Response to reviewer 3,

We thank the reviewer for spending time on the paper improvement. Below, we provide a point-by-point response to the comments, and we list the related changes made to the manuscript. The original review text is indicated in italic blue font and the response in regular black font. New text appearing in the revised paper is indicated by a red color. It is noted that the line number we mentioned here is for the manuscript with the track changes.

The study "SO2 emissions and lifetimes derived from TROPOMI observations over India using a flux-divergence method" by Chen et al. presents emission estimates over India based on TROPOMI observations and a flux-divergence method. The paper generally reads well and presentation quality is good. However, I don't see the main conclusion to be sufficiently supported by the presented results, as detailed below. While I don't think that all the open questions need to be solved within this study before publication, the authors need to extend the discussion substantially and have to present their conclusions more cautious and less absolute.

The main aim in this paper is to update the methodology typically used for deriving SO_2 emissions from satellite data by introducing a lifetime for SO_2 in the inversion calculation. In previous studies it was often considered constant, and thus independent of latitude or season. By calculating a seasonal and latitude dependence into the local SO_2 lifetime, we investigate the effect on the resulting emission estimates. This paper is considered a first step towards addressing the lifetime variability in the inversion methodology.
We have added the text to the manuscript in the last paragraph of the paper to indicate that further work should be done:
For those regions with more Northerly latitudes than 40°N (e.g. Northern China, Eastern Europe), the latitude and season dependent SO_2 lifetime with the improved divergence approach has the potential to significantly improve the top-down derivation of SO_2 emission estimates. This paper is considered a first step towards addressing the lifetime variability in the inversion methodology.

Before publication, the following issues need to be resolved:

Major issues:

1. Title

SO_2 emissions have been derived from TROPOMI observations.
However, the lifetimes have not! They are actually based on CAMS simulations, and the CAMS-based lifetimes are the basis of the conclusions that emissions in CAMS are too high.
Thus, the title is misleading, and "and lifetimes" should be skipped.

Actually, our lifetimes are not directly based on CAMS simulations, but they are calculated based on previous studies while using an OH climatology based on CAMS. However, we agree that the lifetimes are

not based on TROPOMI observations either and the title has been changed to "SO_2 emissions derived from TROPOMI observations over India using a flux-divergence method with variable lifetimes.

2. SO_2 lifetime

The main finding of the study is that TROPOMI SO_2 columns over India are lower than CAMS model simulations, and the conclusion of the study is that bottom-up emissions of SO_2 are too high. However, the discrepancy could also have other reasons, in particular that the modeled SO_2 lifetime is too high.

I see the following aspects that need further discussion:

(a) *OH climatology: The SO_2 lifetime is estimated based on CAMS OH climatology. However, this approach completely ignores the very special conditions within the power plant plumes: In particular due to the co-emitted NOx, plume-OH is probably highly variable and can substantially differ from the climatology!*

We add the discussion of OH chemistry occurring within the NO_x plume in Sec. 7 between line 503-510:

The hard-to-quantify factors influencing the lifetime and emissions are discussed here. First, our grid-averaged (about 40 km ×40 km) OH climatology does not resolve the detailed chemical variation within the pollutant plumes, particularly those involving the interaction between NO_x and OH. Krol et al. (2024) studied the chemistry within the NO_x plumes and observed low OH concentrations near the strong NO_x sources (within an average of 10 km) and high OH away from the sources. This suggests that our 40 km averaged OH climatology cannot capture this OH decline and may underestimate the SO_2 lifetime near the large NO_x sources. Furthermore, the variation of OH concentration between 10 km to 40 km from the source is roughly limited to 10 %, see Fig. 7b from Krol et al. (2024). We have considered these effects in our error estimate of the lifetime.

(b) *) Clear sky: The authors claim that only reaction with OH is relevant, as only cloud free observations were considered. However, this is not completely true:*

- A cloud filter was applied, but pixels with up to 30% cloud fraction are still included! (as I understand from Fig. 9; the cloud threshold has to be added to section 2.1)

Even if a pixel is cloud free at TROPOMI overpass, the observed air mass might have been in contact with clouds over the last hours.

Also heterogenous reactions with aerosols can play a role.

Analysis of the dominant term for conversion in the CAMS system shows aqueous phase chemistry is the dominant term related to sulphate production rather than heterogeneous reactions therefore we assume wet-aerosols are a negligible source term (which typically have low pH and slow sulphate production (Gillani et al., 1981)).

