Author’s response #1

This paper presents a comprehensive understanding of SF_6 emissions worldwide using inverse modeling, which improves our knowledge on global SF6 emissions and their regional (spatial) distributions. It could be the first study that I am aware of presenting SF6 emissions worldwide from an extensive combination of measurements. The manuscript is well-written and well-structured. The analyses are reasonable and conclusions are generally solid. The description of the methods is generally clear. The authors have also acknowledged the uncertainties of the derived emissions and the limitations of the current observation in constraining emissions in several regions including South America etc., and call for attention for enhancing measurement network in these regions, which is important for not only SF6 but others important gases.

The authors have done a very nice piece of work, that will be of interest to the community! I would recommend the publication of this manuscript on ACP. The following are some specific/minor comments, corrections or questions:

We would like to thank reviewer #1 for the valuable and constructive review of our manuscript. The suggestions for improvements were very helpful and we incorporated almost all of them into the final version of the manuscript.

In the response we use 4 different colors. The blue-colored text is the general answer to the reviewer’s comments. Additionally, we show how the text is changed in the manuscript: The original text is colored grey, removed text is colored red, and new text is colored green.

Line 15: I suggest making the potentially increasing emissions in countries other than China (e.g. India) a separate point in the abstract, together with the accompanied uncertainties (arising from the limited measurement sites) which you already stated in point(5). The emissions in these countries are very important for understanding the global SF6 emissions and their variations.

We added:

(5) Our inversions indicate increasing emissions in poorly monitored areas (e.g. India, Africa, South America), however, these results are uncertain due to weak observational constraints, highlighting the need for enhanced monitoring in these areas.

Line 30: I suggest changing concentrations to mole fractions. Concentration is more for something per volume.

done

Line 48: Typo “shwn” to “shown”

done

Line 49: It should be top-down, not bottom-up

done

Line 100: how do you chose the “3h interval”? Auto-correlated errors could still exist within this period (biased systematic errors). Have you tested different intervals?

The choice of this 3h interval is, of course, subjective and can be debated. The choice is always a compromise between getting the most information out of the observation network while trying to limit the effect of error correlations. One option would be a pre-selection of observations in addition to 3h-averaging intervals, (e.g. using only nighttime measurements for mountain stations and afternoon measurements for others, or basing the selection on meteorological conditions (e.g. Lunt et al., 2021)). We also thought about using 1-day averages, but in the end, we decided to stay with 3h intervals for this study, mostly due to the generally limited number of SF_6 observations (especially at the beginning of the study period) and the concerns of discarding too much information.

Line 111: I would like to know more about this 50-day back-trajectory duration. Why do you choose 50 days? Will the uncertainties from the Lagrangian dispersion model increase rapidly when running time grows? I believe it is not a primary task of this study but I suggest adding a brief explanation of the period chosen here in the Method section. You give some details in Lines 261-265 but I do not think the Figure 5b is enough to illustrate your statement in the text.

Certainly! The choice of the backward simulation period was motivated by our last study (Vojta et al. 2022), where we tested the effect of different simulation periods (1-50 days). On one hand side, we found that 50 day-simulation periods resulted in the best model-measurement agreement (e.g. correlation, MSE, Bias). Further, inversion results became less sensitive to large biases in the a priori emissions, when increasing the simulation period from 10 or 20 to 50 days. On the other hand side, observations are most sensitive to emissions occurring during the first few days of the backward simulation and the spatially resolved information content decreases with temporal distance to the measurements, as virtual particles are spread over larger areas. While, with longer simulation periods, more emissions become accessible to the inversion, it also becomes more difficult to extract information on individual emission sources. The benefit obtained from every additional simulation day will, therefore, typically decrease, while computational costs grow. The error of individual trajectories will also grow, however, as simultaneously also the retro-plume grows, we think that the error of single trajectories becomes less and less important (due to the statistical approach of FLEXPART looking at average residence times rather than the individual trajectories). However, if longer model runs result in biases (e.g. unphysical accumulation of particles) this will set a further limit to the simulation period, in addition to the computational resources. Therefore, we also didn’t want to exceed the tested 50 day period and additionally, computational costs of the LPDM runs for the used extensive dataset were already very high.

