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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 the reviewer for the second revision to our manuscript, which has allowed for further improvement of our work. Below we include the original comments by the reviewer in black and our answers indicated in blue. New and modified text is indicated in **bold**.

1 Reviewer 2

1.1 General comments

(a) Line 253: Most of the study is devoted to improving the representation of H_2 in the GEOS-Chem model. As a result, I am still puzzled that vd(H_2) is not calculated dynamically. As noted by the authors, it is the single largest sink of H_2 (>70%) and many (all?) recent models of atmospheric H_2 include such representation (see also Sanderson (2003), Pieterse (2011), Bousquet (2011)).

My understanding is that GEOS-Chem relies on GEOS-FP or MERRA-2 for inputs, both of which do include soil moisture and soil porosity. If I understand properly this recent study (https://www.nature.com/articles/s41597-020-0488-5), these fields are already used to estimate soil NO emissions, which would make it seem as if it should not be too cumbersome to implement the Yashiro model in GEOS-Chem. However, the authors mention in their reply that this is not possible. Could they elaborate?

- To clarify, the main focus of the work is not on improving the H_2 simulation in GEOS-Chem but on testing the impacts of the aldehyde photochemistry (as can be seen in the title, abstract, and introduction). To do so required us to have a reasonable H_2 simulation baseline that we could compare against our sensitivity simulations with the new baseline. As H_2 has not been included in any modern version of GEOS-Chem, we devoted a section of the paper to describing and evaluating our implementation.
- Turning specifically to the dry deposition term, we use the vd(H_2) calculated externally by Yashiro, as the dynamic calculation requires soil variables that are not readily available in the meteorological fields used in GEOS-Chem. We note that GEOS-Chem does not use the GEOS-FP/MERRA-2 products directly, but instead requires post-processed versions of these products to make them compatible with GEOS-Chem. In the post-processing, which is performed by the GEOS-Chem Support Team before providing inputs to the community, only a subset of GEOS-FP/MERRA-2 variables are archived (http://wiki.seas.harvard.edu/geos-chem/index.php/List_of_GEOS-FP_met_fields). Unfortunately, several of the soil variables are not included in this subset, including those we would need to implement the Yashiro parameterisation dynamically. The soil parameters required to implement the dynamic calculation include: soil moisture, soil temperature and soil porosity. We describe below the availability of each of these variables for use in GEOS-Chem, along with comments on what is used in the soil NOx parameterisation in the paper referenced by the reviewer:
  - Soil moisture: The soil NOx emissions calculation in GEOS-Chem uses top soil wetness. The variable used (GWETTOP) corresponds to the ratio of the volumetric soil moisture to soil porosity. Neither soil moisture nor soil porosity are provided directly. This means that in order to use the top soil wetness from GEOS-FP as soil moisture, we also require the soil porosity.
  - Soil porosity: The original meteorological products include a porosity variable. However, this variable is not included in the post-processed version of the datasets that are used as input to GEOS-Chem. It is not used in the soil NOx emissions calculation.
  - Soil temperature: Soil temperature is available in the raw products but not in the products processed for input to GEOS-Chem. The soil NOx code uses the 2-m air temperature as a proxy

for this variable. While it would be possible to use the same approximation for the H_2 deposition calculation, it would add significant uncertainty to the dynamic calculation of the vd(H_2) that should be evaluated appropriately.

- Considering that the calculation of vd(H_2) builds on these three core parameters, we cannot implement the existing scheme with what is currently available in GEOS-Chem. We have clarified this in the manuscript, and also highlighted the importance of future work exploring the possibility of a dynamic sink term, from line 224 to line 229: "The integration of an online H_2 dry deposition calculation from other studies (Yashiro et al., 2011; Ehhalt and Rohrer, 2013; Bertagni et al., 2021) was not performed given that the algorithms require soil variables (e.g., soil porosity, **soil moisture, soil temperature** and depth of soil active layers) that are not available in **the post-processed GEOS-FP meteorological fields used as input to GEOS-Chem. However, the variables are available in the raw GEOS-FP (and MERRA-2) dataset. Future work should explore processing these variables for use in GEOS-Chem and implementing online soil uptake into the model."**

(b) Line 257

(A) Please include the equation for vd. This would make this section easier to follow

- We have included the equation in the supplementary material.

(B) I believe that there are more differences between the two models (e.g., different sensitivity to temperature, moisture, ...). Please clarify.

