Comment on egusphere-2023-208

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Referee comment by Mary Whelan (mary.whelan@gmail.com) on “Sources and sinks of carbonyl sulfide inferred from tower and mobile atmospheric observations” by Zanchetta et al., Biogeosciences Discussion, https://doi.org/10.5194/egusphere-2023-208, 2023.

Dear Authors,

An understanding of atmospheric OCS sources and sinks enable the ability to ascertain plant functioning on an integrated, regional scale inaccessible to other methods. This manuscript presents an effort in untangling OCS gross fluxes over a specific region. Some additional analysis and editing are needed to realize the potential of the study. Below I have some major questions followed by a few minor ones.

The authors would like to thank the referee for the generally positive comments and for the insightful remarks and questions.

The responses will be organized question-by-question in paragraphs formatted similarly to the present one. Major modifications in the preprint will be presented as underlined text together with their respective page and line numbers.

For the first investigation that Kooijmans et al published in 2016, there is an entire year of calibrated data, but the additional data presented here is at a single tower measurement height for 2 months without a calibration cylinder? Is there something missing in the description in the text?

***Answer**: the measurements in January and February 2018 were only performed at 60m height due to necessary maintenance work on the 7m and 40m height sampling lines. Moreover, as the referee correctly underlines, no target cylinders were measured in that period. However, as stated on page 5, line 16: “A reference cylinder was measured every half hour to correct for instrument drift and to calibrate the measurements to the common scales”. Therefore, there was no target gas to independently assess the stability of the measurements, but it was made sure that the measurements were corrected for drift and that they all fell within a common measurement scale.*

In this study, the tower footprints over time were calculated by STILT and the concentrations of the tower were calculated based on assumed fluxes at the surface. Attribution was estimated on page 13 based on footprints during periods of trace gas enhancement.

If we want to do something truly powerful with this data, we can take the known flux estimates as priors and generate new maps of surface fluxes based on observed concentrations at the tower (averaged over afternoons where nighttime inversions have already been dispensed with. Calculating footprints when the PBL is on the move, e.g. at midnight, is error-prone.) This atmospheric inversion would give you a stronger, data-based hint about where the missing sources of the region are and requires no further field measurements.

That said, the uncertainty introduced by using the STILT model is not sufficiently addressed. Derek Mallia at the University of Utah writes articulately about the STILT model and it's application to regional fluxes. The recent update to the STILT model – which version did you use? – makes the analysis more user friendly than previous versions. There has also been work done by Anna Michalak's group in analyzing uncertainties in this type of analysis.

Answer: *the authors agree that an atmospheric inversion approach in combination with tower measurements could provide a powerful tool to locate missing sources at a regional level. The authors also believe it could be interesting to work on a comparative study, to investigate how well local or regional sources inferred from an atmospheric inversion and measured ones would agree. However, the application of this method may be over the scope of this study, which rather aims to introduce a measurements-based technique to identify local sources that could bias tower measurements. A thorough evaluation based on forward model runs and a detailed quantification are prerequisites before applying an inversion. Also, the conclusions from an inversion would be stronger if measurements at several stations rather than at one station could be used to cover a region, which will actually be investigated in our followup study.*
*The STILT model was based on ECMWF-IFS cycle 47r1 (see https://confluence.ecmwf.int/display/FCST/Implementation+of+IFS+Cycle+47r1). The authors acknowledge that uncertainties in transport were not addressed quantitatively and that the inversion modelling approach was not evaluated thoroughly. However, this footprint analysis was performed to identify areas of influence for Lutjewad measurements. Secondly, it aimed to give an order-of-magnitude estimate of the possible impact of newly discovered sources on stationary measurements. Concerning the first application, the authors did not quantify uncertainties in particles transport and footprint locations. Nonetheless, both the extension of possible areas of influence and the spread within anthropogenic COS fluxes magnitude (0-500.4 pmol/(m^2*s) for direct COS, 0-1421.5 pmol/(m^2*s) for CS_2) provided information that the authors considered to be reliable enough for the identification of influential zones (an example is provided in Figure A below, <u>which has also been included in the main text as a replacement of Figure 2</u>). With regard to the impact of newly found sources on the measurements, instead, the uncertainty on fluxes was estimated by performing a Monte Carlo simulation (see Section 3.4 in the preprint), but there was no quantitative assessment of uncertainties for the footprint output. The only sensitivity analysis was applied to CS_2 lifetimes (3 to 10 days) and led to minor differences. The authors acknowledge that this approach is approximated and that*

major uncertainties may arise in particular from the Planetary Boundary Layer height and convective vertical transport. However, these results were considered sufficient for the desired order-of-magnitude estimate and to prove that, on specific dates, local sources could have actually biased stationary measurements in Lutjewad significantly.

