Responses to RC1: 'Comment on amt-2024-4', Simon O'Doherty, 28 Feb 2024

General Comments:

1. This is an important description detailing the calibration strategy used to be able to assign meaningful and traceable mole fraction values to a global network of H_2 flask measurements and is exactly the type of manuscript that should be published in AMT. The difficulty in this “warts and all” description of how the calibration procedures have developed over time is that it makes for quite difficult reading due to the complex nature of the many different tank comparisons performed using many different instruments. I can’t recommend a better way of presenting the data, because ultimately all the useful information is contained within the manuscript and SI. The reader will just have to persevere, jumping between text, Figures, Tables and SI to find what is immensely useful information for setting up a calibration procedure for H_2

Thank you for your detailed review. Your comments and questions are very helpful.

We agree that the manuscript and the SI are covering a lot of information. The WMO H_2 calibration scale adoption and transfer was a long and iterative effort to make the most of existing measurements. We have moved 3 Tables to the Supplementary Information file and removed some redundant text in the main manuscript.

2. Section 3 of the manuscript describes the data quality assurance and quality control of the ~6000 glass flasks that have been collected at a global network of sampling sites between 2009-2021. This is an immensely impressive and useful dataset. I was a little surprise however, that this manuscript describing the analytical detail is being published after a paper whew the measurements have been used to assess the representation of the H2 atmospheric budget in the state-of-the-art GFDL-AM4.1 global atmospheric chemistry climate model (Paulot, F et al., 2023).

I apologize for the timing of this paper’s submission. I very much underestimated the time it would take to get co-authors’ comments back and then the manuscript had to go through a new internal review procedure before submission. The revised H_2 measurements from the Cooperative Global Surface Sampling Network were made available on the NOAA GML public ftp in May 2023. The work and paper led by Fabien Paulot moved fast and we did not want to delay the publication of the modeling findings as there is growing interest among policymakers to understand where the science stands.

3. It is clear from the calibration work that has been undertaken by NOAA, that aluminium cylinders are not stable for H_2. This was recognised by NOAA many years ago and is why the primary calibration standards are filled into stainless steel electropolished Essex cylinders. However, even with this knowledge this hugely

important global network for H_2 measurements has persisted in using aluminium cylinders for secondary and tertiary analysis and then tried to correct for the many different rates of calibration tank drifts. The paper details extensive problems using this approach (under-sampled cylinders, massively different rates of drift on a tank-to-tank basis), all of which propagates uncertainly into the measurements. Why has a different style of tank not been used, which does not suffer from these issues? I realise that Essex tanks (or a similar style of stainless-steel tank) are expensive but surely it is a requirement of a global H_2 network to reduce measurement and calibration uncertainties where practicable by using tanks that don't drift?

Aluminum cylinders work well for CO_2, CH_4, N_2O and SF_6 which have held higher priority historically (and presently) at NOAA GML. Aluminum cylinders are also cheaper and easier to use than stainless steel electropolished Essex cylinders.

A while back, the decision was made to continue using those cylinders for H_2 (and CO) calibration standards and to track their drifts regularly enough to correct for them. Adopting the H_2 gravimetric mixtures prepared in electropolished stainless steel cylinders as our primary standards after they were calibrated by the MPI was a first step. We are still evaluating options to improve the robustness of the H_2 calibration scale transfer. The existence and value of the NOAA H_2 dataset for recent years are becoming more known and we are working on securing some funding to buy more Essex cylinders.

4. I am a little unsure of the purpose of section 3.2.3, the text does not really indicate why the SPO measurements are given their own section (unless the point is to state that H2 stores well in glass flasks and SPO is uninfluenced by emission sources)?

Thank you for this clarification question. Your assumptions for the reasons are correct. We have removed some extraneous information in this section and added this sentence to connect with the WMO comparability goal:

"The average of the absolute differences for H_2 in SPO flask paired samples is less than 2 ppb ($\sigma \leq 1.3$ ppb) and methods S and P H_2 pair averages at SPO agree within 1 ppb on average ($\sigma \leq 1.7$ ppb)."

Specific comments:

1. defined the calibration scale as a WMO scale, whilst L30 defines it a the MPI scale, this is a little confusing so early on in the paper.

   This has been corrected.

2. Grey H_2 not Gray H_2

   Sorry, we use the American English spelling.

