



*Supplement of*

## **Evaluating the contribution of the unexplored photochemistry of aldehydes on the tropospheric levels of molecular hydrogen (H<sub>2</sub>)**

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## 1 Mixing ratios results from the box modelling

The mixing ratios in the baseline simulations provide context for our box modelling results. Selected modelled species from the baseline simulations for London, Cape Verde and Borneo are shown in Figures S1-S3 respectively. The baseline mixing ratio of  $H_2$  increased continuously from its initial value of 530 ppbv to 639.97 ppbv at London and 533.96 ppbv at Borneo. At Cape Verde, the mixing ratio of  $H_2$  decreased during the simulated period to 517.23 ppbv. These changes are equivalent to an increase in  $H_2$  of  $\sim 17\%$  over 12 days for London, an increase of  $\sim 1\%$  over 6 days for Borneo, and a decrease of  $\sim 2\%$  over 12 days for Cape Verde. These final  $H_2$  mixing ratios are not representative of the actual values over the selected locations particularly because of the lack of other relevant physical processes such as emissions, transport and uptake by soil.

For the London and Borneo simulations, the  $H_2$  increase over time in the baseline run was effectively caused by the photolysis of formaldehyde and glyoxal (the only  $H_2$  sources in this simulation). The decrease in modelled  $H_2$  at Cape Verde was a result of imbalances in the chemical sources and sinks in this regime. For the Cape Verde simulation, neither formaldehyde nor glyoxal had available measurement constraints (see Table 1 in the manuscript); however, both were produced chemically, with formaldehyde production from the degradation of methane, ethene, propene, toluene and benzene and glyoxal production from ethene and toluene precursors (Stavrakou et al., 2009). These five precursor species were all constrained in the Cape Verde simulations (see Table 1, footnote b). Figure S2 shows the time series of selected species modelled for Cape Verde, including formaldehyde, which had an average modelled value of  $\sim 800$  pptv ( $\sim 2 \times 10^{10}$  molecules  $cm^{-3}$ ). For comparison, Whalley et al., 2010 reported an average noon value of 328 pptv for their MCM simulations at Cape Verde during May-June 2007 (note that they do not report values for glyoxal). Considering that our modelled formaldehyde mixing ratios were higher than those reported previously by Whalley et al., 2010, and because of the formaldehyde and glyoxal lifetimes of a few hours, we conclude that our simulations included sufficient precursor concentrations and therefore that the decrease in  $H_2$  in the baseline Cape Verde simulation implies that the available  $H_2$  was consumed by OH more rapidly than it could be produced by formaldehyde and glyoxal, yielding an effective loss over the 12 days modelled.

## 2 Dry deposition velocity calculation in Yashiro et al., 2011

The dry deposition velocity on the surface of the inactive layer was calculated by Yashiro et al., 2011 as:

$$Vd = \frac{1}{\frac{\delta}{Ds\theta_a} + \sqrt{\frac{1}{Dsk\theta_a}}} \quad (1)$$

where  $\theta_a$  is volume of gas per unit volume of soil (air filling porosity) [ $m^3 m^{-3}$ ],  $Ds$  is the diffusivity in soil,  $k$  is the biological uptake rate [ $s^{-1}$ ] dependent on soil temperature and soil moisture (see Yashiro et al., 2011 equations 13 to 16). For the diffusivity

$$Ds = Da \frac{\theta_a^{3.1}}{\theta_{sat}^2} \quad (2)$$

where  $Da$  is the molecular diffusion coefficient with a value for  $H_2$  of  $0.611 cm^2 s^{-1}$  and  $\theta_{sat}$  is the maximum aerial or liquid water volume per unit volume of soil (total porosity).

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. Even though both models start from equation 3 (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.

$$Vd = \frac{Fs}{\rho C} \quad (3)$$

Ehhalt and Rohrer, 2013 used equation 4, where  $Ms$  corresponds to the  $H_2$  mixing ratio in the soil air.

$$Fs = -Ds\rho\frac{\delta Ms}{\delta z} \quad (4)$$

On the other hand, Yashiro et al., 2011 used equation 5

$$Fs = -Ds\rho\theta_a\frac{\delta Ms}{\delta z} \quad (5)$$

This equation originated from equations (2), (3) and (4) in Yonemura et al., 2000. The version used by Yashiro et al., 2011 (equation 5) means that the gradient of the gas concentration between the two layers is determined not only by the mixing ratio, but also by the air-filled porosity.