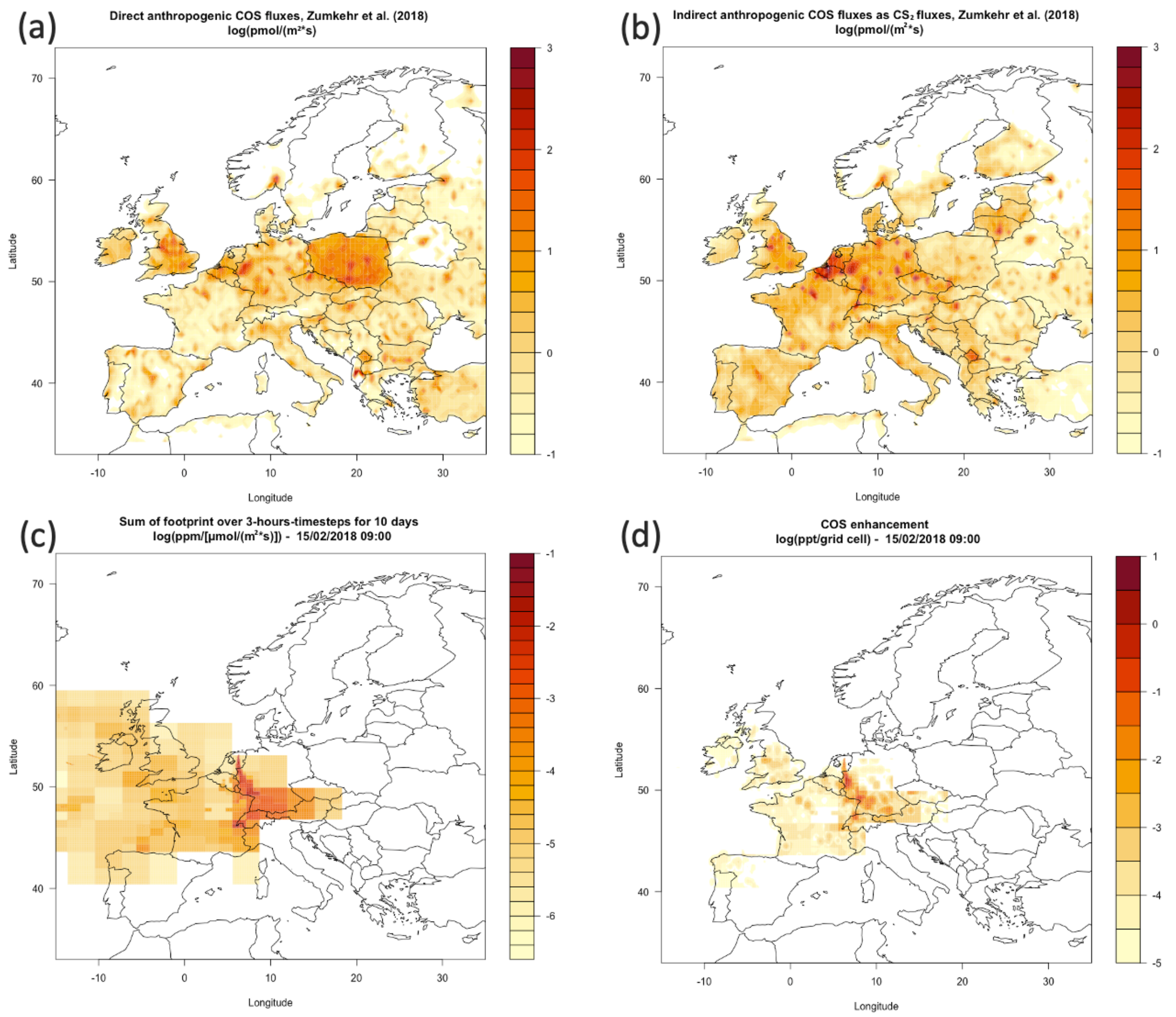


Figure A: (a) direct and (b) indirect anthropogenic COS fluxes, (c) footprints calculated by the STILT model (d) localized effects on Lutjewad measurements obtained by combining (a), (b) and (c) – see main text in the preprint (Sections 2 and 3) for a thorough description.