3. Novelli et al. [1991, 1992] not [1992, 1991]

This has been corrected.

4. 10-200ppb not 10s

   This has been corrected.

5. Why are the Essex cylinders filled with dry air. I understand that Essex cylinders tend to be stable for H_2, however, is there any evidence that drying the air is a requirement for H_2 stability? In my experience Essex tanks filled with undried ambient air are also stable.

   The GML H_2 primary standards in Essex cylinders were prepared gravimetrically by Brad Hall. They were not prepared with ambient air. We do not have experience with H_2 in humidified Essex tanks. We began testing dry air in Essex cylinders after hearing from colleagues that Essex tanks may be stable when filled dry.

6. What is NOAA going to do with the pre-2009/10 ambient air record for H_2

   At this point we are focusing on maintaining the quality of the NOAA H_2 measurements going forward.

   Sadly, the pre 2009/2010 H_2 measurements cannot be revised for reasons detailed in Supplementary text S1. These measurements are marked as rejected in the NOAA GML database and future NOAA H_2 data releases will not include them.

7. L272-276. What caused the tail or noisy baseline? Do you think use of peak height might have caused a bias; what effect did the higher grade of helium have (removed the noise/tail)? Do you use peak height or peak area for the data using the higher-grade helium, are peak height and peak area data comparable now? Why did it take 4-years to decide to use cleaner helium?

   The issue with the peak tail or noisy baseline was very (Airgas) He tank dependent and we found that peak height was less sensitive than peak area in those instances. Colleagues in GML were using Matheson Research Grade He for GC-MS systems and when we tested that He for H_2, the baseline and peak looked good. We get very similar results for peak height and peak area. We still use peak height.

8. The word “few” is not informative.

   We have replaced “few” in this sentence below:

   “GML has performed an H9 instrument response calibration followed by tank calibrations 2 to 3 a few times a year over a 10-14 day period each time.” (Line 298 in final view file)

9. You state that typically H_2 tertiary standards lasted less than a year. However. Figure 3a & b show that many of these tanks lasted much longer than 1-year and most drifted quite appreciably.

   Figure 3a & b shows the calibration records for the MAGICC system tertiary standards. Three (out of 17) tertiary standards were used for more than 14 months (cf. Table 2):

   - on H11: ND46735 had a small quadratic drift < 2.5 ppb/yr and was used for 17 months. ND38963 had a 6.2 ppb/yr linear drift and was used for 16 months.
   - on H8: CA03409 had no detectable drift and it was used for 22 months.

We have revised the text in L 337-338 in final view file:

"Typically, the H_2 tertiary standards used during that time lasted less than a year and most displayed H_2 growth over time. "

to

"Out of 17 H_2 tertiary standards used during that time, 3 were used for more than 14 months and 14 displayed H_2 growth over time. "

10. Why only use 8 or the 11 standards

The three standards that are not used for the H_2 response curve of the MAGICC-3 system exhibit changing H_2 drift behaviors that are not captured well enough by their calibration records. For these 3 cylinders, the residuals of a best fit (quadratic) to their calibration histories span ranges beyond the range [-1.5 ppb, 1.5 ppb], in contrast with the other eight standards.

The suite of standards used for future H_2 response curves may change. Every 1 or 2 years, we will reevaluate the drift corrections and assignments for the 11 cylinders based on new calibration results. If residuals of a standard calibration history to a new best fit function are larger than 1.5 ppb or if H_2 grows beyond 700 ppb in a standard, we may decide to drop that cylinder from the suite of standards. We also may have to go beyond using a single linear or quadratic fit if the observed H_2 drift behavior for one standard will be better captured by a set of different functions.

One sentence was added in the main text (L 376-376 in final view file):

"The three cylinders that are not used exhibit H2 growth that is difficult to capture with periodic calibration episodes."

11. You now define the tanks as working tanks, not secondary or tertiary – why change the tank definition, it is confusing.

We use “working” standards to differentiate from true “tertiary” standards. Secondary standards are only used in GML to transfer the scale to tertiary standards. We are not using secondary standards for H_2 after April 2019.

Section 2 introduction states: “(...) we describe the GML tank air H_2 calibration system and the scale transfer from the primary standards to secondary and tertiary standards (2009-April 2019) or from the primary standards to working standards (after April 2019). The tertiary standards and working standards are used to calibrate the H_2 instrument response on the flask air analysis systems and value assign discrete air measurements.”

