

#Reviewer 2: Estimation of OH in an urban plume using TROPOMI derived NO₂/CO "

1. On line 162, the authors mention that they "account for the chemical transformation of NO_x to HNO₃ in the reaction of NO₂ with OH." However, it isn't clear how this is done - whether a highly simplified mechanism was added to WRF-Chem or whether this was done offline. A more detailed explanation of this would be welcome, even if just in the supplement.

Author Response:

The sentence is added in Line 187 "Instead of a simplified photochemistry solver, we make use of a WRF-Chem module for passive tracer transport for transporting NO_x. This WRF module has been modified to account for the first order loss of NO_x in reaction of NO₂ with OH, using NO_x/NO₂ ratios from CAMS to translate NO_x into NO₂ and CAMS OH fields to compute the chemical transformation of NO₂ to HNO₃ (see Text S1 for detail method).

The larger issue is the choice to use passive tracers with this simplified chemistry rather than one of the established chemical mechanisms in WRF-Chem. Line 180 states that such simulations are considered outside the scope of this paper, but does not explain this reasoning. I could see two reasons for such a choice:

1. To reduce computational cost, making this easier to apply at scale. If this is the case, some measurements of the relative speedup compared to a full chemistry simulation would help support this choice.
2. The framework used in this paper required a specified OH background to permit the calculation of $d[\text{NO}_x]/d[\text{OH}]$ in a straightforward manner. With a full chemistry simulation, I suspect it would be much more difficult to impose a constant increase or decrease in OH for this purpose.

Whatever the reason for the choice to use passive tracers, I urge the authors to explain their reasoning behind this choice, given (as they mention) the potential impact of other NO_x loss pathways.

Author Response:

So the main motivation is indeed computing time, which for a single day is not restrictive, but to apply the method to longer-term averages or a list of TROPOMI observed cities it is. The sentence is added in Line 155 - 159 :

"Here, we used the passive tracer transport function instead of the encoded chemistry in WRF to speed up the model simulation and reduce the computational cost. In addition, the passive tracer option helps in separating the influences of meteorology, OH and the rate constant of the NO₂+OH reaction ($K_{\text{NO}_2,\text{OH}}$) on the NO₂/CO ratio in the downwind city plume. Compared to previously used methods by Beirle et al., (2011);Valin et al.,(2011) which did not use a transport model at all, we consider this an important improvement. "

Second, at line 404, the authors state that "the optimization method can be used for a single TROPOMI overpass and does not require yearly averaged NO₂ data." This is contrasted with the EMG approach, which does need a significant amount of data to generate reliable results. However, the ability of the optimization method described in this paper to estimate OH for individual days is not clearly demonstrated in this paper. Since this seems to be one of the main advantages of the authors' optimization method over the EMG method, this should be shown in more detail. At least a timeseries plot of daily OH concentrations obtained by this method would help by showing that we

do get reasonable OH values with a single day of data. Further, I expect that there is a minimum amount of clear sky pixels over a city required for this method to work effectively. Assuming that clouds are uncommon over Riyadh, this could still be explored by withholding increasing percentages of the available pixels for a given day and testing how the estimated OH deviates with the reduction in data.

Author Response:

We agree with the reviewer that it would have been better to demonstrate the application of our method to single satellite overpasses. The following subsection was added:

3.5 WRF optimization using a single TROPOMI overpass

To demonstrate the application of our WRF optimization method to single TROPOMI overpasses, results are presented in this subsection for August 18th, 2018. This date was selected for clear sky conditions with most of the TROPOMI NO₂ and CO pixels passing the data quality filter. During this day, the urban plume is transported in southwestern direction over Riyadh. The spatial distribution of $XNO_{2,WRF}$ ($r^2 = 0.76$) and XCO_{WRF} ($r^2 = 0.65$) matches quite well with TROPOMI (see Fig S21). The optimized ratio, XNO_2 and XCO for a single day fit well with TROPOMI ($X^2 = 0.1, 0.3$ and 0.7) comparable to the summer averaged plumes indicating that the optimization method can be applied to single TROPOMI overpass. The ratio optimization increases the emission ratio and CAMS OH respectively by $111 \pm 18.4\%$ and $37.9 \pm 6.2\%$ respectively, whereas the background is reduced by $51.5 \pm 5.2\%$ (see Fig S22 a). The XNO_2 optimization increases the EDGAR NO_x emission by $25.5 \pm 5.1\%$ and CAMS OH by $32.3 \pm 4.4\%$, whereas the NO_x background is reduced by $54.4 \pm 7.0\%$ (see Fig S20 b). The CO optimization doubles the EDGAR CO emission and reduces the background by $6.1 \pm 0.97\%$ (see Fig S20 c). The optimized NO_x and CO emission for August 18th is 8.9 ± 1.7 kg/s and 18.9 ± 4.0 kg/s respectively and differs by <25 % with the summer optimized emission (see Table 2 and S5). The optimized OH derived from a single TROPOMI overpass is $1.73 \times 10^7 \pm 0.3$ molecules cm⁻³ differs by < 5 % from the summer averaged OH i.e. $1.7 \times 10^7 \pm 0.3$ molecules cm⁻³ confirming that the method yields realistic results for a single overpass.