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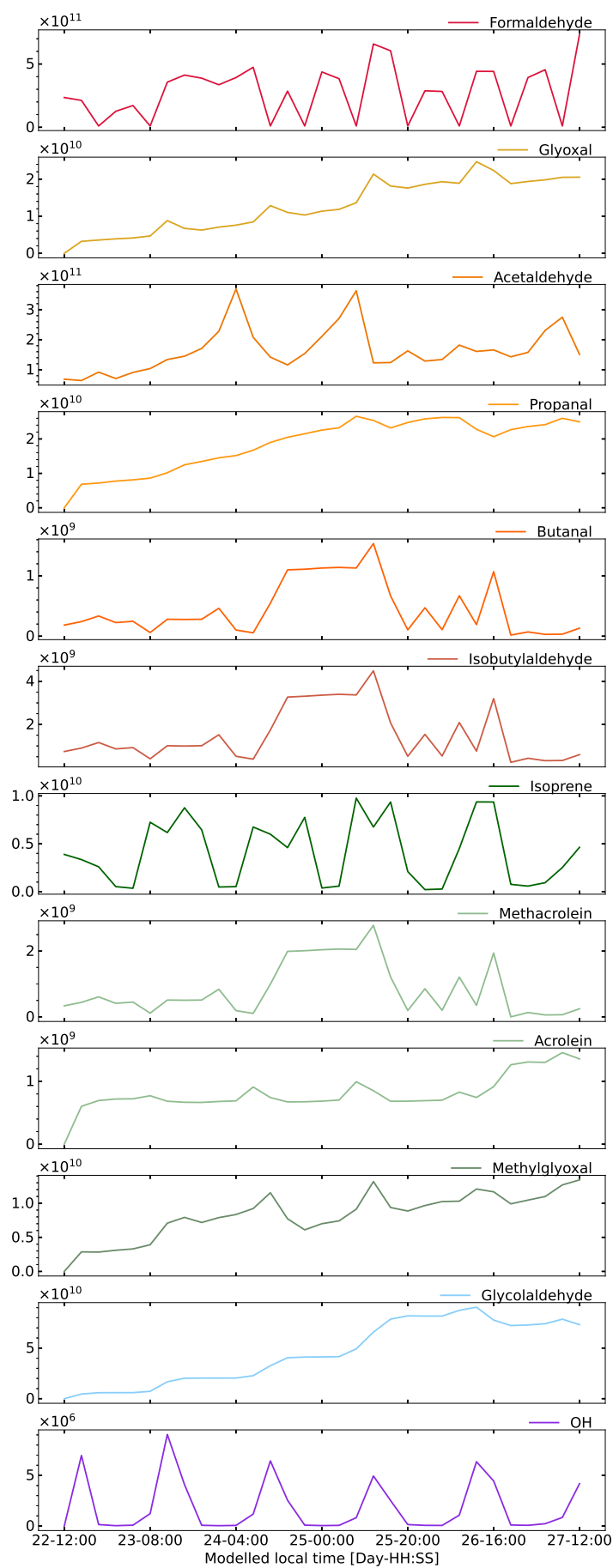


Figure S1: Time series for selected modelled species in molecules  $\text{cm}^{-3}$  from the baseline box model simulation in London starting at noon on the 22<sup>nd</sup> of July 2012.

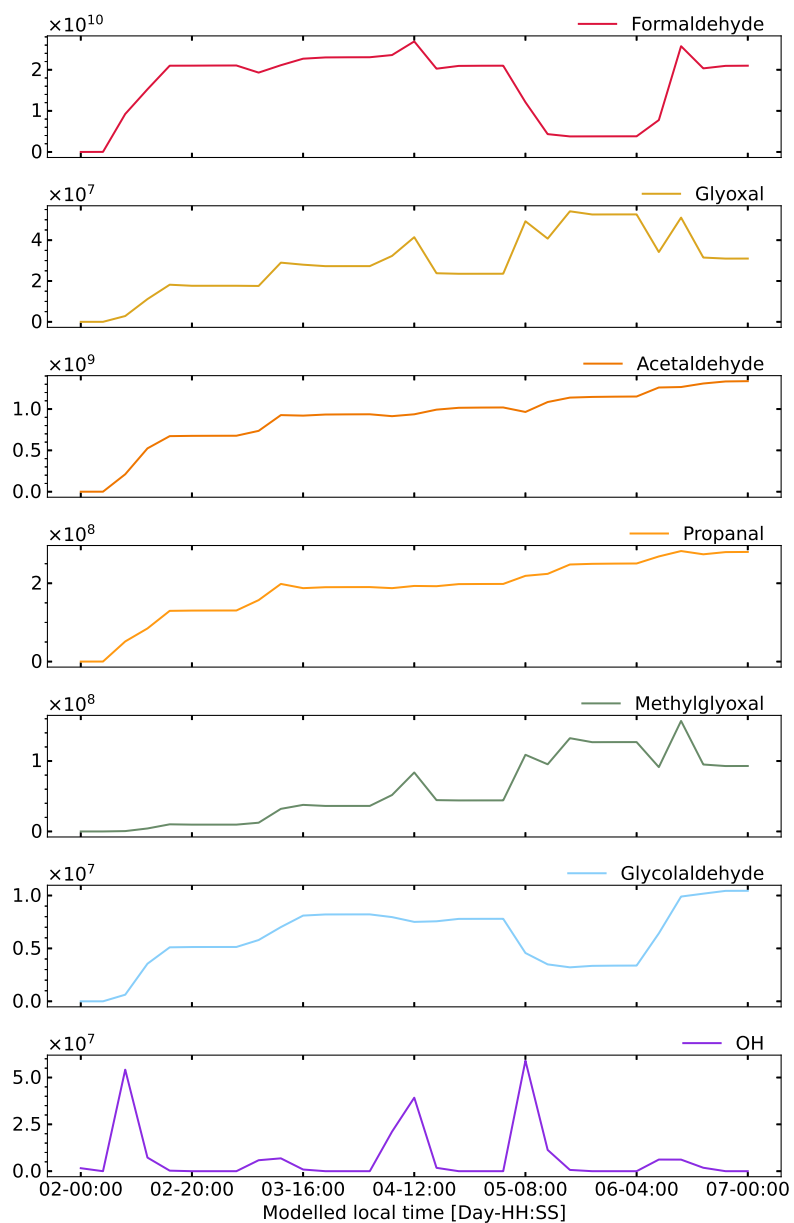


Figure S2: Time series for selected modelled species in molecules  $\text{cm}^{-3}$  from the baseline box model simulation in Cape Verde starting at midnight on the 2<sup>nd</sup> of January 2015.

