Review of “Understanding the influence of combustion on atmospheric CO2 over Europe by using satellite observations of CO2 and reactive trace gases”

December 13, 2021

Sadiq et al. “Understanding the influence of combustion on atmospheric CO_2 over Europe by using satellite observations of CO_2 and reactive trace gases” examines the relationship between emissions ratios of NO_x:CO_2 and CO:CO_2 using high resolution emission inventories for Europe, observations of CO_2 from OCO-2 along with NO_x and CO from TROPOMI, and the GEOS-Chem model. They calculate enhancements of NO_x, CO, and CO_2 over the Pacific ocean background values for both the satellite and model column data. They find that the GEOS-Chem enhancement ratios do not match the emissions ratios in the inventories driving the GEOS-Chem simulation, demonstrating that one must account for confounding effects (including photochemistry and other sources) when trying to use these ratios to determine top-down estimates of CO_2 from combustion sources.

Given the upcoming satellite missions expanding our observing system for these gases, such a study could be valuable to establish best practices for future work combining these species in top-down emissions estimates. Judging from the authors’ response to the first reviewer, they appear to have invested significant work to address those comments. Given those changes, I only have one additional methodological concern I suggest the authors investigate, and one general suggestion about the writing of the paper. I will detail these below; if both are addressed, I recommend publication.

Writing and focus

In my opinion, the main message about how well observed NO_x:CO_2 and CO:CO_2 enhancement ratios can constrain emissions ratios gets lost in the discussion of results. Section 3.1 discussion the variation in emission ratios among countries, lines 244–259 in Sect. 3.2 discuss how discrepancies between the model simulation and TROPOMI data vary by country, and the first two paragraphs of Sect. 3.3 discuss how the enhancement ratios vary by country.

While I understand that this is meant to guide the reader through the data, the emphasis on understanding differences between countries gave me the impression that the authors' were trying to identify errors in the inventory's emission ratios, rather than test the ability of satellite-observed enhancement ratios to constrain emissions based on emission ratios.

The discussion of the relationship between the enhancement and emissions ratios does not begin until the third paragraph of Sect. 3.3, and then only consists of three paragraphs outside of the concluding remarks. This seems like a very small portion of the manuscript devoted to its main point. Additionally, this section does not explore the question of how to best use NO_2 and CO measurements to constrain CO_2 emissions in much depth.

My suggestion is to reorganize the paper and expand the discussion of how to best use obseved NO_x:CO_2 and CO:CO_2 ratios to constrain CO_2 emissions. One option would be to make Sect. 3 the comparison of the GEOS-Chem simulations with observations (including the new comparisons to in situ), making clear that the purpose of the comparison is to validate the model for the next section. Then a new Sect. 4 would become a more detailed discussion of the best approach for combining NO_x, CO, and CO_2 observations. A possible avenue to expand this discussion would be to compare CO_2 emissions that would be derived by different methods that previous work (such as the papers cited on lines 47–48 of the introduction) in order to quantify the error introduced by e.g. not accounting for photochemistry. Other approaches could also be interesting, but it is important that the discussion provide concrete suggestions for how to improve the synergistic use of NO_x, CO, and CO_2 measurements and place those improvements in the context of previous work.

Choice of background

My primary metholoogical concern is the choice of the Pacific Ocean as the background sector when calculating the column enhancements. While I understand that the Pacific Ocean is often used to calculate a global background, given the prevailing winds, does not air mostly come into Europe from the east, thus making the Atlantic a more obvious background for this study? That way any influence of North America emissions would be directly accounted for.