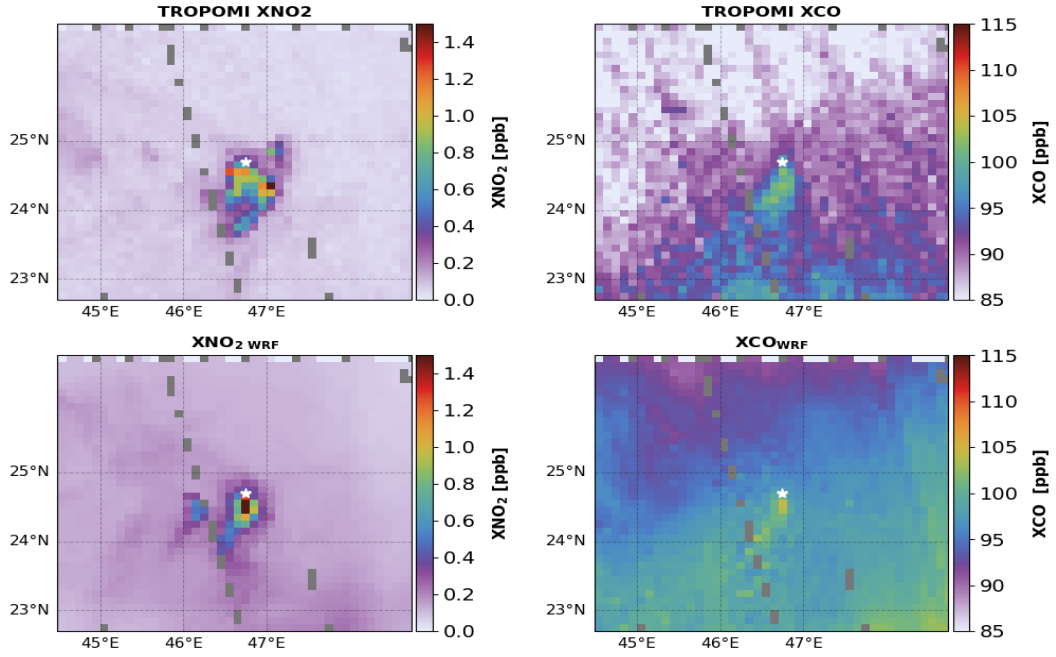


Figure S21. Comparison between XNO₂ (left) and XCO (right) from TROPOMI and WRF over Riyadh for 18th August , 2018 . Top panels show TROPOMI data and bottom panels the corresponding co-located WRF results. $XNO_{2\text{ WRF}}$ is derived by adding $XNO_{2\text{ (emis,OH)}}$ and $XNO_{2\text{ Bg}}$. $XCO_{\text{ WRF}}$ is derived by adding $XCO_{\text{ emis}}$ and $XCO_{\text{ Bg}}$. The white star represents the centre of city. TROPOMI and WRF results are gridded at $0.1^\circ \times 0.1^\circ$.