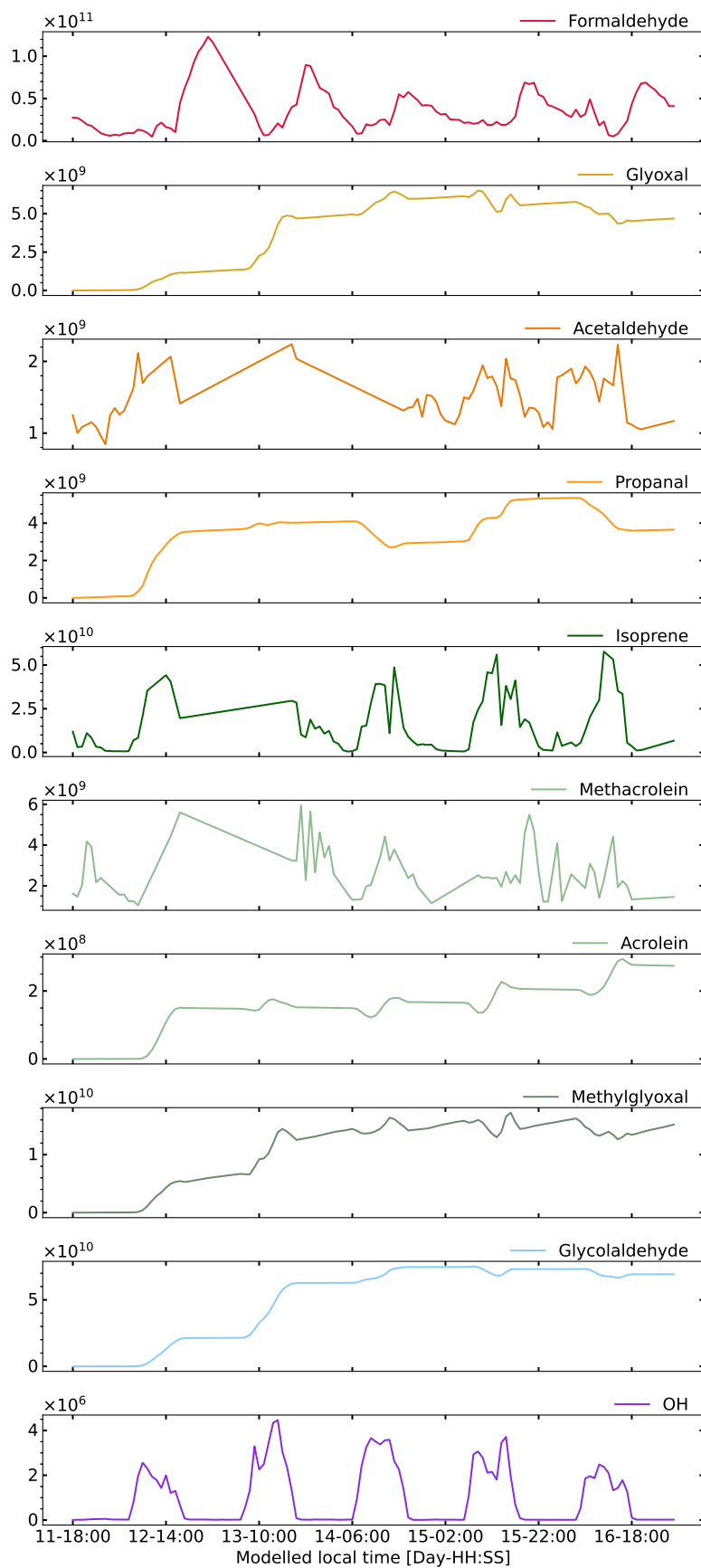


Figure S3: Time series for selected modelled species in molecules  $\text{cm}^{-3}$  from the baseline box model simulation in Borneo starting at 18:00 on the 11<sup>th</sup> of July 2008.

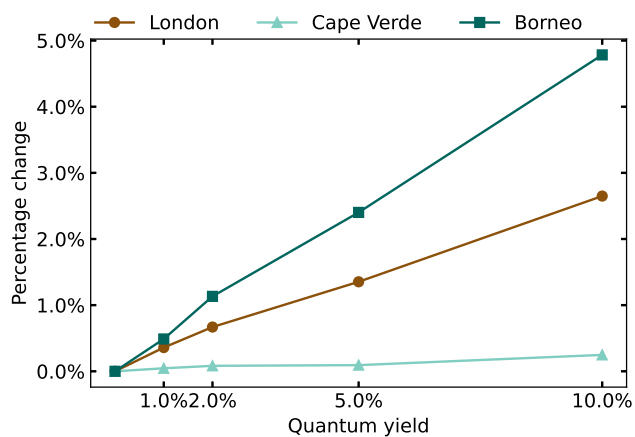


Figure S4: Percentage change in the total rate of production of  $H_2$  from aldehydes for varying quantum yields calculated relative to the baseline simulation at the three tested sites for 1 modelled day (local time)