More generally, I'm not convinced that a single curtain background like this is sufficient to resolve differences in emissions on a sub-continental scale. While it will certainly work for areas on the upwind shore, enhancements for cities or countries more inland would need to use a background that accounts for upwind emissions between them and the ocean. To illustrate this, I did a quick 1D calculation (Fig. R1) where CO_2 emissions are constant, but CO emissions are higher in the middle five boxes. For simplicity, CO is assumed to have no chemical loss on this timescale. When using cell 0 (the left boundary condition, with mixing ratio = 0 for both species) as the background, the first five boxes' enhancement ratios (blue line, bottom panel) match their emission ratios (top panel), but the middle five boxes' enhancement ratios are too low. Using box 5 as the background (red line) fixes that. While this is a deliberate exaggeration of the variation in CO:CO_2 emission ratios, it demonstrates how using the same background for the whole continent will obscure differences in emissions ratios.

I recognize that there are technical difficulties in defining a unique background for each region. However, it would be helpful to at least see a discussion of this effect, and ideally some quantification of how much error it introduces in the enhancement ratios.

Minor comments

First I will give comments on the original manuscript.

- Like the first reviewer, I would also like to see more explanation of how the CO_2 GEOS-Chem simulation was handled. Did you actually run two simulations, one with the full chemistry mode and one using the CO_2 mode?
- Line 222: "the oxidation of anthropogenic VOCs dominates over biogenic" - the cited references seem to point to biogenic dominating (Palmer et al. 2003 says this is true for urban environments only in the introduction, Abbot et al. 2003 and Fu et al. 2007b both mention isoprene dominating in North America.) Perhaps this needs qualified?
- Line 260: I'm not convinced that it is solely CO's longer lifetime that lead to the smaller bias. If the emissions were biased, the columns would still be biased. It also implies that CO is more affected by your boundary conditions. However, I do agree that the longer lifetime means errors in chemistry won't affect the CO bias as much.
- Line 312: the argument that the negative correlation between the NO_2:CO_2 enhancement and emissions ratios is an interesting hypothesis, but it would really depend on the chemical regime. Since the authors included new analysis in the response to reviewer 1, this seems to be less important. However, if this conclusion is still in the revised paper, I recommend checking that instantaneous lifetime (NO_x/loss(NO_x)) is negatively correlated with NO_x concentration in the GEOS-Chem simulation to confirm that the model is in the regime where larger emissions lead to more loss.
- Line 326: another reason for the smaller variation in the ΔCO:ΔCO_2 ratio than the emissions ratio could be the choice of background; as my Fig. R1 shows, in the simple 1D case, using a fixed background will damp the response of the enhancement ratio to changes in emissions ratio.

Since the authors have already responded to the first review and included descriptions of some significant changes, I will include some comments on those changes here.