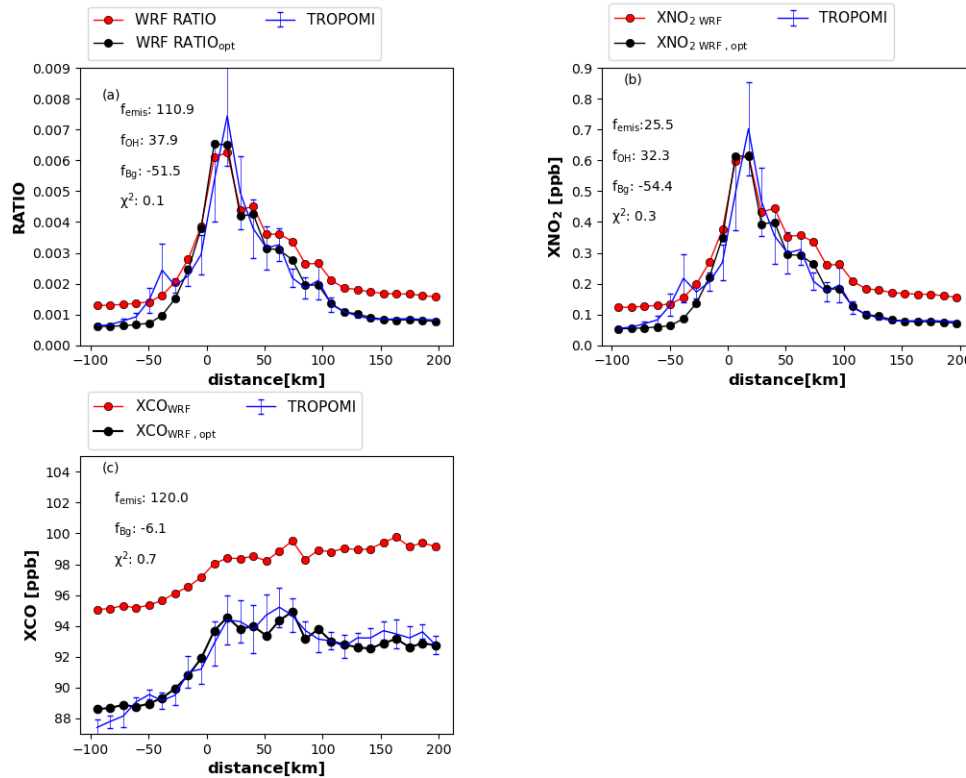


Figure S22. Comparison between TROPOMI and WRF, before and after optimization for 18th August, 2018.

a) XNO₂/XCO ratio, b) XNO₂ and c) XCO in comparison to TROPOMI. f_{OH} , f_{emis} and f_{Bg} are optimized scaling factors obtained iteratively for OH, emissions and background by least square optimization method. f_{emis} , f_{OH} and f_{Bg} are derived by accounting the total change in emission, OH and background using the corresponding scaling factors obtained from 1st and 2nd iterative step. The unit of scaling factor is in percent (%).

Third, the efforts to test this optimization approach described in the manuscript are a good foundation, but could be improved. My understanding is that there are three elements to the testing, covered in Sect. 3.3:

1. Tests in which NO₂ and CO fields generated by varying the scale factors in Eq (5) are input to the optimization algorithm and it has to reproduce the scale factors used.
2. Comparing the NO₂ and CO line densities and their ratio produced by the optimization against those from TROPOMI, in Fig. 4 and 5.
3. Comparing the OH concentrations, NO_x emissions, and NO_x lifetimes output by the optimization to those derived from the EMG method (Table 2)

These are important tests, but each have weaknesses. Sources

- For #1, because the framework that generated the synthetic NO₂ and CO fields is the same framework used to match them, it cannot account for chemistry or other confounding factors outside that framework.

- For #2, the optimization was given the goal of matching the TROPOMI NO₂ & CO values and their ratio. Thus, showing that it can do so proves that the optimization has sufficient degrees of freedom and that the underlying model simulations include enough of the physics to reproduce the observations. It does not necessarily show that it obtains the right answer for OH.
- For #3, the EMG method makes a similar assumption to the optimization approach that the OH + NO₂ pathway dominates NO_x loss. This may well be true in Riyadh, but cannot give any information on errors from unsimulated chemistry.

One way to address these issues would be to repeat the first experiment, but using NO₂, CO, and OH from a full chemistry simulation of WRF-Chem. Even if computational costs limit the runs to only a few days each in the summer and winter, comparing the OH returned by applying this optimization approach to the NO₂ and CO columns simulated in the full chemistry WRF-Chem to the OH in that WRF-Chem run would be a useful metric of the error introduced from ignoring other NO_x loss processes. Additionally, going back to my second main suggestion, this would be a useful way to demonstrate that this optimization approach works for individual days.