The analysis in 3.1 may belong in the supplement with Figure S1. It is a look at wind direction and deviation from a calculated seasonal average. Using the flux-gradient method or approach, a flux estimate could be made based on concentrations measured at two different heights (along with high frequency wind and temperature data). However, the conclusion of the analysis here is unsatisfying – we are no closer to knowing the sources and sinks of OCS in this region, but rather again acknowledge that atmospheric mixing affects OCS concentrations. At the same time, it seems like a great effort was made to calculate nighttime fluxes with Rn, with no further use of the flux estimates.

***Answer**: the authors agree that referring to sources and sinks in Section 3.1 would be an overstatement. The title has been modified as "<u>Observed deviations from seasonal cycles by wind directions during stationary measurements</u>". Section 3.1 and Section 3.2 report the results that contextualized the measurements and the model applications described in the following paragraphs. However, the authors recognize that Section 3.1 and the consequent discussion in Section 4.2 are not well contextualized within this study. They were therefore moved to the supplementary material as Section S1 and Section S1.1, respectively. New numbers were assigned to the remaining Sections in the main text, following the new structure. With regard to Rn measurements, they were performed to identify soil emissions and, consequently, the nighttime COS and CS_2 fluxes described in Section 3.1 (previously Section 3.2). The following sentence was introduced in Section S1.1:*

"In general, we find depletions of COS only coming from inland, which is likely driven by terrestrial vegetation and soil. <u>This last, in particular, was measured to be a COS sink during nighttime, as reported in Section 3.1.</u>"

*Further applications of these findings within this study were rather limited. SiB4 data for Lutjewad were requested only for January and February 2018. The average COS nighttime flux was estimated at Lutjewad coordinates over these two months and resulted to be -2.1 ± 0.2 pmol/(m^2*s). On page 10, Lines 22-24, the following sentence was added:*

"<u>The average SiB4 COS nighttime (9PM – 6AM) flux was retrieved for Lutjewad (53.4°N, 6.3°E) for January and February 2018 and was estimated to be -2.1 ± 0.2 pmol m^{-2} s^{-1}</u>." However, in spite of the limited application presented with the current data, the authors believe these results could provide valuable knowledge for further analyses and/or flux modelling in future studies.

This study misses some context. For example, there are other places in Europe collecting OCS concentration data and an extensive N American dataset that could be used to figure out the seasonal cycle. Some recent efforts to better quantify anthropogenic sources by Sauveur Belviso, who I see has already reviewed this manuscript, would be prudent to include in the interpretation.

In short, this project moves us towards answering several interesting questions in our community, but the analysis is incomplete.

***Answer**: this remark is consistent with the comments of the other referee (*Sauveur Belviso*) for this study. The authors agree that a further contextualization was needed for this case study, in particular concerning other measurement sites in Europe. The following text has been added to the manuscript:*

Page 3, Lines 21-28: <u>Tropospheric COS molar fraction is only monitored in a few sites in Europe. Among these, four monitoring sites are located in Western Europe, within 48°N and 53°N: Mace Head, Ireland (Montzka et al., 2007), Gif-sur-Yvette and Trainou, France (Belviso et al., 2022) and Lutjewad, the Netherlands (Kooijmans et al., 2016). Moreover,</u>