About the lines 261-265, We agree. We still think, it is very nice to see, that with 50-day simulation periods, there are increments over the baseline caused by emissions within the last 50 days, even at a remote station like Ragged Point and the optimization of these emission contributions can be seen. However, it is of course true that we don't show the situation for shorter periods. For this, we refer the read to Vojta et al. (2022).

We added:

The choice of the 50-day simulation period was motivated by the findings of Vojta et al. (2022) who tested the effect of different simulation periods (1-50 days), and found that 50-day simulations resulted in an improved model-measurement agreement and in more robust inversion results in comparison to shorter periods (e.g. 1, 5, 10, or 20 days).

And removed:

"Figure 5b further illustrates the advantage of choosing a rather long 50-day backward simulation period. With this long simulation period, we can see that this remote station is also directly influenced by emissions (i.e., enhancements over the baseline) that can be directly optimized. With shorter simulation times (e.g., 5-10 days), no emission contributions above the baseline could be seen, thus rendering this station useless for emission optimization. For a detailed discussion about the LPDM backward simulation period see Vojta et al. 2022}."

Line 119: I suggest adding the observation error term to eq (1).

In this case we would like to keep it as it is, as y represents the modeled mole fractions

Line 133: I suggest changing "cannot be determined well" to "may not be determined well". You need to combine with your error reductions to decide whether these emissions can be constrained well, which I suggest adding in the results and discussion section.

done

Line 157: Here you are using the "UP" a priori emissions to drive the baselines. What is the reason for choosing this? You stated later that you cannot determine which prior is better (Line 239-240), but eventually find in line 448 that EDGAR is actually the most reliable estimate for SF6 emissions. Why not using EDGAR in generating the mole fraction field?

Yes, we concluded that EDGAR provides the best estimate for the total sum of all the emissions in poorly covered regions. On the other hand, we also saw that EDGAR is overestimating emissions in the U.S., so the choice is not totally clear and dependent on the region. Overall, indeed, EDGAR might be better suited for generating the mole fraction field. However, that is an outcome of our study and we didn't have this information when we produced the mole fraction fields. We also thought it wouldn't be right to use this outcome a priori and re-calculate the mole fraction fields (apart from the very high computation costs), since this would mean to use a posteriori information as an input to the inversion. Further, tests showed, that the produced 3-d fields were not very sensitive to the emission inventory used. The comparison between the produced mole fraction fields and the measurements showed a very good agreement (also for observations not used for nudging), so we were quite happy with the produced fields.

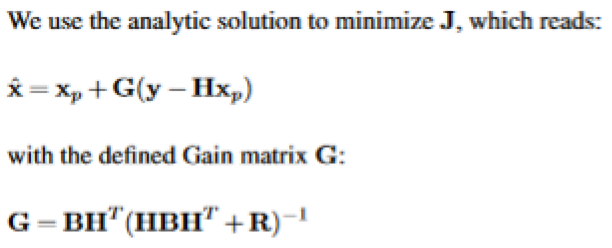
Line 219: It is good to show the available number of observations each year.

We added: .... "ranging from a minimum of 5841 (2005) to a maximum of 11901 (2016), which is related to the number of available observations each year (see Fig. S1)"

Line 226: Eq (3), I would like to know whether you apply the same inequality constraints for a posteriori baselines? Give more details of how the baselines, posterior error matrix for emission and baseline, prior and posterior uncertainty for y (observation error matrix) etc. are determined or calculated.