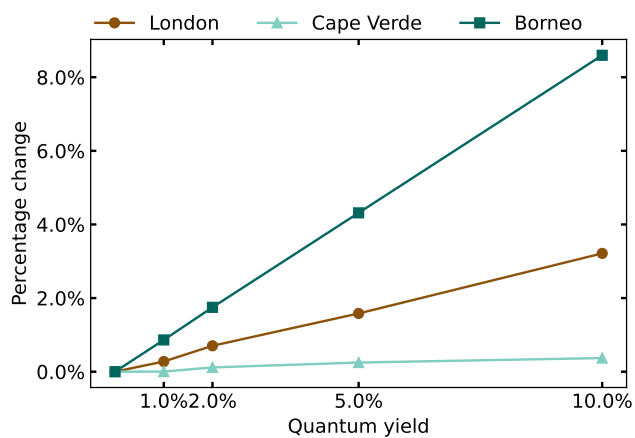


Figure S5: Percentage change in the total rate of production of  $H_2$  from aldehydes for varying quantum yields at the three tested sites for 5 modelled days (local time)

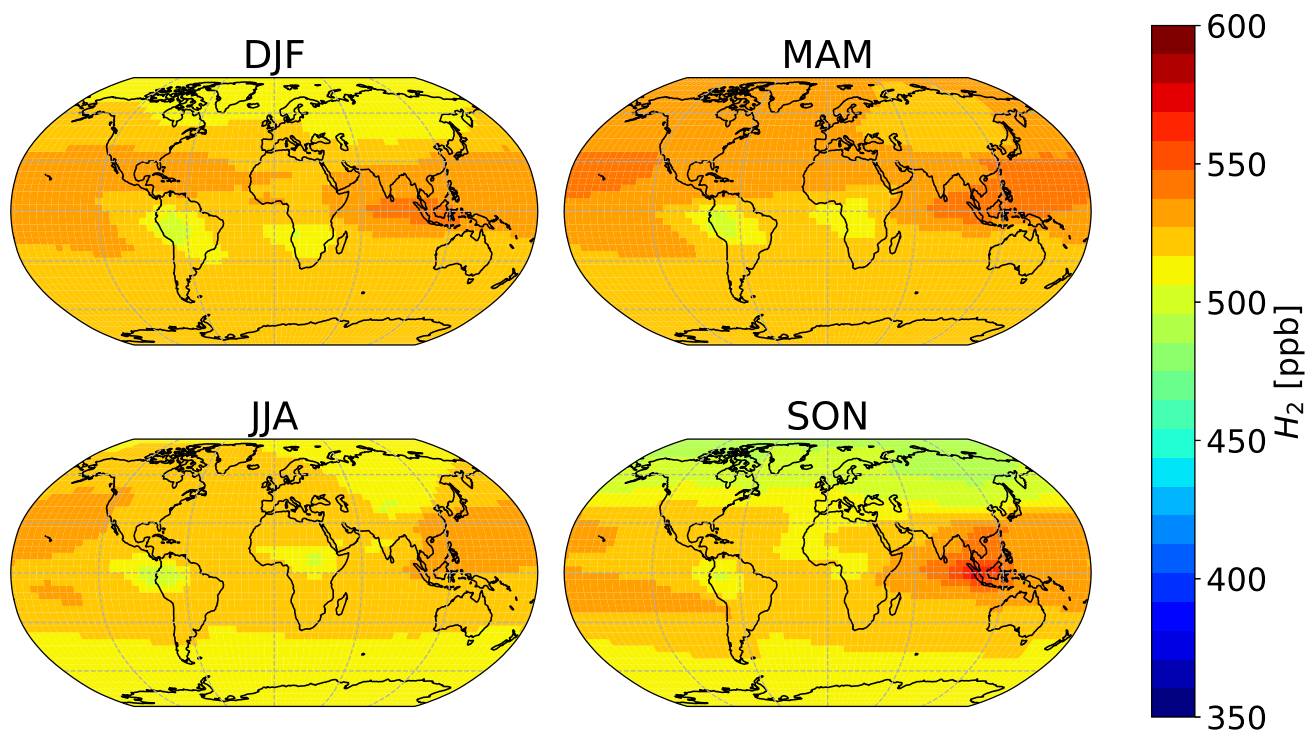


Figure S6: Average modelled mixing ratios of H<sub>2</sub> per season estimated with GEOS-Chem at 500 hPa for 2015 and 2016.

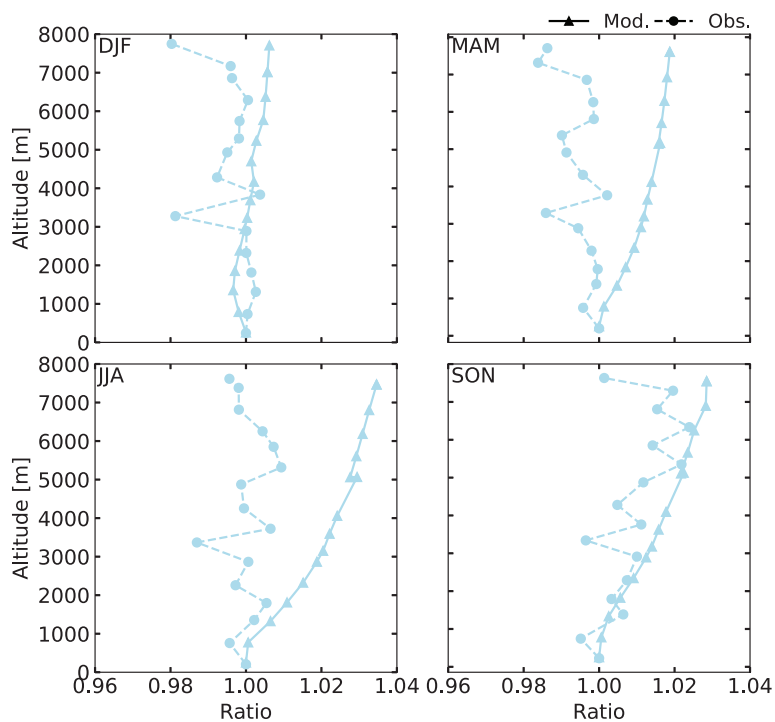


Figure S7: Seasonal comparison between average modelled (triangles) and average observed (circles) H<sub>2</sub> estimated ratios at different heights with respect to the surface layer. Modelled averaged values are from 2015 and 2016. Observations averaged values are those from the Aircraft (AIA) flask sampling data from Krummel et al., 2021r