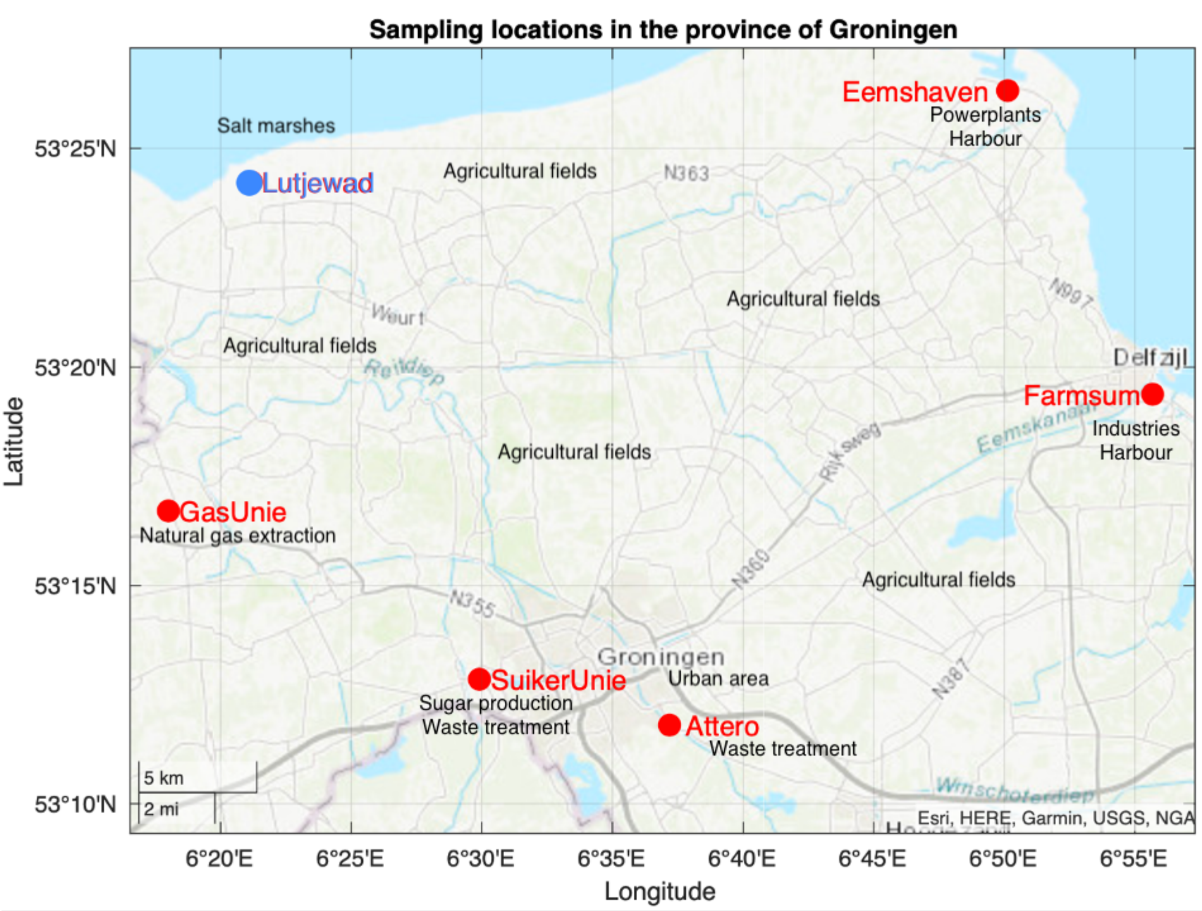
COS has been recently monitored discontinuously in Utrecht, the Netherlands (Baartman et al., 2022). Comparing these observations show higher autumn and winter COS molar fraction in the Netherlands than in the comparable sites listed above. This calls for a more thorough investigation of possible local sources in the Netherlands at a local and regional scale.

Page 20, Lines 19-23: This approach, combining COS stationary measurements, mobile measurements and models, could be applied in other existing measurement locations. It could allow a broader assessment of local anthropogenic influences, to prevent biases in COS budget and seasonality estimates.

Minor Comments

Figure 1 and site description: the site description gives context to the Lutjewad tower that is lacking in the map. Maps are difficult to make well and I found myself sketching a separate map to understand the greater context. It would be useful to mention that the ocean, aluminum smelting, wetlands, and winter wheat are all known sources of atmospheric OCS. Figure 1 and several other figures need a more robust caption.

Answer*: the authors agree that the map could have been drawn in a more informative way. Figure 1 and its caption were modified as follows:*



<u>Figure 2: location of Lutjewad and of the sampling locations in the province of Groningen (NL). The map reports also the major features of the sampling locations and their surrounding areas. Only the locations where emissions were detected will be described in the text.</u>

Table 1: Is ploughing a source of OCS? Or is the ploughed soil?

Answer*: currently, it is believed that the source could be identified in outgassing from the ploughed soil. However, the emissions in this case could not be distinguished between ploughing activites (e.g. agricultural vehicles, fertilization) and ploughed soil. The "source type" description was therefore modified to <u>Ploughing, soil</u>.*

P6, L18: Mentioning why these extra cylinders were collected would be helpful here, even if the details are included in the supplement.