No, the inequality constraint was only applied to the a posteriori emissions:

Certainly, we added:



We use the analytic solution to minimize $\mathbf{J}$, which reads:

$$\hat{\mathbf{x}} = \mathbf{x}_p + \mathbf{G}(\mathbf{y} - \mathbf{H}\mathbf{x}_p)$$

with the defined Gain matrix $\mathbf{G}$:

$$\mathbf{G} = \mathbf{B}\mathbf{H}^T(\mathbf{H}\mathbf{B}\mathbf{H}^T + \mathbf{R})^{-1}$$

and:

"FLEXINVERT+ assumes a diagonal observation error covariance matrix R, and therefore, does not account for possible error correlations. The diagonal elements represent the sum of measurement and model errors, where we assume the latter to be dominant. Our error estimates are based on a number of initial inversion runs, where we assessed the model error according to the a posteriori model residuals (difference between observed and a posteriori simulated mole fractions), and such that the reduced chi-square value (the value of the cost function at minimum divided by the number of observations and divided by 2) is close to 1. The a posteriori emission error covariance matrix **B** is calculated as

$$\hat{\mathbf{B}} = \mathbf{B} - \mathbf{GHB}$$

Line 230ff: Do you show the results of the sensitivity tests somewhere? I would suggest doing so in Supplement.

We added a section about sensitivity tests in the supplements and added:

(see Sec. S7)

Line 243: suggest revising it to "observed and modeled mole fractions (before and after the inversion) at the Gosan observation station....., using the E7P emissions field as the a priori in the inversion", to make it clear.

done

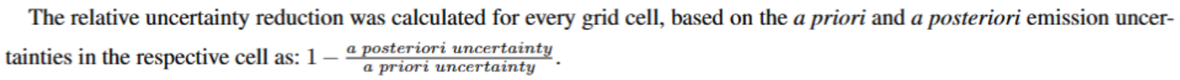
Line 259: define "detrended" here when it first appears.

We added:

(detrended; i.e. removing the 2005-2021 trend from the time series)

Line 268: add how you calculate the uncertainty reductions in the Methods section. It will be easier for readers without inversion expertise. Do you use the Averaging Kernal? Will the posterior uncertainties the same with analytical solution when no inequality constraints are used?

We added to the methods section:

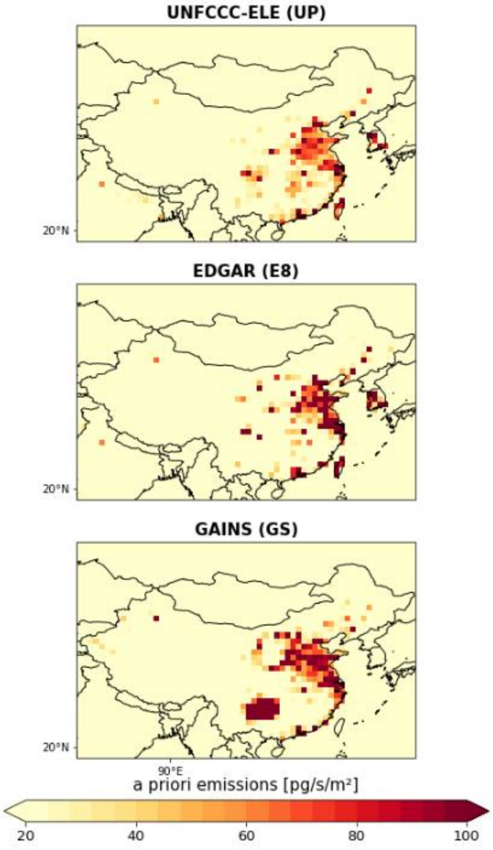


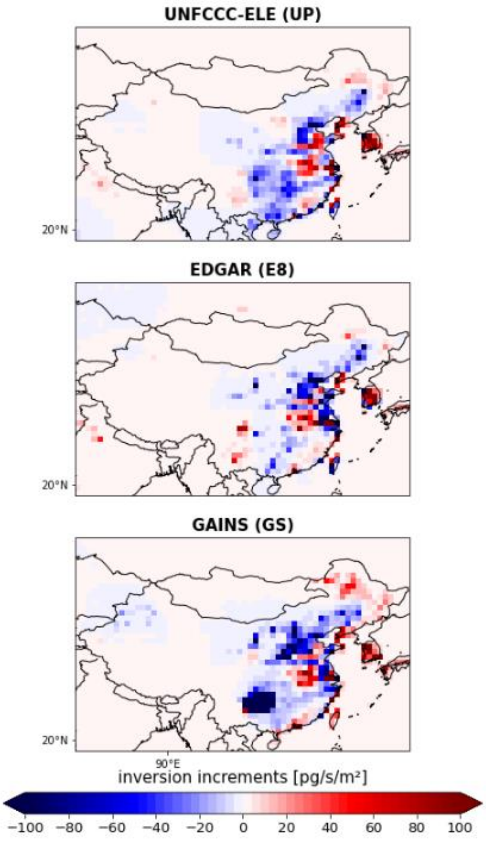
The relative uncertainty reduction was calculated for every grid cell, based on the *a priori* and *a posteriori* emission uncertainties in the respective cell as: $1 - \frac{a\ posteriori\ uncertainty}{a\ priori\ uncertainty}$.

The inequality constraint only affected the *a posteriori* emissions but had generally only little effect on the inversion results. The a posteriori uncertainties were not affected.

Figure 6: I am curious about the increments in the very northeast region of China. In the prior distribution, emission is already very high in this region. Is there any explanation for this? In addition, you are using the average of different variations of a priori as the inversion results, but here you are showing the increments and uncertainty reductions for only one of the variation. Suggest showing the average here, or show plots for all the variations in a separate supplement file.

Yes, the values in the very northeast region of China appear very high due to the logarithmic color bar. We also thought about using linear color bars, as this might be favorable for individual countries (such as China), however, for the global emission distribution one needs a logarithmic scale, so we decided to go with lognormal color bars. When we use a linear color bar for the Chinese a priori emissions and increments comparable to e.g. An et al. 2024, those high values “disappear”, and emissions appear in a similar (maybe more familiar) pattern. However, in case of the GAINS inventory higher positive increments can be seen in the northeast region compared to EDGAR or UNFCCC-ELE.





We included the 3 remaining a priori emission fields, increments, error reductions and all 6 *a posteriori* emission fields in the supplements.

Figure 7: I would like to see the separate posteriori emission spatial distributions from 6 different prior distributions. Also, in Line 235-236, you claim that inversion results using different variations are similar, I suggest showing them in SI Figure.

Done – see last comment

Line 304: I hope you can discuss a bit about the interannual variations in the posterior emissions, e.g., the increase in 2019-2020 then drop. I am curious if the authors have any insight into this.