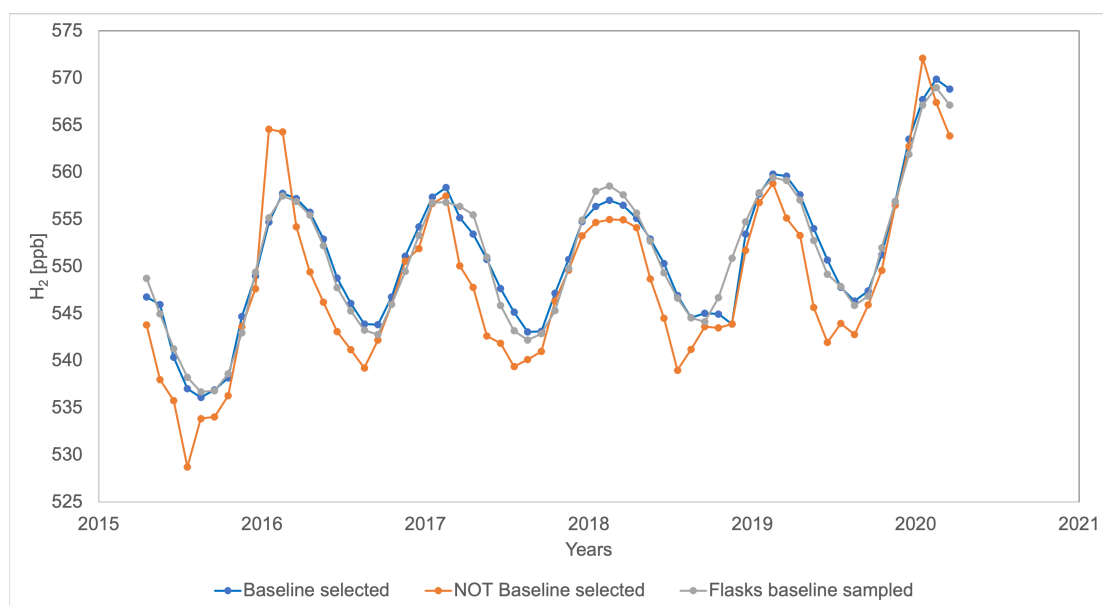


Figure S8: Comparison between baseline-selected in-situ data, baseline-sampled data measured with a PDD detector (blue and orange line) and flask baseline sampled by CSIRO at Cape Grim from April 2015.

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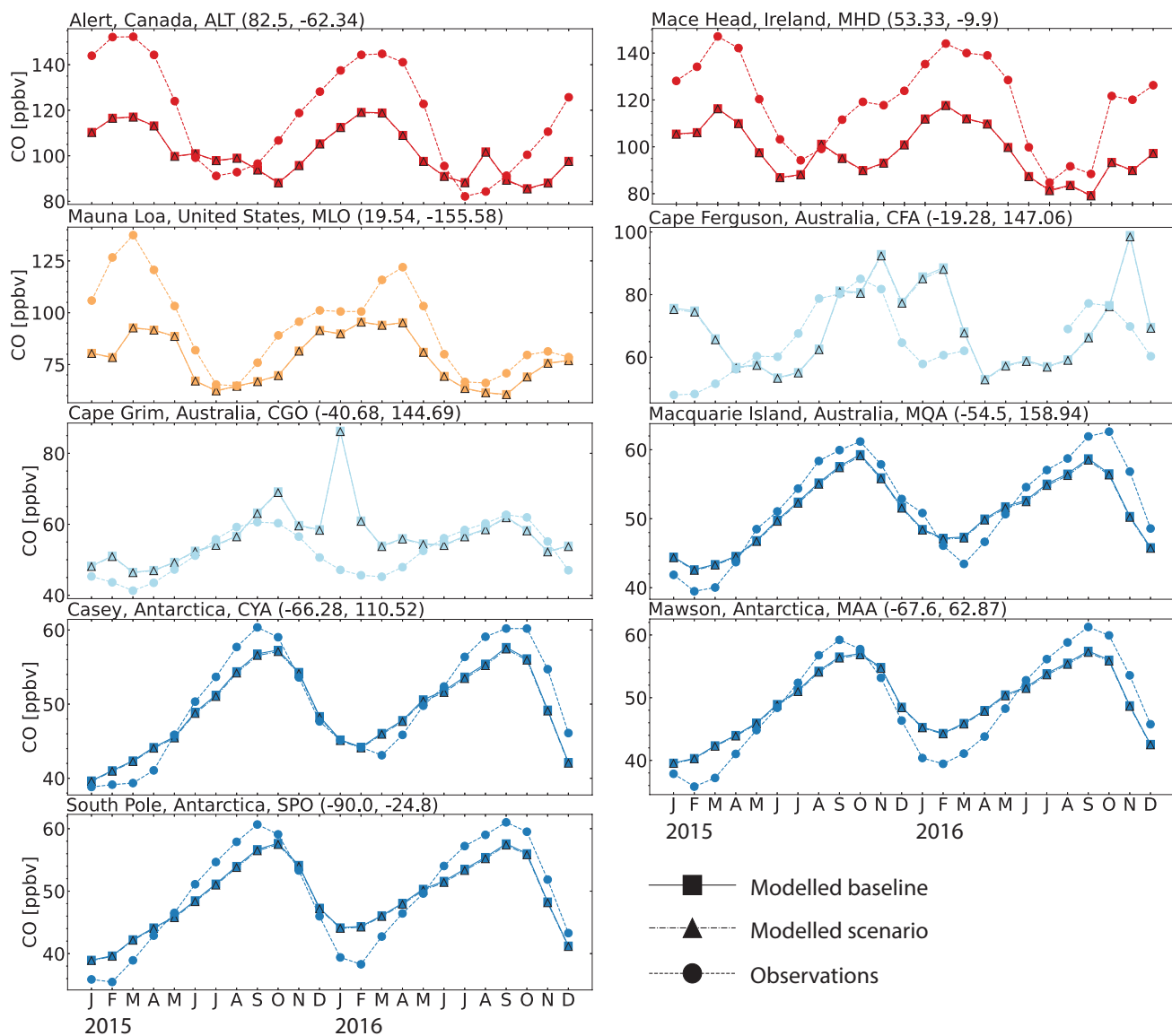