Answer*: it is unclear to the authors if the referee was referring to the standard cylinders or to the sampled flasks. Regarding the cylinders, the authors believe that the whole measurement technique and its relative calibration procedure, described in Kooijmans et al. (2016), have been summarized thoroughly in Section 2.2.1. To make it clearer to the reader, the paragraph at page 6, lines 11-18 was modified as follows:*

"<u>Field standard cylinders are calibrated against NOAA standards in the laboratory before and after each measurement period, to test for drift in molar fraction of gas species</u>. The COS mole fraction measurements of nine cylinders are available, and five cylinders changed less than 2.5 ppt/year, two cylinders decreased by ~10 ppt/year and 2 cylinders decreased by ~30 ppt/year. The four cylinders that drifted more than 10 ppt/year were not used as reference cylinders in the data processing. All of the cylinders were uncoated aluminum cylinders, which, according to experience at NOAA, are more prone to COS mole fractions drift than Aculife treated aluminum cylinders."

Regarding the flasks, the paragraph at page 6, line 20 was modified as follows:

"<u>To investigate COS seasonal cycle amplitude in Lutjewad,</u> besides the in-situ measurements, we also measured flasks that were sampled at 60 m…"

P7, L17: Emission rather than exhalation? Or is this a term specific to Rn?

Answer*: exhalation is indeed a specific term for Rn.*

P7, L23-24: Is simply taking the average the "done" thing for dealing with Rn emission variability? Can you cite another group or two who have done this and perhaps did a sensitivity analysis or similar?

Answer*: this is also a specific method for Rn exhalations estimates (Alhamdi & Abdullah, 2021; Levin et al., 2021; Thabayneh, 2018). In particular, Levin et al. (2021) focuses on* *radon-tracer method applications and limitations and, while stressing the advantages of high-frequency measurements and a day-to-day variability oscillating between ±10% and ±30%, employs monthly averages in their analyses.*

P7, L26-27: The methods are cited, however, can you give a 1 sentence explanation for why the method only works at night? It seems earlier in the paragraph there is a comparison between daytime and nighttime PBL. While we'd expect photosynthesis to cease at night, making the nighttime fluxes easier. Is that's what's happening here? I know you cite the papers that include more detail on the methods and I could read those and piece it together myself, though as it stands the paragraph here is confusing.

Answer: *more than a photosynthesis issue, it is a convection issue: given that the ^{222}Rn-tracer method is based on vertical gradients in stable (non-convective) conditions, in presence of (vertical) turbulence the method becomes difficult to apply.*

An example is given for clarification, citing van der Laan et al. (2010): "Another source of uncertainty is the fact that the ^{222}Rn flux method is based on (vertical) atmospheric gradients which are observed mostly in the evenings and nights when the atmosphere is in general more stable (Fig. 10). Our method is therefore less suitable for estimating surface emissions in the afternoon when vertical mixing is more pronounced. Most of the day is, however, well covered and also the traffic peaks in the mornings and evenings are generally included in our data set. Figure 10 shows furthermore that there is no significant correlation between the height of the flux and the time of the events, which is probably because each event represents a single integrated value that usually includes emissions over several hours during day and night.".

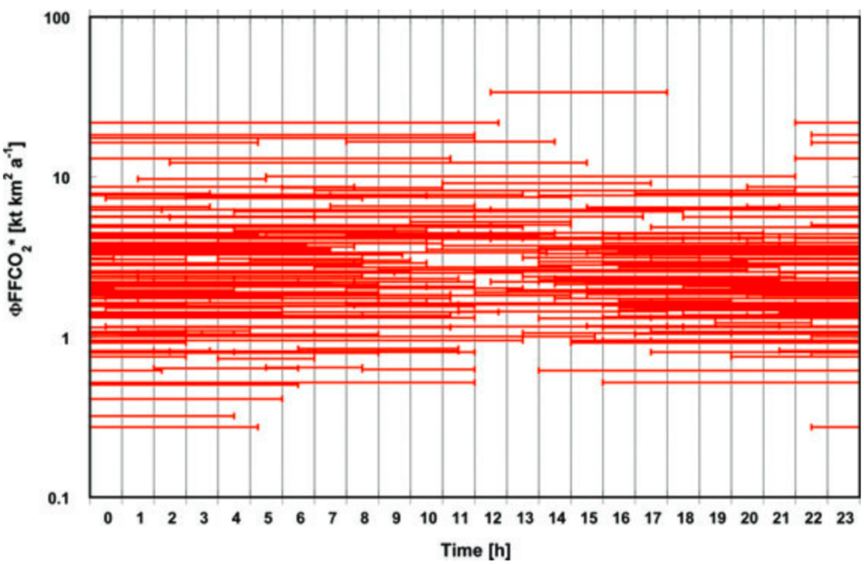


Fig. 10. Distribution of the selected events during the day. Fewer events are observed during 10:00–16:00 when vertical mixing is more pronounced.

