the prior inventory. Additionally, the weaker weekly emission cycle observed in winter could be influenced by the effect of vehicle cold starts. On weekdays, vehicles are typically started early in the morning, while on weekends, car usage tends to begin later, closer to the TROPOMI overpass time. Weekend day emissions could then show up higher than without cold starts, dampening the weekly cycle."

Technical / language comments

l. 6 MicroHH: what does the name stands for? MicroHH is the name of the CDF model itself and is to our knowledge not an abbreviation. But for clarity in the abstract, we added that it is a computational fluid dynamics model.

l. 49 "to estimate the NOx and predict CO2 emissions...": not clear why one is estimated and the other predicted. You could replace by "estimate NOx and CO2 emissions".

This has been corrected as suggested.

Legend of Fig. 1: why "grey arrow"? There are several (apparently) black arrows.

This has been changed to "black arrows".

l. 95 Delete second "on"

This has been corrected.

Fig. 3 Use same distance units (preferably km) for all panels

The axis units have been changed to km for all panels of Figure 3, as well as Figure 2.
l. 139 "the observed NO2 columns"

This has been corrected as suggested.

l. 152 Make a new sentence "It amounts to..."

This has been corrected as suggested.

l. 210 Figure 4b,d (not 4c,d)

This has been corrected.

l. 243 "Computation of..."

This has been corrected

l. 244 Remove the first sentence since this step is elaborated in the following paragraph.

This has been corrected. We removed this sentence and moved the information about the quality filtering to the previous section.

l. 275 "in between"

This has been corrected.

l. 317 Missing dot after parenthesis.

This has been corrected.

l. 340 Did you really filter data for weekdays? Isn't it for weekends?

We agree that this was phrased unclearly. We changed the phrasing to "We filtered the data by excluding weekends, lockdown periods and the Summer holiday period".

References author reply

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