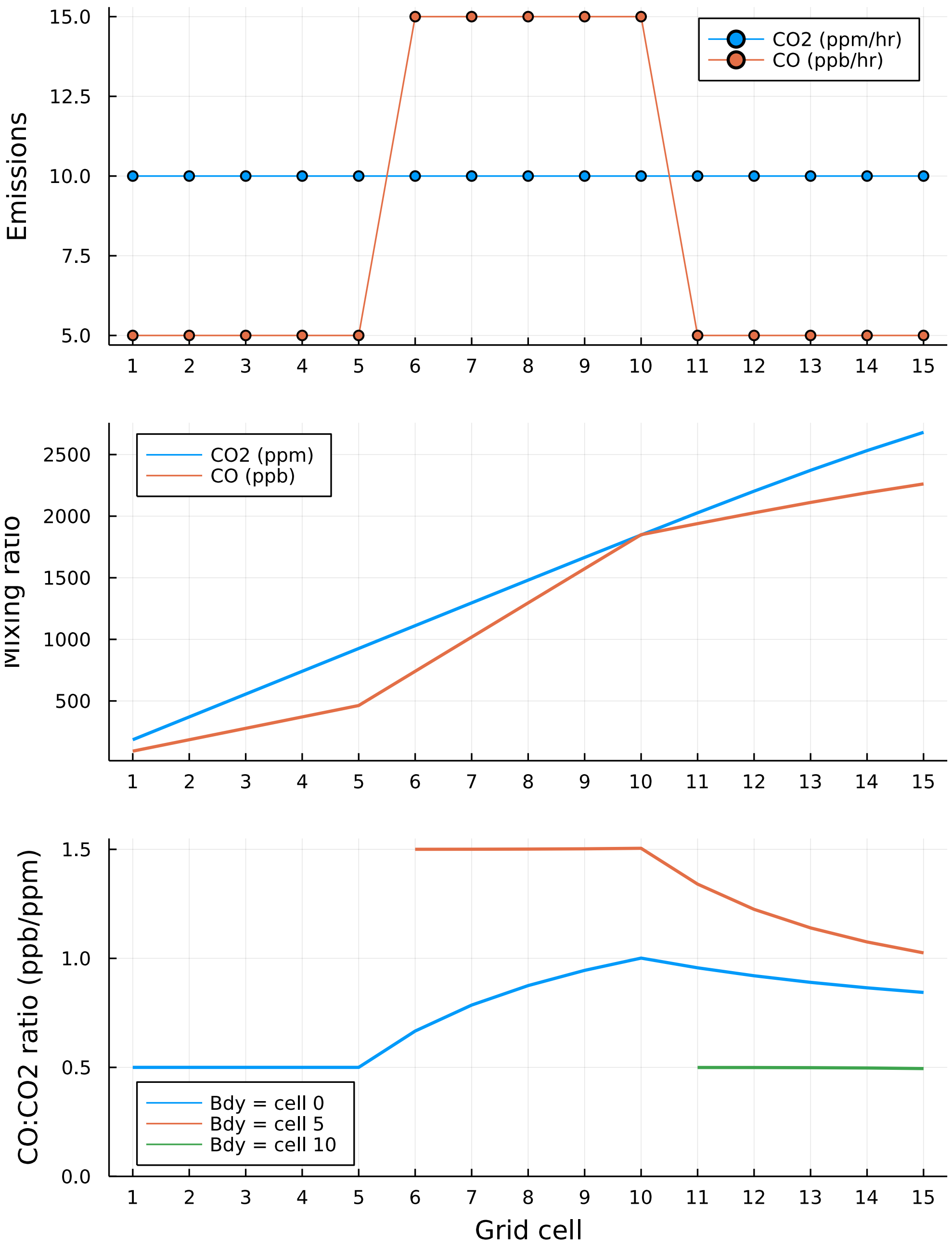

Figure R1: Simple model example of background selection on enhancement ratios. Top: emissions of CO and CO_2 in each grid cell. Middle: mixing ratios at steady state, assuming left-to-right transport and open boundary conditions. Bottom: enhancement ratios calculated using difference grid cells as the background. Each grid cell is 200 km so that five grid cells is roughly the width of France.

- *Edits regarding HCHO:* I support the authors in retaining the conclusion that HCHO is not useful, as this negative result can inform future studies' approaches.

- *Updated model validation:* It would be helpful to include a proper correlation of matched GEOS-Chem and AirBase data for validation purposes, not just the maps. Also, in Fig. 1c of the response to reviewer 1, why is GEOS-Chem afternoon NO_2 so high over the English Channel? That seems like more than just the influence of shipping emissions.

- *Updated TROPOMI CO filtering:* In Fig. 5 of the response, is the white area of the TROPOMI CO (panel c) missing data or data below the colorbar's lower limit?

- *Updated Fig A7:* In the response, the authors indicate that they see a negative correlation between the NO_2:CO_2 enhancement and emission ratios for the UK, Italy, and Poland. I'd advise caution here: the R values do not imply a particularly strong correlation—is the p value < 0.05? Does a bootstrapping analysis consistently return a similarly negative R, or does it depend greatly on what points are included? For the UK and Poland, the negative relationship appears largely driven by only a few points. Italy has a stronger case, but is still driven by a small subset of the data.