P8, L13: What does it mean for a footprint to be negligible?

***Answer**: typically, footprint values decrease with the timesteps taken from the start of the simulation. An example is provided in Figure C. This trend changes for every simulation, depending on the parameters leading the model. In the example provided, which refers to 15/02/2018, 9:00 AM, the sum of footprint values starts at 0.57 for the first timestep back in time and decreases to ~0.001 at timestep 38 (4 days and 6 hours back in time), after which it remains stably at 0. For other simulations, these conditions were reached after 8 to 9 days (64 to 72 timesteps). For clarity, page 8, lines 23-26, were modified as follows: "<u>In this analysis, footprints are reliably negligible (their sum over the selected domain being at least 3 orders of magnitude lower than the beginning of the simulation) after 8 to 9 days. Therefore, the simulation timespan is set on 10 days to confidently cover all the potentially significant footprint values</u>".*

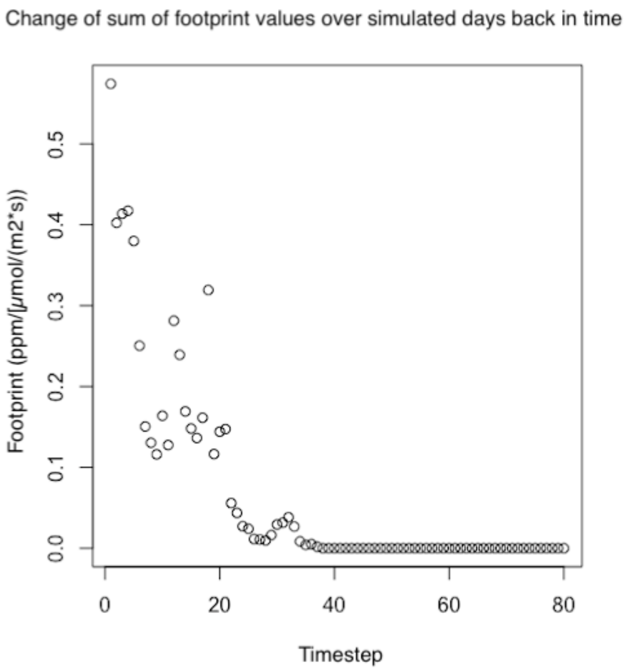


Figure C: sum of footprint values over timesteps from the start of the simulation (3-hours timesteps for 10 days, for a total of 80 days).

P16, L25: For a guassian distribution to be a useful model here, certain assumptions must be met. A justification of these would be useful here.

***Answer**: the authors acknowledge that major simplifications were made to apply the Gaussian dispersion model for these estimations. The peaks measured during the mobile sampling campaign closely followed a Gaussian shape. Unfortunately, there were no 3D-sonic measurements coupled with this sampling campaign. Furthermore, in most cases the exact source of the emissions remained unknown (e.g. it was not possible to see any industrial chimney, or there was no visible plume). Therefore, it was necessary to assume that emissions occurred at the sampling height. The emissions were reconstructed using the parametrization of σ_y and σ_z defined after Pasquill-Gifford stability classes (Csanady, 1973), estimated after a Monte Carlo simulation based on distance from the source and wind speed (obtained from approximated estimates from Google Maps and weather data).*

This, in fact, results in fluxes uncertainties that range between 44% and 92% of the estimated flux means. The authors would like to stress that the Gaussian plume modelling was applied to obtain some rough estimate; the used approach is not considered a reliable representation of reality, but rather a tool to get the best estimate possible given the available data.

P17, L19 and on: this goes into discussion rather than results.