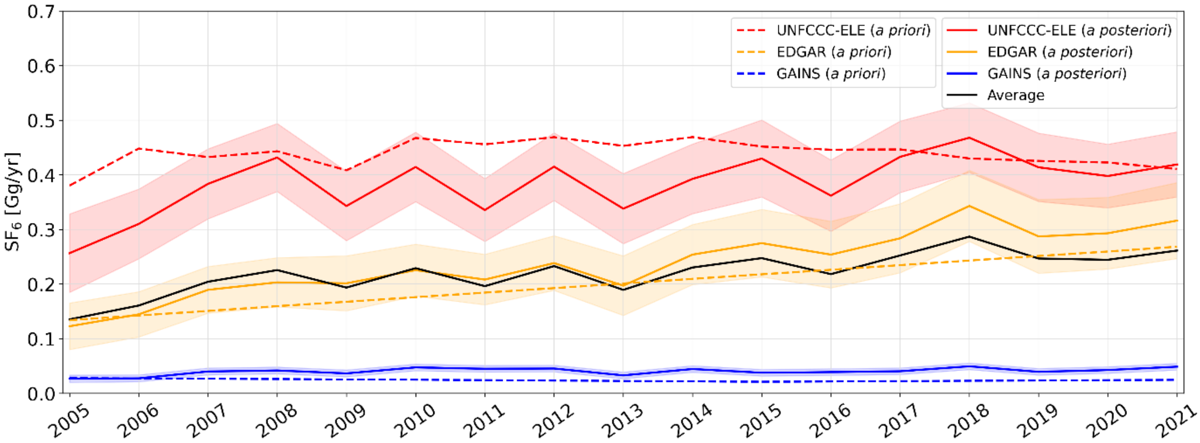
Yes, we thought a lot about this peak in European emissions in 2021, but our ideas were all too vague to imply it in the discussions. An obvious suspicion would of course be, that it is related to the start of the Corona pandemic. Maybe maintenance of equipment and control mechanisms were reduced in that period, leading to more leakage. However, we could not find any more indication for this suspicion. Another idea was, that it is related to the emissions from soundproof windows. Especially in Western Europe, starting in 1975, SF_6 was filled in double-glazing windows to dampen acoustic pressure and improve the sound-insulating effect. In Germany, for instance, six percent of the manufactured and installed glazing contained SF_6 in 1990. Since the end of the 90's there was a transition away from the use of SF_6 for windows and the EU banned its use in 2008. The expected lifetime of soundproof windows is about 25 years and emissions of soundproof windows are still substantial in Germany (estimates are around 0.13 Gg/yr which is a huge fraction) and therefore also in Europe (since Germany is by far the biggest emitter in Europe and we see the same peak if we only look at German SF_6 emissions). Regarding this timeframe, it would fit that around 2020 the lifetime of a lot of windows that were built in the 90's come to an end which could lead to an emission increase followed by a decline. However, it is not so likely that a gradual replacement of such windows would cause a clear peak in a single year. The least exciting explanation would be, that this peak is a result of methodological uncertainties. Many inverse studies seem to show unrealistic interannual variability in posterior emissions, which could have its origin in the interannual variability of available observations, model errors, or a poor characterization of the emission and observation uncertainties. The 2020 peak is not particularly pronounced, so could well be an artifact.

Line 351: the citation here is the conference abstract version and I do not think they provide insight into whether there is any underestimation from Simmonds et al., neither in An et al. 2024. Perhaps just remove the citation here. As you claim that your emissions in China are more influenced by Gosan site, you can look further in to the reason for the difference between Simmonds and other emissions, rather than refer to a previous publication.

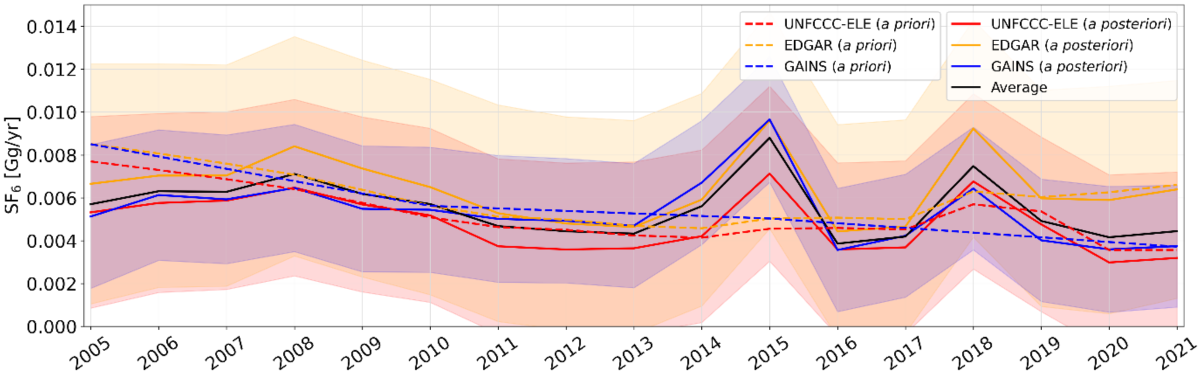
Yes, we removed the citation!

Line 359ff: I suggest that the discussion of emissions in these potentially less-constrained regions is accompanied by the discussion of error reductions. For GAINS prior, have you tried to increase the prior uncertainty and test it? You stated in the methods part that you did the relevant sensitivity tests with different prior emission uncertainties. I am afraid the inversion cannot constrain this region at all when using GAINS prior (no error reduction in Fig. 6).

