Evaluating the contribution of the unexplored photochemistry of aldehydes on the tropospheric levels of molecular hydrogen (H$_2$): Response to reviewers

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We thank both reviewers for the thorough reading of our manuscript and all the helpful comments. Their insight has contributed to the betterment of our work. In what follows we address each reviewer comments, the original comments are in black and our answers are indicated in blue. New text is indicated in **bold**.

1   Reviewer 1

The authors analyzed the contribution of aldehydes on the chemical production and tropospheric levels of H_2 using a box model and a 3-D atmospheric chemical transport model. The authors concluded that their results imply that the previously missing photochemical source is a less significant source of model uncertainty than other components of the H_2 budget. Overall, the paper is well written and well organized.

We thank the reviewer for the positive feedback about our paper.

1.1   Major comment

(a) My only concern is that the global model simulations were conducted with a resolution of 4x5. As the authors found in Section 2, the conditions over urban environments and regions with substantial vegetation are very different. Urban size is usually smaller than this scale. Can the model properly represent that with this resolution?

- We have added a clarification into the main text in Section 3.3 **"Even tough the box modelling showed a marked difference on the aldehydes that produce H_2 between urban and densely vegetated environments, the global model simulations are not intended to capture the fine-scale detail of such regions. Aiming at estimating how the aldehyde photochemistry compares to other H_2 global sources, the coarse resolution used in the baseline is maintained to test the reactions."** The 4x5 resolution used here is sufficient for the purpose highlighted now from lines 363 to 366. **"Even tough the box modelling showed a marked difference on the aldehydes that produce H_2 between urban and densely vegetated environments, the global model simulations are not intended to capture the fine-scale detail of such regions. Aiming at estimating how the aldehyde photochemistry compares to other H_2 global sources, the coarse resolution used in the baseline is maintained to test the reactions."** Also, the applied resolution is similar to other global H_2 budget simulations, such as the one by Derwent et al., (2021), that used a resolution of 5x5. Detailed accounting of the budget in urban environments would require a higher resolution model as noted by the reviewer, but that is beyond the scope of the work presented here.

1.2   Minor comments

(1) Line 95: "The the" to "Then the"?

- The correction in line 95 has been made.

(2) Line 216: Here it is "GFED4" but later it was denoted "GFEDv4s". Please make it consistent.

- The abbreviation for the Global Fire Emissions Database v4 was standardized as GFEDv4s throughout the text.

(3) Line 345: Change "difference between observations and predictions" to "difference between observations and model simulations"?

- As suggested by the reviewer, the sentence has been changed.

(4) Figure 1. The colors are hard to differentiate especially the orange colors.

- Figure 1 has been updated to help the reader differentiate the colors better.

2   Reviewer 2

In this study the authors estimate the contribution of aldehyde photolysis on the production of H_2.

Using a chemical transport model, the authors conclude that this recently identified source makes a very small contribution to the overall H_2 budget.

This analysis is performed using a newly-developed simulation of H_2 in the GEOS-Chem model.

The findings are interesting but require additional analysis for publication in ACP.

2.1   Major comments

(a) Section 2

(1) Given the limitations of the box model, the interpretation of the simulated H_2 concentration is quite challenging as pointed out by the authors. I suggest to focus on the production rates [i.e., remove lines 125 to line 146]

- Following the suggestion from the reviewer we have placed the interpretation of the mixing ratios into the Supplementary material.

(2) Fig. 1. Please indicate the H_2 production associated with aldehyde photolysis at each site and the time period considered. What is the production of H_2 from the photolysis of formaldehyde and glyoxal at these sites? If the production from aldehydes is very small relative to that from formaldehydes and glyoxal, the authors need to clarify why they expect a different result from the global model.

- The H_2 rates of production at each site are now included in the caption of Figure 1. We also now explicitly state that the production of aldehydes was small relative to that of formaldehyde and glyoxal from lines 166 to 168 **"The aggregated rates of production from the tested aldehydes here was less than 1% of the total rate of production at each modelled site, with formaldehyde and glyoxal remaining the main photochemical sources of H_2 in the box model simulations."** We did not anticipate a different result with the global model. However, as explained in lines 171-175, we turned to the global modelling to be able to appropriately quantify the impact by including other processes that are relevant to the H_2 budget, accounting for spatial variability in environments, and extending the simulation time to allow the model to reach steady state.

(3) It's unclear why the authors restrict themselves to these 3 sites. Would it be possible to perform the same type of analysis using data from NOAA/NASA airborne intensive campaigns (acetaldehydes and glycoladelhydes are often measured)? This would help better constrain the importance of this process.