Answer*: the authors recognize that parts of this paragraph may sound like a discussion. The paragraph at page 18, lines 16-24*

<u>*"However, it is good to mention that the model resolution might have not been high enough to reproduce the dispersion of emissions in such a limited zone. Moreover, it is possible that other sources could be present nearby Lutjewad, or in general in the areas influencing the observations at the tower. Furthermore, the vertical mixing parameter of the model may have been too fast to correctly simulate the plume transport in such a limited area with stable night conditions. Also, possible indirect emissions of CS2 were not considered in this simulation. In other words, a model with a higher resolution and/or a more detailed database would probably produce a different and more accurate estimate for the missing source in the area. Therefore, the number stated above should be considered as a rough estimate."*</u>

<u>*has been adapted and moved to page 19, lines 15-24.*</u>

P19, L20: The word "prove" is too strong here.

Answer*: the sentence was modified: "The results presented in Section 3.4 <u>demonstrate</u> the presence of local sources of COS in the province of Groningen."*

P19, L20-30: Too much faith is being put into the STILT analysis. Note that the model is run with imperfect data, the PBL height is often off and this effects the size of the "box".

Answer*: please see the answer to the following point.*

P20, L29-31: I'm not sure this conclusion is justified.

Answer*: the authors thank the referee for these valuable remarks and would like to underline how the purpose of this study was not to quantify missing sources with a complete inversion analysis. Rather, the intention of this STILT application was to gain a (qualitative) description of regions that can be influential for COS measurements in Lutjewad. However, while recognizing this model's application limits and flaws, it is interesting to notice how the estimated influences of some known sources are still well in line with the measurements, when combined to STILT simulations. This is particularly noticeable for CO_2 (see, for instance, the peaks in Period 1, 2 and 4 in Figure 5 in the main* *text and the relative linear regressions of modelled results vs measurements in Figure S3 in the supplement). On the other hand, while applying the same model on other periods in time (Period 3) or other species (COS), the same method produces clearly less accurate results. Within this framework, the authors found it reasonable to conclude that in this case the cause for mismatch could be found in missing sources – or peculiar events – rather than in the model's limitations.*

P20, the rest of section 4.2: This reads like speculation when you have an analysis with associated uncertainty to rely on.

Answer*: the authors acknowledge a speculative aspect in Section 4.2, which was meant to cover some qualitative aspects of the results presented in Section 3.1. As stated earlier in this response, these sections <u>have been moved to the supplementary material together as Section S1</u> (previously, Section 3.1) <u>and Section 1.1</u> (previously, Section 4.2).*

P21, L26: In conclusion, this inversion analysis is incomplete.

Answer*: the authors agree this study does not present a thorough inversion analysis. As mentioned previously, this study was not aiming to test the STILT model validity or to estimate missing sources with an inversion approach, but rather to present a case-study application of STILT with known and newly-discovered COS sources. Given the lack of weather data and a rather restricted coverage of the emission ranges in the identified emitters, it was not possible to infer a parametrized emission value for the local sources. However, this approach could be extended to other measurement stations and to more detailed model analysis to provide a proof of concept for the identification of possibly missing sources or sinks surroundings stationary measurements.*

Thank you for your efforts so far. This is an interesting dataset and is moving towards the most interesting application of atmospheric OCS observations.

Mary Whelan

References used in the responses (excl. web links in the text):

Alhamdi, W. A., & Abdullah, K. M. S. (2021). Determination of Radium and Radon Exhalation Rate as a Function of Soil Depth of Duhok Province—Iraq. *Journal of Radiation Research and Applied Sciences*, *14*(1), 486–494. https://doi.org/10.1080/16878507.2021.1999719

Levin, I., Karstens, U., Hammer, S., DellaColetta, J., Maier, F., & Gachkivskyi, M. (2021). Limitations of the radon tracer method (RTM) to estimate regional greenhouse gas (GHG) emissions – a case study for methane in Heidelberg. *Atmospheric Chemistry and Physics*, *21*(23), 17907–17926. https://doi.org/10.5194/acp-21-17907-2021

Thabayneh, K. M. (2018). Determination of radon exhalation rates in soil samples using sealed can technique and CR-39 detectors. *Journal of Environmental Health Science and Engineering*, *16*(2), 121–128. https://doi.org/10.1007/s40201-018-0298-2

van der Laan, S., Karstens, U., Neubert, R. E. M., Laan-Luijkx, V. D., & Meijer, H. A. J. (2010). Observation-based estimates of fossil fuel-derived CO_2 emissions in the Netherlands using Δ14C, CO and ^{222} Radon. *Tellus B: Chemical and Physical Meteorology*, *62*(5), 389–402. https://doi.org/10.1111/j.1600-0889.2010.00493.x