Yes, for these regions the minimal a priori emission (and thus, also assumed uncertainty) is the driving variable. In some regions, e.g. Africa, we saw, that increasing the (minimal) emission uncertainty by a factor of 5 resulted in higher GAINS *a posteriori* emissions and a positive trend (see Figure below), which appears reasonable when comparing to the other inventory estimates. So, while the inversion is of course limited in these regions, we think that results could give at least an indication of the direction in which emissions should be corrected. We think the error reduction alone might give an incomplete picture here. It depends a lot on the estimated a priori emission uncertainty and on the a priori emission field itself. While the inversion very likely can not improve priors close to the "true" values in these regions, it is more likely to reduce large biases. Also, we see that the inversion leads to a positive trend for all tested a priori fields.



In other regions, e.g. Australia, also higher assumed prior uncertainties (5 times higher minimal a priori emission error - see Figure below) do not substantially change inversion results except leading to more inter-annual variability.



Line382: "see Sec. 3" in the bracket. please specify the specific section here for the prior uncertainty assignment.

done

Line 402ff: for AGAGE 12-box global SF6 emissions, you can refer to the latest ozone assessment report (providing emissions up to 2020) or An et al. 2024 (providing emissions up to 2021).

[Laube, J. C. & Tegtmeier, S. Chapter 1: Update on Ozone-depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol. in *Scientific Assessment* *of Ozone Depletion: 2022* vol. 278 (World Meteorological Organization, Geneva, Switzerland, 2022).

An, M. *et al.* Sustained growth of sulfur hexafluoride emissions in China inferred from atmospheric observations. *Nat Commun* **15**, 1997 (2024).]

Yes, thank you. We exchanged the extrapolated values with the updates from 2019-2021.

We changed the corresponding text to:

To judge the quality of our a posteriori global emission, we compare our results with the global emissions calculated by Simmonds et al. (2020) for the years 2005 to 2018 using the AGAGE 12-box model (e.g., Rigby et al., 2013), which we linearly extrapolated until 2021. -> To judge the quality of our a posteriori global emission, we compare our results with the global emissions calculated by Simmonds et al. (2020) for the years 2005 to 2018 and updated until 2021 (An et al., 2024; Laube et al., 2023) using the AGAGE 12-box model (e.g., Rigby et al., 2013).

And some values in the comparisons slightly changed:

….while the UNFCCC-ELE \textit{a posteriori} global emissions are on average **16%** higher. -> ….while the UNFCCC-ELE \textit{a posteriori} global emissions are on average **18%** higher.

….emissions show on average almost no bias (**0.1%)** compared to the reference values -> emissions show on average almost no bias **(<1%)** compared to the reference values

The average of the total global emissions of the different discussed cases provides a very good estimate for the global SF6 emissions, showing an average bias of +**1,4%** compared to both, the AGAGE box model and the NOAA growth rate emissions ->

The average of the total global emissions of the different discussed cases provides a very good estimate for the global SF6 emissions, showing average biases of +**2,2% and 1.4%** compared to the AGAGE box model and the NOAA growth rate emissions

with average biases to the box model and NOAA growth rate emissions of **+16%, 0.1%, and -15%** for UNFCCC-ELE, EDGAR, and GAINS respectively

with average biases to the box model and NOAA growth rate emissions of +**18%, -15%, and <1%** for UNFCCC-ELE, GAINS and EDGAR respectively.

Line 418-419: I do not believe this could be the case. The ocean is very heterogeneous and the ocean flux is highly dependent on the locations (see Gruber et al. 2001). I suggest you discuss the potential uncertainties from that previous study you cite (Ni et al. (2023)) arising from scaling measured flux from a region (with potential strong sink) to global (with strong sources at other regions). Your explanation in lines 425ff seems plausible. Also, in this paragraph, always clarify that the overestimation is specific to the UNFCCC-ELE inversion, not all the inversion in the study, to avoid confusion.