Since the authors state that full chemistry simulations are beyond the scope of this paper, I accept that this specific approach may not be practical. However, something like this - effectively an OSSE experiment in which NO₂ and CO columns simulated with more complete chemistry are ingested by the optimization framework proposed in this paper, and the optimum OH from this framework compared with known OH in the original simulation - would help quantify the uncertainty introduced by omitting VOC-NO_x chemistry from this framework.

Author Response:

To strengthen the link between the TROPOMI observed NO₂ decay and OH we have decided to follow the suggestion made by the reviewer to extend our OSSE tests with an additional experiment in which the VOC-NO_x chemistry in WRF-chem is used to test if OH can be recovered using our method. Section 3.3 has been extended with:

To obtain a more realistic estimate of the uncertainty in least squares optimization derived OH, TROPOMI data have been replaced by NO₂, CO and NO₂/CO ratio derived from WRF-chem using the Carbon Bond Mechanism Z (CBM-Z) gas-phase chemical mechanism (Zaveri and Peters, 1999). EDGAR based VOCs, NO_x and CO emission have been used in combination with boundary condition for NO, NO₂, CO, ozone (O₃) from CAMS to run WRF-chem for August 17th, 2018 and November 18th, 2018 representing a summer and winter day, respectively.

For August 17th, 2018, the ratio and XNO_2 optimization increase the CAMS based prior OH of 1.19×10^7 molecules/cm³ by 15.7 % and 13.4 %, respectively (see Figure S17). In the WRF-chem full online chemistry simulation the boundary layer averaged OH for the box of 300 km x 100 km amounts to 1.33×10^7 molecules/cm³, which <5 % lower than the optimized OH value that is derived using our method. The optimized NO_x and CO emission differs by <11% than the emission input in full online chemistry. In winter, optimization increases CAMS based OH of 1.03×10^7 molecules/cm³ by 19.4%. The OH derived from WRF-chem full online chemistry is 1.07×10^7 molecules/cm³ and lower by 15.2% than the optimized OH value. The component wise optimization increases the EDGAR NO_x and CO emissions by 23.1 % and 10.5 %, respectively. Overall, the uncertainty in optimized NO_x, CO emission and OH derived from this test is <11 % in summer and 10 % to 23 % in winter. Since the lifetime of NO_x is determined by other reactions in addition to the oxidation to HNO₃ considered in our method, it is expected to overestimate the real OH value. The test using WRF full chemistry confirms that this is indeed the case.

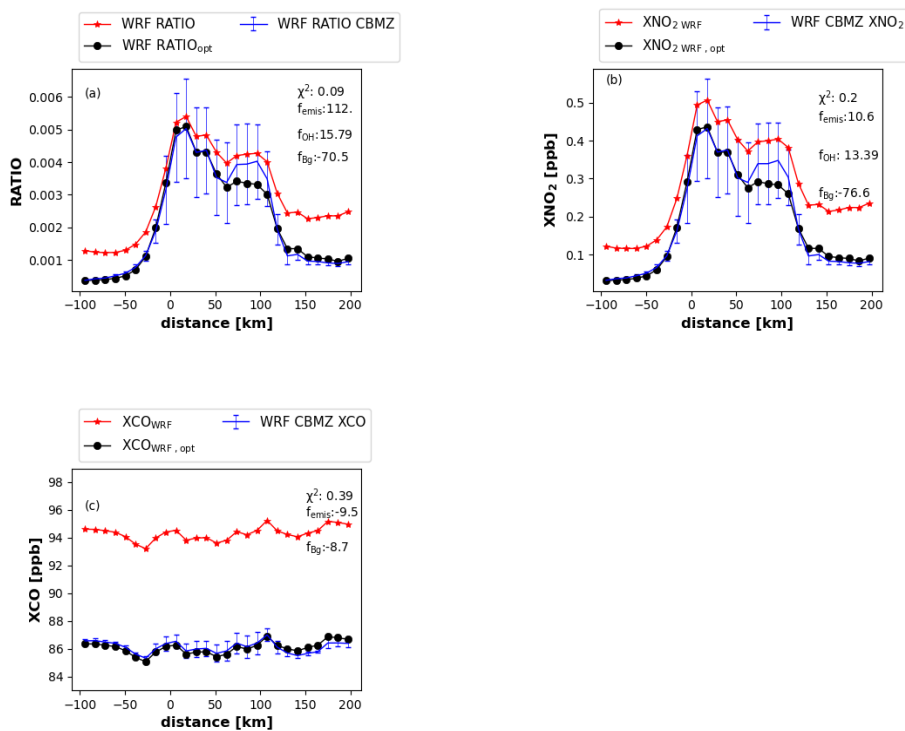


Figure S17. WRF derived a) XNO_2/XCO , b) XNO_2 and c) XCO before and after optimization in comparison to WRF using full chemistry with CBMZ chemical scheme for 17th August, 2018.