- The goal of the work was to determine the relevance of the so-far unaccounted for photochemistry of some aldehydes and their role in the chemical production of H_2. This was clarified from lines 83 to 87 **"The box modelling aimed to determine which aldehydes contribute meaningfully to the primary chemical production of H_2 in different types of environments. We choose 3 indicative sites to explore distinctive environments, each with different expected mixing ratios of aldehydes (urban, pristine oceanic and pristine forested). The direct production of H_2 from the photolysis of aldehydes evaluated with AtChem further helped to configure the global model (see section 3.3)."** While simulating more observation campaigns would give a more nuanced view of the distribution of H_2-forming compounds, it would not fundamentally change our understanding of the chemistry or of the most important aldehydes to include in our simulations.

(b) Section 3

(1) Emission inventory.

The authors use a constant emission factor to convert anthropogenic CO emissions to H_2 emissions. Instead Ehhalt et al (2010) recommended using different emission factors for transportation.

Similarly, Akagi (2011) et Andreae (2019) reviews provide biome-specific emission factors for H_2. It's unclear why the authors didn't use these.

Indeed, the Akagi estimates are already used by GFED4s.

- As suggested by the reviewer, we modified the scaling factors used for anthropogenic fossil fuel emissions making a distinction for automobile emissions. The new scaling factor for automobile emissions was 0.036 g H_2 / g CO as summarized by Ehhalt. Added to this, we changed the use of a single scaling factor for biomass burning emissions from CO emissions, and instead applied the biome-specific emission factors from Akagi et al., (2011) and Andreae (2019), as also done by Paulot et al., (2021), to the GFEDv4s implementation in GEOS-Chem. With this modifications we re-ran both the baseline and the aldehyde photolysis scenarios. The changes are reflected in the budget estimates and the values in the text have been updated (see section 3.2).
  The resulting changes were small, and both our original and updated budgets are within the range found in previous estimates. For example, Paulot et al. (2021) determined a range for biomass burning emissions of 7.3-12.6 Tg H_2/yr over a 1995-2014 simulation. Our original estimates for 2015-2016 with a single CO scaling factor were 6.5-9.2 Tg H_2/yr. These values have been updated to 7.6-9.2 Tg H_2/yr (see Table 2 and Figure 3). All figures and the text have been updated to reflect the changes, but we note that there is no change to any of our conclusions following this modification.

(2) Deposition velocity

  (1) The authors need to discuss how the Yashiro model differs from the one presented by Ehhalt (2013). The Ehhalt model parameterization was used in two recent studies (Bertagni (2021) and Paulot (2021)). It would be interesting to test the model against observations collected at Harvard Forest by Meredith (2017)

    - We have now added a clarification on how the model used by Yashiro et al., (2011) differs from the one used by Ehhalt et al., (2013) from lines 229 to 233 **"The parameterisation to derive the dry deposition velocity for H_2 used by Yashiro et al., (2011) implements the same variables as the ones used by the Ehhalt et al., (2013). The Ehhalt et al., (2013) parameterisation, applied in other recent modelling studies Paulot et al., (2021), differs from the one by Yashiro et al., (2011) in that the latter considers the diffusivity in the soil to be uniform from the soil surface to a sufficient depth, while Ehhalt et al., (2013) uses two different soil diffusivities."** We agree that it would be interesting to compare simulated dry deposition models against the H_2 fluxes measured by Meredith et al., (2017), but this is beyond the scope of our work which focuses on the untested aldehyde photochemistry at global scales (and does not attempt to update or evaluate dry deposition schemes).

  (2) It's unclear why the authors do not calculate vd(H_2) dynamically in the model using the parameterization described by Yashiro and soil moisture/temperature available from reanalysis (see Bertagni (2021), for instance). This would provide a significant improvement over the approach used by Price (2007) that solely (but interactively) accounts for the impact of snow cover and temperature.

    - While we would have preferred to calculate vd(H_2) dynamically in the model, this is not possible in the GEOS-Chem CTM. Unlike in the examples cited by the reviewer (climate models that integrate with a land model Paulot et al., (2021)), GEOS-Chem does not have access to several of the soil variables required by the Yashiro et al., (2011), Ehhalt et al., (2013) and Bertagni et al., (2021) parameterisations, such as soil porosity and depth of soil active layers. We added a clarification to this in the main text from line 225 to 228 **"The integration of an online H_2 dry deposition calculation from other studies (Yashiro et al., 2011; Ehhalt et al., 2013; Bertagni et al., 2021) was not performed given that the algorithms require soil variables (e.g. soil porosity and depth of soil active layers) that are not available in our model."**. The implementation of the dry deposition algorithms dynamically in GEOS-Chem would require extensive modification of the model. For this reason we do not calculate the vd(H_2) dynamically. We note that the offline vd(H_2) fields used here still represent a significant improvement from the approach used by Price et al., (2007).

  (3) I am not sure that I understand the benefit of using daily vd(H_2) derived for a different period from the one considered here. This will not account for the significant swings in H_2 removal associated with soil moisture (see Bertagni (2021) for instance).