Figure S9: Seasonal cycle comparisons of CO at five sites from the CSIRO dataset (Krummel et al., 2021a, 2021b, 2021c, 2021d, 2021e, 2021f, 2021g, 2021h, 2021i) reported Flask Data for 2015 and 2016, the dash line with circle markers corresponds to observed values and the continuous line with triangle markers corresponds to modelled values in GEOS-Chem.

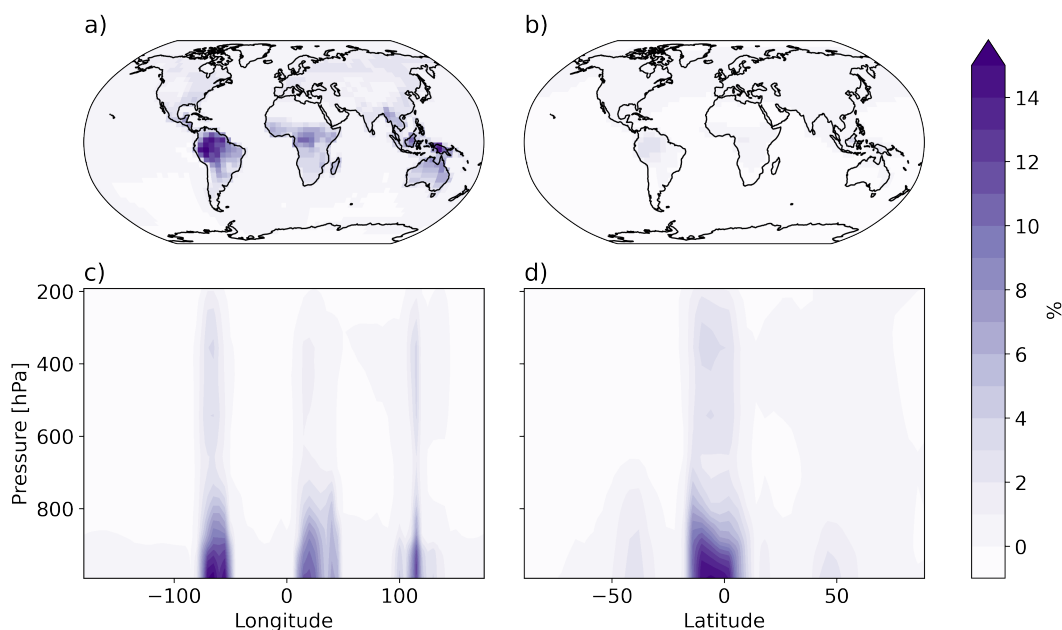


Figure S10: Percentage difference on the chemical production of H<sub>2</sub> between the 1% production of H<sub>2</sub> scenario and the baseline for a year a) At the surface level, b) At 500 hPa, c) Longitude section at 2 N and d) Latitude section at -70 W

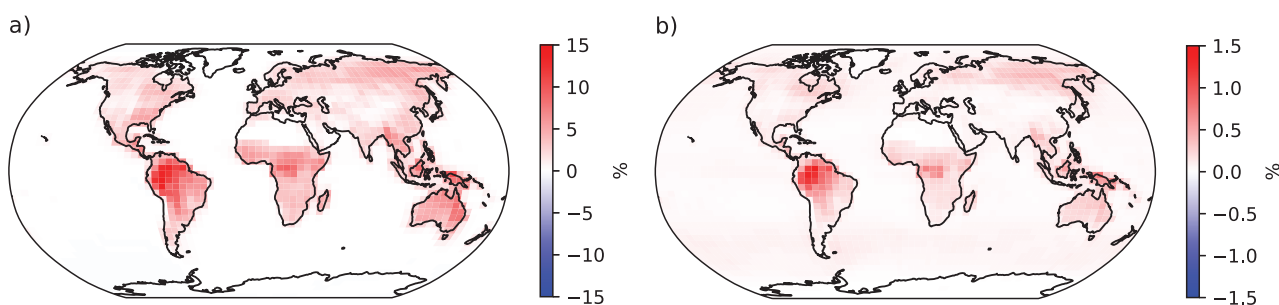


Figure S11: Percentage difference on the chemical production of H<sub>2</sub> between the 1% production of H<sub>2</sub> scenario and the baseline for a year at the surface layer from the photolysis of a) methylglyoxal b) acetaldehyde, HPALD, glycolaldehyde, methacrolein, lumped aldehydes with more than 3 carbon atoms RCHO (integrated)