We have added the text between line 510 and line 519:

Second, we did not consider the heterogenous SO_2 reactions on wet aerosols. We suppose this impact on SO_2 lifetime can be neglected in our study. Analysis of the dominant term for conversion in the CAMS system shows aqueous phase chemistry is the dominant term related to sulphate production rather than heterogeneous reactions. We therefore assume wet aerosols are a negligible source term (which typically have low pH and slow sulphate production (Gillani et al., 1981)). Even though the atmospheric SO_2 in gas phase can convert to aqueous phase and be oxidized to form sulfate on aerosol wet surface or within clouds, these reactions typically occur on hazy days with high relative humidity and PM2.5 level (Ge et al., 2021). These meteorological conditions are generally not favored on days with minimal cloud coverage, as achieving the necessary high relative humidity is difficult with ample sunlight at noon.

TROPOMI can only "see" SO_2 from point sources located at the surface for cloud-free pixels. It means only cloudless area SO_2 can be measured by TROPOMI even though up to 30% clouds may exist. The TROPOMI retrievals for the whole pixel are based on the cloud-free part only. Therefore, we calculate an effective lifetime for cloud-free conditions. In theory, it might be possible that plumes originate under the cloud and later become visible in cloud-free pixels. We assume that these cases are rare and will only lead to a small additional uncertainty.

We added an extra explanation about the uncertainty of the SO_2 lifetime we described.

To emphasize that we only calculate the SO_2 lifetime in the cloudless area, we have added new text between line 188 and 190:

Notably, TROPOMI can "see" SO_2 only in the cloud-free part of the pixel, leaving SO_2 concentrations within or beneath clouds being unmeasurable. We assume that the resulting SO_2 has had no interaction with clouds, thus the resulting lifetime derived for SO_2 pertains to cloud-free conditions in a constrained region.

We add the text in Section 3.2.3 between line 233 and 236:

Comparing the SO_2 lifetime derived here with those proposed in the literature shows that our estimates are similar to other independent model-based lifetime estimates (Lee et al., 2011) and ground-measurement based lifetime estimates (Hains et al., 2008). We therefore argue that on average our calculated SO_2 lifetime is reasonable. Furthermore, it has a latitude and seasonal dependency that is often lacking in other inversion methods.

And we add extra discussion of clouds effect on lifetime in Section 7 between 519 and 521:

Finally, we only calculate the lifetime for SO_2 in cloud-free regions, excluding the SO_2 wet deposition and the reactions within the clouds. This is actually the lifetime we need in our inversion since the TROPOMI observations of SO_2 plumes are limited to cloud-free scenes.

My strongest concern about the main conclusion is actually raised by Fig. 9: While the difference in SO_2 columns is clear, this could indeed be due to input emissions, but also due to the loss processes in CAMS. It is hard to tell from the Figure alone, but it looks like CAMS (even if values would be halved) shows substantial outflow of SO_2, e.g. over the oceans, that is not observed from TROPOMI. Thus I would conclude that the CAMS SO_2 lifetime is definitely too high.

The OH concentration is the major controlling factor of SO_2 lifetime under cloud-free conditions. We firstly compare the Indian OH concentration in CAMS with those in previous studies. Hewitt and Harrison (1985) summarized the early papers and found the OH concentrations were typically measured or simulated at around 10^6 radicals/cm^3, which is comparable to CAMS OH levels. Then we found that Indian CAMS OH levels are similar to those in Lelieveld et al. (2004) study (2.0-4.0×10^6 radicals/cm^3) (Fig R1), while slightly higher than the values in Lelieveld et al. (2016) study (1.2-1.8×10^6 radicals/cm^3). We suggest this difference arises because Lelieveld et al. (2016) reported OH concentrations averaged throughout the troposphere, whereas our focus is specifically on PBL-averaged OH concentrations. We also change the color bar range of Fig. 9 to fit their own maximum values and show it here (Fig. R2). Many strong source signals are shown in west of India on the CAMS map while not being visible on the TROPOMI map. Therefore, we suggest that the discrepancies in Fig. 9 mainly resulted by the overestimation of model input emissions. But we have added the text to the manuscript between line 469 and 476 to make this conclusion less absolute (See the text below the figure).