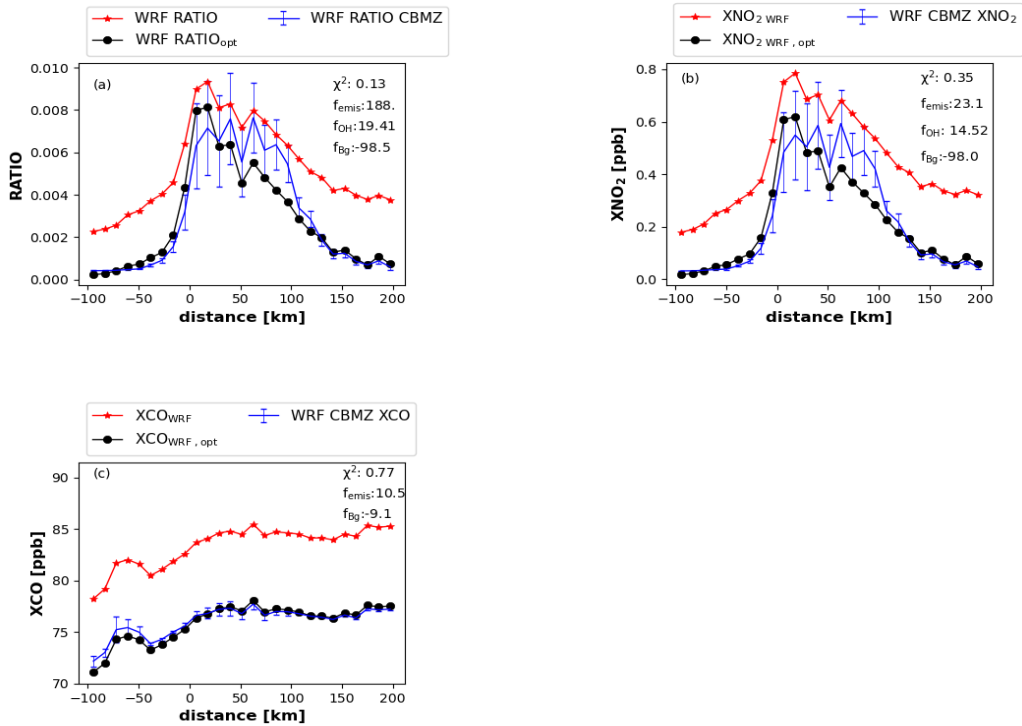


Figure S18. Same as Figure S17 but for 18th November, 2018.

Furthermore, to check if the size of the error matches the expected contribution of other NO_x removal pathways the Chemistry Land-surface Atmosphere Soil Slab (CLASS) (van Stratum et al., 2012) model has been used. CLASS provides Ox-NO_x-VOC-HO_x photochemistry scheme with 28 different chemical reaction including the loss of NO_x via N₂O₅ to HNO₃. We run the CLASS model for a summer and winter day representative of Riyadh. During the summer mid-day, NO_x loss is dominated by OH (93.4 %) in CLASS. The heterogeneous N₂O₅ loss accounts for 6.6 % (see Figure S26), in close agreement with the full chemistry WRF test. During the winter mid-day, the N₂O₅ loss increases to 21.4 % and NO₂+OH accounts for 78.6 % of the total NO_x loss (see Fig S26), which is larger than the mismatch in the full chemistry test, but within its uncertainty.