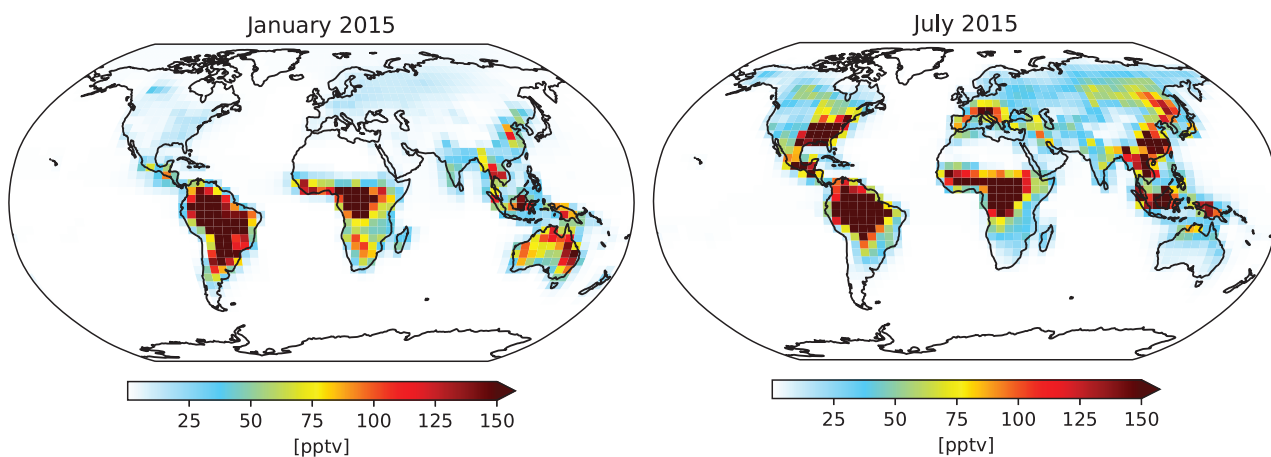


Figure S12: Simulated mixing ratios of methylglyoxal at the surface layer for January and July 2015. The modelled magnitudes of methylglyoxal in our GEOS-Chem simulation are comparable to those shown by Fu et al., 2008 in their Figure 2b.

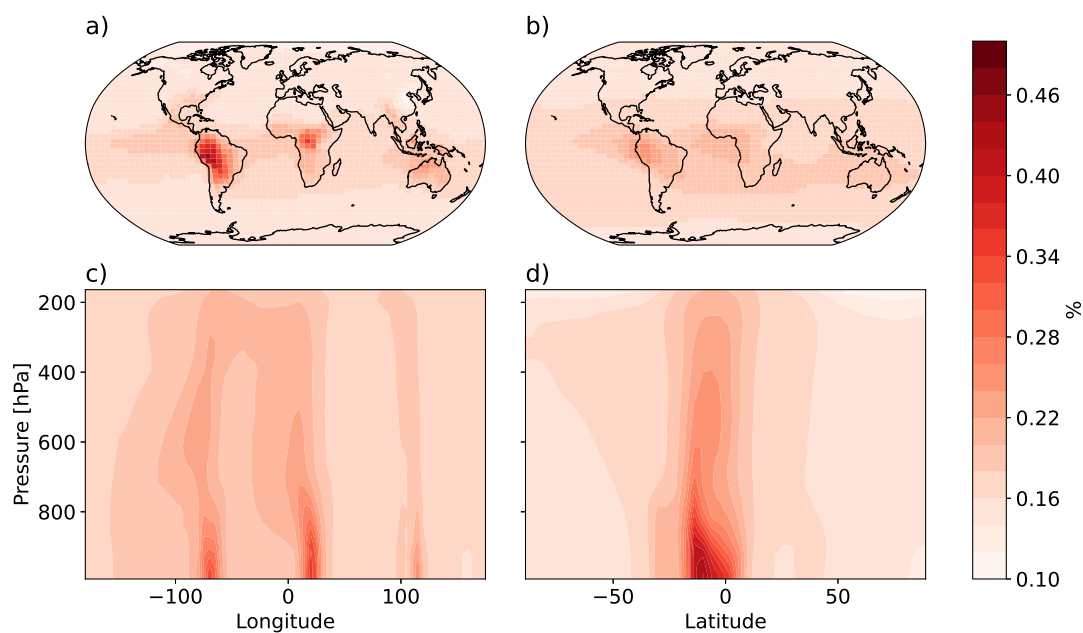


Figure S13: Percentage difference on the modelled mixing ratios of  $H_2$  between the 1% production of  $H_2$  scenario and the baseline for a year a) At the surface level, b) At 500 hPa, c) Longitude section at 2deg N and d) Latitude section at -70deg W

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Table S1: List of aldehydes in the MCM, along with photolysis products and rates ( $J$  [ $s^{-1}$ ]) for the  $H_2$  channel estimated with 1%, 2%, 5% and 10% quantum yields applied across wavelengths.