- We have expanded on the differences between the two and moved the discussion to the Supplementary Material Section 2, *Dry deposition velocity calculation in Yashiro et al., 2011* In addition to including the relevant equations (as requested above), the section now reads as follows: **"The parameterisation to derive the dry deposition velocity for H_2 used by Yashiro et al., 2011 implements the same variables as that used by Ehhalt and Rohrer, 2013. The Ehhalt and Rohrer, 2013 parameterisation, applied recently by 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 (because the diffusivity is within the first layer of the parent land model.), while Ehhalt and Rohrer, 2013 use two different soil diffusivities. Further, the biological activity (uptake rate k), soil moisture and soil temperature dependencies are also different between Yashiro et al., 2011 and Ehhalt and Rohrer, 2013. Yashiro et al., 2011 follow the variation of the biological activity from Smith-Downey et al., 2006, while Ehhalt and Rohrer, 2013 rely on the dependencies from the reanalysis performed by Ehhalt and Rohrer, 2011. Also, the thickness of the inactive layer used by Yashiro et al., 2011 is considered to be uniform (with a value of 0.7 cm) while Ehhalt and Rohrer, 2013 provide values that are a function of the average volumetric soil water content."**
- We also refer to this section of the supplement in the main text when we describe our implementation of the dry deposition sink.

(C) Most importantly, although Yashiro and Ehhalt start from the same equation, if I am not mistaken they seem to arrive at a different result. Take delta=0, equation (13) of Ehhalt implies vd=sqrt(k Theta D) while equation (11) of Yashiro implies vd=Theta sqrt(k*D). I believe the former is correct. At any rate this should be clarified.

- We have added a brief discussion of this difference to the Supplementary Material (new Section 2)" **"Even though both models start from equation 1 (where Fs is the flux and C is the mass concentration of H_2) to derive the dry deposition velocity as a function of the H_2 flux and diffusivities, the two models differ when the thickness of the inactive layer $\delta = 0$ as a consequence of the difference in the definition of the flux.**

$$Vd = \frac{Fs}{\rho C} \tag{1}$$

Ehhalt and Rohrer, 2013 used equation 2, where Ms corresponds to the H_2 mixing ratio in the soil air.

$$Fs = -Ds\rho\frac{\delta Ms}{\delta z} \tag{2}$$

On the other hand, Yashiro et al., 2011 used the equation 3

$$Fs = -Ds\rho\theta_a\frac{\delta Ms}{\delta z} \tag{3}$$

This equation originated from equations (2), (3) and (4) in Yonemura et al., 2000. The version used by Yashiro et al., 2011 means that the gradient of the gas concentration between two layers is determined not only by the mixing ratio, but also by the air-filled porosity.". Note that Eq. 6 in Yonemura et al. (2000b) misrepresented the porosity (as is not the combination of Eq. 3 Eq. 4), and so Yashiro et al. considered that $V_d = \theta\sqrt{kD}$ more relevant.

(c) Line 382: I don't follow the argument. If the simulated OH is biased, wouldn't you underestimate the flux of H_2 from CH4?

- We have clarified this in the manuscript in lines 359 to 361: **"We do not expect the oxidation of CH_4 to be a possible source of our H_2 model bias because CH_4 is constrained to observations at the surface in our simulations."**

1.2 Minor comments

(a) Line 380. Did you try to estimate the oceanic flux of H_2 that would be required to reduce the model bias?

- We did not attempt to determine the required oceanic flux to reduce the model bias observed for H_2, as this is beyond the scope of our work (focused on the photochemistry). We have clarified this in lines 356 to 359 "Given the large ocean area in this part of the world, underestimated ocean H_2 emissions are a possible driver of the bias, **although we did not estimate the magnitude of the emissions that is required to overcome such bias.** Improvements to ocean H_2 emission parameterisations with particular emphasis on the Southern Ocean should be a priority for future model development."

(b) Line 214. How do you assess that the model is indeed spun-up? Did you run longer spin-ups? If I am not mistaken, your IC is the same throughout the atmosphere. Given H_2 long lifetime, I would expect that it would take significantly longer to achieve a proper spin-up.

- We tested the impact of different spin-up times for January 2015 using longer spin-up times (18 months and 2.5 years, compared to our original 6 months). Over background regions, the difference between using our 6-month spin-up and longer spin-up times was less than 0.5%, and so we consider that our spin-up time was sufficient. We have clarified this in lines 187-189 **"Tests with 18-month and 2.5-year spin-ups showed differences in H_2 mixing ratios were smaller than 0.5%, showing that the six-month spin-up was sufficient."**