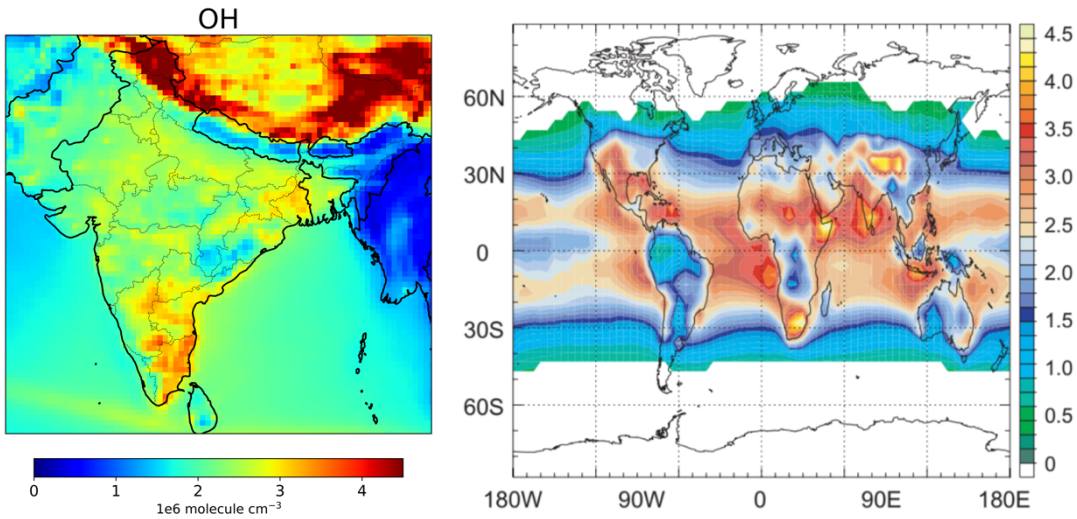

Figure R1. Left: Annual mean OH concentration from CAMS model averaged from 2019 to 2023 in our study. Right: Annual mean OH concentrations near the earth's surface calculated with a chemistry-transport model (Lelieveld et al., 2004). The units are 10^6 radicals/cm^3.

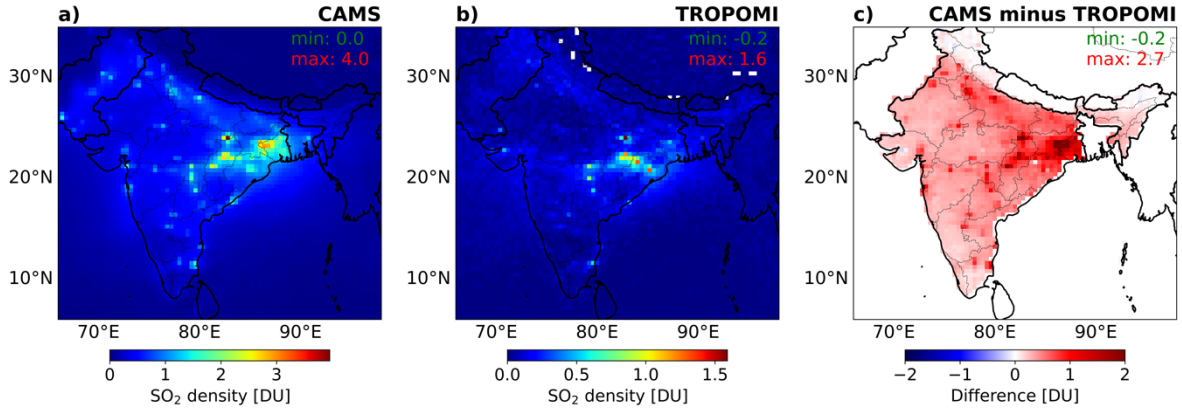

Figure R2. Indian SO_2 vertical column densities (VCDs) averaged in 2023 from (a) CAMS global composition forecast dataset, and (b) TROPOMI Level-2 COBRA dataset (at about the overpass time of 6 UTC). We integrate the TROPOMI observations to a resolution of 0.4° × 0.4°, the same as the CAMS datasets.

The emissions at the large source locations show big differences between the two maps. Many strong source signals in the west of India are shown on the CAMS map while not visible on the TROPOMI map. Considering the low uncertainties of the TROPOMI observations (Theys et al., 2021; De Smedt et al., 2021), we suggest that the difference in Fig. 9 is primarily due to a positive bias in model input-emissions. It is noted that the SO_2 lifetime in CAMS may be overestimated and contributes to the higher simulated SO_2 concentration, even though the OH level, which mainly determines the SO_2 lifetime under cloud-free conditions, are similar between CAMS results (Fig. S10) and previous studies (Hewitt and Harrison, 1985; Lelieveld et al., 2004; Duncan et al., 2024)

The authors need to

- include a discussion about plume chemistry (affected by strong local NOx emissions) on OH and how far it is appropriate to use the OH climatology here,

- be aware that "cloud free" does not really mean free of any clouds, and heterogeneous reactions on clouds and aerosols need to be discussed as well, which actually results in lower SO2 lifetimes,

- include a discussion about remaining uncertainties, and the possibility that the CAMS lifetime is actually too long, as indicated in Fig. 9.