Aldehyde	MCM ID	Photolysis products <sup>a</sup>	JID	$J$ 1% qy	$J$ 2% qy	$J$ 5% qy	$J$ 10% qy
Formaldehyde (Methanal)	HCHO <sup>b</sup>	H2 + CO	J12	-	-	-	-
Glyoxal (oxaldehyde)	GLYOX <sup>b</sup>	CO + CO + H2	J31	-	-	-	-
Acetaldehyde	CH3CHO	CH2CO <sup>c</sup> + H2	J62	4.37E-07	8.74E-07	2.18E-06	4.37E-06
Propanal	C2H5CHO	C2H4 + H2 + CO	J63	5.68E-07	1.14E-06	2.84E-06	5.68E-06
Butanal	C3H7CHO	C3H6 + H2 + CO	J64	6.76E-07	1.35E-06	3.38E-06	6.76E-06
Isobutylaldehyde	IPRCHO	C3H6 + H2 + CO	J65	5.49E-07	1.10E-06	2.74E-06	5.49E-06
Acrolein (2-propenal)	ACR	C2H2 + H2 + CO	J66	2.44E-06	4.89E-06	1.22E-05	2.44E-05
(2-methylprop-2-enal)	MACR	C3H4 + H2 + CO	J67	3.05E-07	6.09E-07	1.52E-06	3.05E-06
Methylglyoxal (2-oxopropanal)	MGLYOX	CH2CO <sup>c</sup> + H2 + CO	J68	4.42E-07	8.83E-07	2.21E-06	4.42E-06
HPALD (2-hydroperoxyacetaldehyde)	HCOCH2OOH	H2 + Other products	J69	4.65E-08	9.30E-08	2.32E-07	4.65E-07
Glycolaldehyde (2-hydroxyacetaldehyde)	HOCH2CHO	HCHO + H2 + CO	J70	1.07E-07	2.15E-07	5.37E-07	1.07E-06
3-Hydroxy Methylpropanal	HOIPRCHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
Lactaldehyde	CH3CHOHCHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
3-Oxopentanal	CO3C4CHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
3-Hydroxy-pentanal	HO3C4CHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
3-Hydroxypropanal	HOC2H4CHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
2-Hydroxybutanal	HO3C3CHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06
4-Hydroxybutanal	HOC3H6CHO	H2 + Other products	J71 <sup>d</sup>	6.76E-07	1.10E-06	3.38E-06	6.76E-06

<sup>a</sup> Expressed with the identification used in the MCM.

<sup>b</sup> Species in MCM that already include the photolytic generation of  $H_2$ . The photolysis rates were kept the same for all tests.

<sup>c</sup> The ketene  $CH_2CO$  generated in the photolysis channel was replaced with glycolaldehyde as described in the text.

<sup>d</sup> In absence of aldehyde-specific cross section measurements, the photolysis rate of butanal was used as a surrogate in each case.

Names in parenthesis are IUPAC names

Table S2: Calculated metrics at each measuring site from the Krummel et al., 2021j, 2021k, 2021l, 2021m, 2021n, 2021o, 2021p, 2021q dataset

Site ID	Site name	Lat	Lon	Hemisphere	Lat. band	Gas	Start <sup>a</sup>	End <sup>b</sup>	N. obs <sup>c</sup>	Mean Mod. [ppb]	Mean Obs. [ppb]	r	RMSE	MB	NMB	MFB	NME	FE	FB
ALT	Alert	82.4991	-62.3415	NH	HNH	H2	2015-01	2016-12	24	494.86	489.93	0.93	9.30	4.93	1.01	0.01	1.62	1.63	1.00
MHD	Mace Head	53.33	-9.9	NH	HNH	H2	2015-01	2016-12	24	502.40	515.91	0.95	15.99	-13.51	-2.62	-0.03	2.62	2.70	-2.70
MLO	Manna Loa	19.5362	-155.5762	NH	LNH	H2	2015-01	2016-12	24	530.12	536.51	0.54	11.53	-6.39	-1.19	-0.01	1.60	1.62	-1.21
CFA	Cape Ferguson	-19.2773	147.0584	SH	LSH	H2	2015-01	2016-12	20	483.79	546.30	0.52	60.87	-60.26	-11.03	-0.10	11.03	9.74	-9.74
CGO	Cape Grim	-40.6822	144.6883	SH	LSH	H2	2015-01	2016-12	24	508.42	547.37	0.74	39.44	-38.95	-7.12	-0.07	7.12	7.39	-7.39
MQA	Macquarie Island	-54.4985	158.9385	SH	SHS	H2	2015-01	2016-12	24	513.94	547.78	0.84	34.04	-33.84	-6.18	-0.06	6.18	6.38	-6.38
CYA	Casey	-66.2833	110.5167	SH	SHS	H2	2015-01	2016-12	24	516.11	546.93	0.87	30.98	-30.82	-5.64	-0.06	5.64	5.80	-5.80
MAA	Mawson	-67.6047	62.8706	SH	SHS	H2	2015-01	2016-12	14	516.20	551.72	0.54	34.05	-33.90	-6.14	-0.04	6.14	3.70	-3.70
SPO	South Pole	-89.9969	-24.8	SH	SHS	H2	2015-01	2016-12	24	516.12	547.13	0.87	31.16	-31.01	-5.67	-0.06	5.67	5.83	-5.83

<sup>a</sup>Corresponds to the first date available in the measurements from Krummel et al., (2021a-i) used in the calculation of metrics.

<sup>b</sup>Corresponds to the last date available in the measurements from Krummel et al., (2021a-i) used in the calculation of metrics.

<sup>c</sup>Number of measurements used to compare during the period covered by the start <sup>a</sup> and end <sup>b</sup> dates.