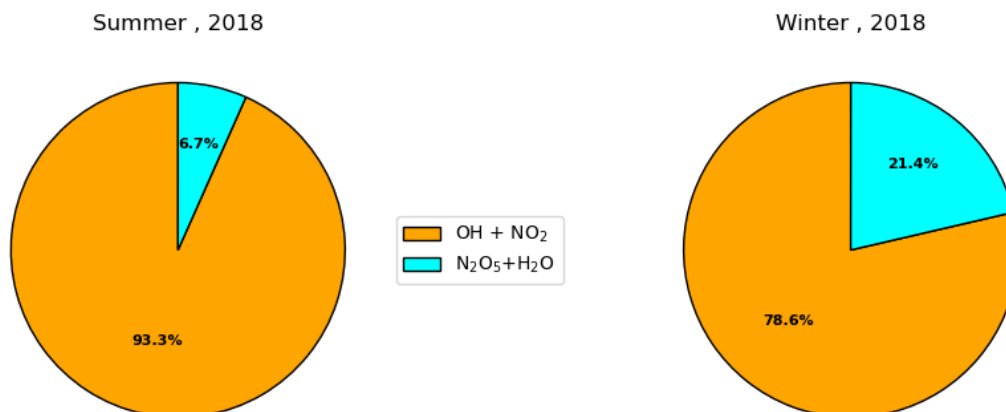


Figure S26. The different pathways of NO_x loss over Riyadh at the time TROPOMI overpasses during summer (left) and winter (right) , 2018.

Minor comments

- Title should be "Estimation of OH in an urban plume" or "Estimation of OH in urban plumes" (singular/plural mismatch in the current title) (done)

Author Response

-Changed as suggested

- Recommend defining XNO₂ in the abstract, since it is less common to use column-average mole fractions for NO₂ than for CO or CO₂.

Author Response :

In line 12 to 14, this sentence has been added: "A new method is presented for estimating urban hydroxyl radical (OH) concentrations using the downwind decay of Tropospheric Monitoring Instrument (TROPOMI) derived dry column mixing ratios of nitrogen dioxide (XNO₂)/carbon monoxide (XCO) ratios combined with Weather Research Forecast (WRF) model simulations."

- At line 49, recommend mentioning that the EMG method assumes that OH+NO₂ is the only loss route so that this is clear from the start.

Author Response :

In line 57 to 58, this sentence has been added: "In the EMG method, the satellite observed exponential decay of NO₂ downwind of the city centre is used to quantify the first order loss of NO₂, which is used to quantify the hydroxyl radical (OH) neglecting other NO_x removal pathways."

In Sect. 2.6, do you use the average pressure and temperature over the same time period as the EMG fit when computing the rate constant? Over what vertical distance?

Author Response:

In line 264, this sentence has been added: "Rate constants at the time of TROPOMI overpasses are obtained from WRF by averaging the IUPAC second order rate constant from the surface to top of the planetary boundary layer."

- Recommend reiterating that f_{emis} , f_{OH} and f_{Bg} in Eq. (5) are the scale factors alongside the other variable descriptions following Eq. (10). Also please explain why they are divided by 10.

Author Response

This sentence has been added in line 293 to 294 "The scaling factors f_{emis} , f_{OH} and f_{Bg} obtained from the ratio optimization have been multiplied by 10 % (i.e. divided by 10) as they represent changes in emission ratio, OH and Bg by 10 %."

This sentence has been added in line 308 to 309 "The scaling factors f_{emis} , f_{OH} and f_{Bg} are divided by a factor 10, because $\Delta XNO_{2\ emis}$, $\Delta XNO_{2\ OH}$ and $\Delta XNO_{2\ Bg}$ are defined as 10 % changes in NO_x emission, OH and background level. "

- Fig. 3 caption - I'm not sure "zonally" is the right term, that implies averaging along latitude lines. Should this be perpendicular to the wind direction?

Author Response :

The caption of Figure 3 has been changed to: "Comparison of WRF and TROPOMI averaged across the wind direction for a) XNO₂, b) XCO and c) WRF Ratio (XNO₂/ XCO) without CAMS background d) WRF Ratio (XNO₂/ XCO) with background and TROPOMI as a function of distance to the center of Riyadh for summer (June, 2018 to October, 2018). "

- Fig. 3 caption - "with background as a function of distance" is ambiguous - does it mean that the background value depends on distance or is it saying that each of the quantities described previously (XNO₂, XCO, WRF Ratios) are plotted versus distance.

Author Response:

This comment is accounted for also by the new formulation of the figure 3 caption.

- Line 357 - the OH uncertainties of 11% to 15% are probably underestimated because VOC chemistry is not accounted for. Please note that here.

Author Response:

The OH uncertainties arising from different NO_x removal pathways have been included in section 3.4. The sentence is added in Line 400 "For summer and winter, the uncertainties of the optimized OH concentrations is <17 % and < 29 % respectively. For NO_x and CO emissions, the uncertainty is < 29 % in summer and winter."