[Gruber, N., Gloor, M., Fan, S.M. and Sarmiento, J.L., 2001. Air-sea flux of oxygen estimated from bulk data: Implications for the marine and atmospheric oxygen cycles. *Global Biogeochemical Cycles*, *15*(4), pp.783-803.]

We agree that the estimates of Ni et al. are probably highly uncertain and added:

They estimated this global oceanic sink by scaling up calculations of sea-air fluxes based on simultaneous measurements of SF_6 concentrations in the atmosphere and surface seawater of the Western Pacific and Eastern Indian Ocean. However, since the ocean fluxes are highly inhomogeneous (strong oceanic sources might exist in other regions), we suspect the up-scaled estimate to be very uncertain. Nevertheless, we

……

increase of the global emissions by the inversion -> increase of the global **UNFCCC-ELE** emissions by the inversion

There is a better explanation for our too-high \textit{a posteriori} emissions. -> There is a better explanation for our too-high \textit{a posteriori} **UNFCCC-ELE** emissions.

L440: "underestimation of the emission residuals between the global and the Chinese emissions", clarify that it is in GAINS prior emissions.

done

L454-456: consider the uncertainties for the trend for both global and China.

We changed:

Notice that the average global trend of 0.20\;Gg/yr is slightly smaller than for Chinese emissions (0.21 Gg/yr), supporting the finding of An et al. (2024) that Chinese emissions alone have offset the overall decreasing emissions from all other countries --> Notice also, that the average global trend (0.20 Gg/yr) is similar to the Chinese emission trend (0.21 Gg/yr),

L457-458: state here that your bias may be especially in the poorly-observed regions.

We added:

Despite some potential problems with our inversion setup that can lead to biased a posteriori global emissions (as could be clearly seen and explained with the UNFCCC-ELE and GAINS a priori emissions in poorly-observed regions)

Line 488-490: is there any result to support your statement here that your results are mainly driven by the high-frequency data in the U.S.? In addition, you can also have a look at the mole fraction enhancements, either in the observations or the posterior simulated ones, to check the seasonality in mole fraction enhancements. Do you have any data with reference (e.g., the high power transmission in summer in Line 490-491) to help justify your seasonal cycle?

No, you are right, this was more of an assumption.

We rephrased:

In addition, our inversion results for the USA are mainly driven by the high-frequency measurements from Trinidad Head (THD) and Niwot Ridge (NWR), which have not been used by Hu et al. (2023) -> In addition, high-frequency measurements from Trinidad Head (THD) and Niwot Ridge (NWR), have not been used by Hu et al. (2023)

Yes, thank you, we actually looked at observed mole fraction enhancements at background stations, however, those analyses didn't provide us with a clear picture.

Yes, for instance, data from the U.S. Energy Information Administration. We added:

(see e.g. https://www.eia.gov/electricity/).

Line 520ff: Again, you need to consider the uncertainties. If the two trends are not significantly different, then I suggest you remove this bit in the conclusion. In addition, I suggest also mentioning that the China's official voluntary reports are improved in the latest reports compared to the top-down results (Figure 10), and also discussing this in the main text.

We added:

The values from the more recent reports in 2017 and 2018 are, however, closer to our inversion results, indicating an improvement in Chinese reports.

We removed:
The derived trend is slightly steeper than the global total SF$_6$ emission trend (0.20 Gg/yr), supporting the suggestion that Chinese emissions alone have more than offset the overall decreasing emissions from other countries \citep{Minde_an_2024}

We added: however, the latest reports in 2017 and 2018 seem to be improved.

References:

Lunt, M. F., Manning, A. J., Allen, G., Arnold, T., Bauguitte, S. J.-B., Boesch, H., Ganesan, A. L., Grant, A., Helfter, C., Nemitz, E., O'Doherty, S. J., Palmer, P. I., Pitt, J. R., Rennick, C., Say, D., Stanley, K. M., Stavert, A. R., Young, D., and Rigby, M.: Atmospheric observations consistent with reported decline in the UK's methane emissions (2013–2020), Atmos. Chem. Phys., 21, 16257–16276, https://doi.org/10.5194/acp-21-16257-2021, 2021.