We already shown the text we added in the manuscript above. Considering the added text is mostly in Section 7, I put the whole Section 7 here for the convenience of reading.

7. Discussion

The hard-to-quantify factors influencing the lifetime and emissions are discussed here. First, our grid-averaged (about 40 km × 40 km) OH climatology does not resolve the detailed chemical variation within the pollutant plumes, particularly those involving the interaction between SO_2 and OH. Krol et al. (2024) studied the chemistry within the NO_x plumes and observed low OH concentrations near the strong NO_x sources (within an average of 10 km) and enhanced OH away from the sources. This suggests that our 40 km averaged OH climatology cannot

capture this OH decline and may underestimate the SO_2 lifetime near the large NO_x sources. Furthermore, the variation of OH concentration between 10 km to 40 km is roughly limited to 10 % (See Fig. 7b from (Krol et al., 2024). We have considered these effects in our error estimate of the lifetime. Second, we did not consider the heterogenous SO_2 reactions on wet aerosols. We suppose this impact on SO2 lifetime can be neglected in our study. Analysis of the dominant term for conversion in the CAMS system shows aqueous phase chemistry is the dominant term related to sulphate production rather than heterogeneous reactions. We therefore assume wet aerosols are a negligible source term (which typically have low pH for this slow sulphate production). Even though the atmospheric SO_2 in gas phase can convert to aqueous phase and be oxidized to form sulfate on aerosol wet surface or within clouds, these reactions typically occur on hazy days with high relative humidity and PM2.5 level (Ge et al., 2021). These meteorological conditions are generally not favored on days with minimal cloud coverage, as achieving the necessary high relative humidity is difficult with ample sunlight at noon. Finally, we only calculate the lifetime for SO_2 in cloud-free regions, excluding the SO_2 wet deposition and the reactions within the clouds. This is actually the lifetime we need in our inversion since we only consider cloud-free scenes measured by TROPOMI.

With these open questions, I consider the given uncertainties of 35% (monthly) and 10% (annually) to be far too low.

We change the uncertainty to 40% for monthly SO_2 emissions and explain this in the new text between line 380 and 383:

Although the measured SO_2 plume has no interaction with the clouds during the TROPOMI overpass, the SO_2 may interact with clouds before and after this time to influence the effective SO_2 lifetime. Therefore, we take an uncertainty of 40%, which is larger than the averaged uncertainty (35%), for the derived monthly emissions,

3. Implementation of the derivative

The authors state that the analysis was performed on 0.4° grid, on 0.1° grid, and "TROPOMI measured pixels".

It is not clear to me what the latter actually means:

Is the analysis done on a regular grid with 5.5 km × 3.5 km resolution (as indicated in line 267)?

Or is the original "grid" of the TROPOMI measurements (along x across) used for calculating the derivative?

I would not understand the first option, and I see problems with the pixel size changing across the swath.

If the second option is meant, this should be explained and motivated in more detail, and a reference to de Foy and Schauer, 2022, who proposed this approach, has to be added.

We conduct the divergence calculation on original TROPOMI pixels (along · cross, about 5.5 km×3.5 km at nadir). Because this is the finest resolution that we can use to calculate the divergence for TROPOMI data. Although the final emissions are on the same grid size of 0.1°, the divergence calculated on original TROPOMI pixels performs better than the one calculated directly on 0.1° regular grids. Thus, our emission is derived based on the divergence map with the second option. Overall, we suppose the emission map resolution can be improved by enhancing the grid size but will be finally limited by the pixel scale of TROPOMI.

To make it clear, we make the changes in the manuscript between line 279 to 281:

Original sentence: The divergence can also be calculated based on the TROPOMI measured pixels (5.5 km× 3.5 km) and later integrated to the regular grid cells of 0.1°× 0.1°.

Revised sentence: Since the emission map resolution is limited by the pixel scale of TROPOMI, we also calculate the divergence based on the original TROPOMI measured pixels (on an along × across track grid, about 5.5 km× 3.5 km at nadir varying with the viewing angle) and later integrated to the regular grid cells of 0.1°× 0.1° (de Foy and Schauer, 2022).