- Lines 358 to 368 - the discussion here is difficult to follow because the results for OH, emission ratio, and background ratio vs. CAMS are very spread out and (in one case) given in different ways, e.g. the amount by which CAMS is overestimated and optimized value. It would help significantly to gather the results from the ratio-optimized and component-optimized tests into a table along with the CAMS values and provide the actual values. Describing the optimization results as percentages by which CAMS is overestimated is awkward to follow while reading.
- Author Response:

Table S4 has been added to summarize the prior and optimized emission ratios, OH, and background ratios obtained from the ratio and component wise optimizations.

Table S4. Overview of optimized emission ratio, OH and background ratio using ratio and component wise optimization.

Variables	Summer			Winter		
	Prior	Ratio optimization	Component optimization	Prior	Ratio optimization	Component optimization
Emission ratio (NO _x /CO)	0.79 (8.2/10.34)	2.01±0.33	0.55±0.091 (11.6/21.09)	0.93 (9.4/10.1)	1.46±0.8	0.36±0.18 (7.8/21.6)
OH (10 ⁷ , molecules/cm ³)	1.3	1.7± 0.32	1.66±0.29	0.86	1.3±0.38	1.28±0.37
Background ratio (XNO _{2Bg} /XCO _{Bg})	0.002 (0.22/92.13)	0.00068± 6.12e-05	0.00059 (0.053/88.41)	0.0016 (0.15/92.58)	0.00053 ±0.00015	0.00054±0.00015 (0.049/90.54)

Lines 365 to 371 - the discussion of why the component and ratio optimizations yield different emissions ratios isn't convincing. Whether directly optimizing the ratio or the NO_x and CO amounts, the algorithm has information on the ratio of NO₂ to CO, so how can it come up with emissions ratios that vary from 0.38 to 1.05 (if I understood the ratio optimization result correctly)? If the component optimization matches TROPOMI NO₂ and CO well, it should by definition match the TROPOMI NO₂/CO ratio too.

Author Response :

The ratio inversion has enough degrees of freedom to get the observed NO₂/CO ratio correct. However, as different emissions can have the same emission ratio, the degree of freedom of the absolute emissions is larger as was explained in the manuscript already. It puzzled us also why even the emission ratio could be different between the ratio and component wise optimization. It turned out the emission ratio is sensitive to the background. This can be understood considering that the NO₂/CO ratio over a city is the sum of the contributions of the background and the city emission. The relative weight of the two is determined by the absolute background levels and absolute emissions of CO and NO₂. In the ratio inversion these absolute values are not well constrained, as the data only inform about ratios. This is our explanation of why the optimized solutions can have different emission ratios. According to our tests, however, the OH concentration derived from our method is not affected as it is not sensitive to the background.

- Lines 371 to 376 - please provide the Lama et al. (2020) values for comparison.

Author Response :

In line 405, this sentence has been added "Lama et al., (2020) inferred an NO₂/CO emission ratio over Riyadh of 0.47 ± 0.1 for 2018 from TROPOMI favoring the Monitoring Atmospheric Chemistry and Climate and CityZen (MACCity) emission ratio over that of EDGAR."

- Lines 391 to 392 - "Both methods result in higher NO_x emissions and shorter lifetimes in summer; lower NO_x emissions and longer lifetimes in winter." In summer, the prior values are within the EMG uncertainties. To claim that the EMG values are higher than the prior, given the uncertainty range, requires a t-test or other statistical test to determine if that difference is significant.

Author Response :

Here, the higher and lower values are not meant relative to the prior, but relative to each other as a quantification the seasonal changes which happen to be consistent between the two methods and in line with the expected seasonal differences.

- Line 411 - the simplified OH + NO₂ chemistry used here will also be a barrier to more general use. It would be good to acknowledge that any such simplified approach in the future will either need to (a) account for other paths for NO_x loss, or (b) prove that neglecting those paths introduces an acceptable error in the OH concentrations.

Author Response

In line 459 to 461, the sentence has been added "In the future, the accuracy of our method can be further improved by accounting other NO_x removal pathways. "

- Line 442 - this paragraph could use a stronger topic sentence. It's not clear what the main point of this paragraph is.

Author Response

The paragraph has been removed.