    - We use the daily dry deposition velocities from Yashiro et al., (2011) from 1997 to 2005 to construct a multi-year mean climatology that provides a reasonable estimate of the seasonal changes associated with different soil moisture and temperatures. We have added a comment to this effect to the main text from line 235 to 237.
    "We used the dry deposition velocities from Yashiro et al., (2011) to create a

climatology for an "average" year with daily temporal resolution to represent typical seasonal variability, which was then used in our 2014-2016 simulations" While we could have used monthly means, that would have introduced an assumption that step changes occur at the same time each year (e.g. end of each month). Averaging the daily values across years provides for smoother transitions that are more representative of the real interannual variability. We do not expect to capture specific fluctuations associated with changes in temperature or soil moisture, and indeed do not show results at sub-monthly resolution

(3) Impact of hydrogen.

The authors need to describe how the improved representation of H_2 in GEOS-Chem impacts the lifetime of CH_4, the tropospheric and stratospheric O_3 budget, and the stratospheric H_2O budget. As detailed in many studies (Derwent et al. (2000,2020), Field (2021), Paulot, (2021), Vogel (2012))), these are critical to understanding the indirect impact of H_2 on radiative forcing.

- The goal of this paper is to evaluate the impact of the changes in chemistry on the H_2 budget, not to understand the role of H_2 on the climate system. Evaluation of changes in follow-on parameters such as CH_4 and O_3 is beyond the scope of this work. In any case, the change in CH_4 cannot be determined from our simulations as the GEOS-Chem Standard simulation used is nudged to CH_4 observations. The change in the O_3 fields is very small with differences <1%.

(4) Evaluation Why aren't airborne observations discussed (Fig. S7)? This is a unique dataset and the model does show significant biases that should be discussed.

- The airborne dataset is discussed very briefly in the supplementary material, this discussion has been moved into the main text. To note is the fact that the comparison showed is a climatological one. The measurements used were performed from 1991 to 2000.

2.2 Minor comments

(1) Fig. 1 Please use IUPAC names for chemicals.

- As suggested by the reviewer, the IUPAC names were included in the Table S1 to allow for some of the more common names (as glycolaldehyde) to be consistent throughout the text.

(2) Fig. 3 is very difficult to read. Please use different colors for model and observations.

- Figure 3 shows sources and sinks for the two modelled years and makes no comparison against observations. The caption of the Figure has been updated to avoid further confusion.

(3) Are the authors using the results of the box model to select the aldehydes used in GC?

- We used the box model result to determine which aldehydes could be tested in GEOS-Chem, this is now clarified from line 360 to 362 **"Here we tested the impacts of the direct formation of H_2 from photolysis of the rest of the aldehydes in GEOS-Chem (with the exception of dihydroperoxide dicarbonyl as it was not present in the box modelling test). This was supported by the findings made in section 2.2, that showed the more relevant aldehydes to the photochemical formation of H_2."**

(4) A fairly recent H_2 budget was provided by Paulot (2021), which could be added to Table 2.

- The H_2 budget estimated by Paulot et al., (2021) has been added to Table 2.

(5) The AGAGE network provides H_2 observations at Mace Head that should be considered.

- The observations at Mace Head in Ireland have been included in the evaluation. The addition can be seen in Figures 4, 5, S9 and in Table S2.

(6) The lifetime of H_2 is 2.5 years. Isn't a 6-month spin up much too short?

- We set the initial H_2 mixing ratios to 530 ppb based on observations to enable the model to stabilise more quickly, and found that the model reached steady state after a 6-month spin-up. We have now clarified this in the main text.

(7) Fig. 5. Are these dry mixing ratios?

- The mixing ratios in Figure 5 are dry mixing ratios. We have added this to the figure caption.

(8) Line 348. The model seems to be biased low everywhere. Isn't CH_4 oxidation another possible culprit.

- CH_4 is constrained to the measurements in our GEOS-Chem model simulation. The model biases in the Southern Hemisphere are much larger than in the Northern Hemisphere, which suggests they are more likely attributable to low oceanic emissions, as we would expect a CH_4 oxidation bias to be more uniform. An addition in the main text in in lines 349 and 350 has been done **"Another possible source of model bias is the oxidation of CH_4. However, we do not expect it to represent the main source of the bias because CH_4 is constrained to observations at the surface in our simulations."**

(9) Fig. 2a. I cannot distinguish between brown and red

- Figure 2a has been updated by changing the color for the anthropogenic emissions to purple and biomass burning emissions to red to aid the reader.

(10) Fig. 5. Please show the impact of aldehydes on the simulated H_2 profile.

- Figure 5 has been modified to show the modelled scenario with H_2 photochemical production from aldehydes.