The information content of the divergence term comes from the change of horizontal flux from one pixel to the next.

For this, a resolution of 0.4° is far too coarse.

I would expect that (a) calculating the divergence on the TROPOMI grid and (b) re-gridding and averaging it afterwards on high spatial resolution (0.05°) yields high-resolution information about the location of SO2 point sources, without the need for modifying the difference quotient.

We use the resolution of 0.4° for the closed-loop validation only. The emissions calculated from the observations are in 0.1° and original TROPOMI pixel scales. Calculating SO_2 emissions at different scales reveals that increasing resolution can reduce but not eliminate the spreading effect inherent in the divergence method. Using different scaling factors further mitigate the effect based on the given resolution. We highlight the limitations of the current divergence method and introduce an improved approach that enable other users to enhance emission map resolution and quality without requiring higher resolution and, consequently, computational cost. Based on the tests we had, we thought the resolution of 0.1° is suitable. There are about 50 out of 450 pixels larger than 5.5×10 km in a line of across-track pixels. Since the TROPOMI track shifts daily and divergence is averaged seasonally, each regular cell captures divergence from both big and small pixels. This can mitigate the error introduced by integrating divergence from large pixels (>0.1°) into a 0.1° grid. In future studies, we will constrain SO_2 emissions in a finer resolution, e.g. 0.05°.

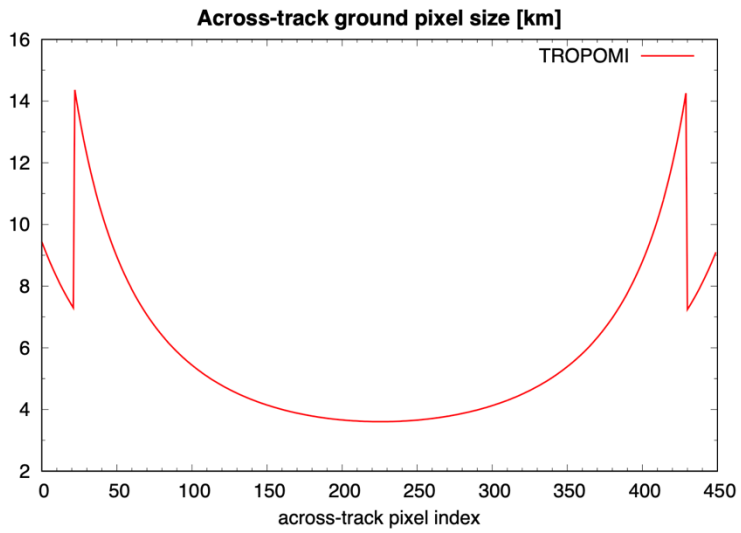

Figure. R3. The across-track ground pixel size of TROPOMI. On average the pixel size across-track is about 6 km.

We change the sentence between line 123 and 125 to:
The spatial resolution for the center of the swath is approximately 5.5 km × 3.5 km (7 km × 3.5 km before August 6, 2019) in nadir, and 5.5 km × 6 km on average over the swath.

Additional comments:

Line 103: "and its divergence": "its" refers to the sink term, whereas the divergence is derived from the horizontal flux.

Original sentence: The flux-divergence method, i.e. adding the independently derived SO_2 sink term and its divergence to obtain local emissions, is used for the emission estimation.
Revised sentence: The flux-divergence method, i.e. combining the independently derived SO_2 sink and divergence, is used to obtain local emissions.

Line 127: Please specify the version of the COBRA SO_2 product.

We use the COBRA dataset v01.00.01 and it is added in the manuscript.

Line 349: This pixel size is valid for nadir. Towards the swath edges, pixels become significantly larger (even larger than 0.1°!)

Most TROPOMI pixels are finer than 0.1°, with about 50 out of 450 pixels per across-track line exceeding 5.5 × 10 km. To make the sentence more precise, we changed the original sentence in the manuscript and show it below.

Original sentence: We subsequently adopt method B to calculate divergence at the resolution of 0.1°×0.1° (about 10 km×10 km) and at the finer scale of the TROPOMI measured pixels (5.5 km × 3.5 km), respectively.
Revised sentence: We subsequently adopt method B to calculate divergence at the resolution of 0.1°×0.1° (about 10 km×10 km) and at the original TROPOMI measured pixels (along × cross, about 5.5 km × 3.5 km at nadir), respectively.

Figure 9: Resolution is poor. Lat/lon numbers should not be bold.

Revised in the manuscript.

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