12. Why change at 250 psia, is there evidence that the tank drifts at pressures below this?

A tank pressure of 250 psi is a cutoff GML uses as there are no or very small changes in the tank mole fraction for the GHG measured in GML, especially CO_2 [WMO. 2016; Schibig et al., 2018].

GML rarely uses standards with lower pressures. It did happen for example for CC305198 (A) and we noticed an acceleration in its H_2 drift rate (SI Table 2). The H_2 growth in aluminum tanks is suspected to be caused by a surface process (see next question’s response and [Jordan and Steinberg, 2011]) and therefore the drift rate could be influenced by pressure in the tank.

Schibig, M. F., Kitzis, D., and Tans, P. P.: Experiments with CO2-in-air reference gases in high-pressure aluminum cylinders, Atmos. Meas. Tech., 11, 5565–5586, https://doi.org/10.5194/amt-11-5565-2018, 2018.

WMO: 18th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13–17 September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.

13. Do you know why H2 drifts in air filled aluminium cylinders? If a non-drifting tank is reused, is it still non-drifting and vice versa with a drifting tank?

Jordan and Steinberg, AMT, 2011 (section 3.1, Figure 5) discuss the stability of reference air in various high pressure cylinder types. They analyzed > 100 cylinders over 1-6 years and found that “highly variable storage properties were observed in aluminium cylinders.” They go into more details about cylinders made with different alloys and propose that different alloys and manufacturing processes may impact the integrity of the cylinder surface.

We do not have a lot of repeated fills for tanks used for H_2 work. For TST air cylinders which are refilled regularly and have 4 or more tank calibrations, it seems that AL47-104 and AL47-108 always exhibit significant drift in H2 for the 2 or 3 fills plotted, while AL47-113 shows no drift for 3 successive fills and AL47-145 had a very large drift for fill E and more

moderate drifts for fills F and G. We are paying attention to this issue and hope to understand more soon to avoid cylinders with large drifts.

14. If the tank shows signs of large initial growth in the first 0.5-2 years, why not fill then store a tank for this time before use?

Yes, it seems that waiting at least 2 years could help with some tanks. We now know we need to wait longer after a fill or document its behavior for a while before adopting them as a standard or a target tank. Our colleague MM has been screening cylinders over several months with regular analysis in the flask lab to pick reference air tanks with ambient level and stable H_2.

13. L451-452. I assume the three tanks are aluminium filled with dry air? – this information is not detailed in the text or Figures.

Yes this is correct, the MENI cylinders are 10 L Luxfer UK aluminium cylinders (AA6061) filled with dried air.

This information has been added, L 430.

15. SI L281. Figure 5 (a) is missing.

I am very sorry. The missing figure has been added. Thank you for noticing.

16. SI Figure 5. To understand the year in year comparisons it would be useful for the to have the error bars plotted.

See below, merged answer with the next question.

17. SI Figure 5. The data in 5(b) are not that easy to understand. Why are the NOAA (2018) and MPI (2019) data carried out a year apart quite similar, but the NOAA (2021) and MPI (2022) a year apart quite different (~2 ppb). There are also very few NOAA data points to compare with MPI.

The MPI MENI tanks go to other laboratories besides NOAA for analysis of a suite of gases (CO_2, CH_4, N_2O, SF_6, CO, H_2) and CO_2 stable isotopes (^{13}C, ^{18}O). Delays can happen. We have added the reported reproducibility as error bars to the plots. The MPI BGC GC-RGA measurements (April 2020) have larger standard deviations and that instrument has a reported reproducibility of 2 ppb compared to the 0.5 ppb reported for the MPI BGC GC-PDD measurements.

18. L 462-463. You state the MENI program provides an important on-going check from MPI X2009 H2 calibration scale transfer in GML. What is not clear is how the results presented in SI Figure 5 are used?

As you point out these measurements are not very frequent but they still provide an independent on-going comparison directly with the CCL. If we ever see large differences, we will know we need to investigate and fix a problem. We replace the word “important” with “valuable” in the main article section 2.3.2.

19. Does the restating the information about the flask sampling systems need its own section (3.1), why can't the information be contained in Section 3.

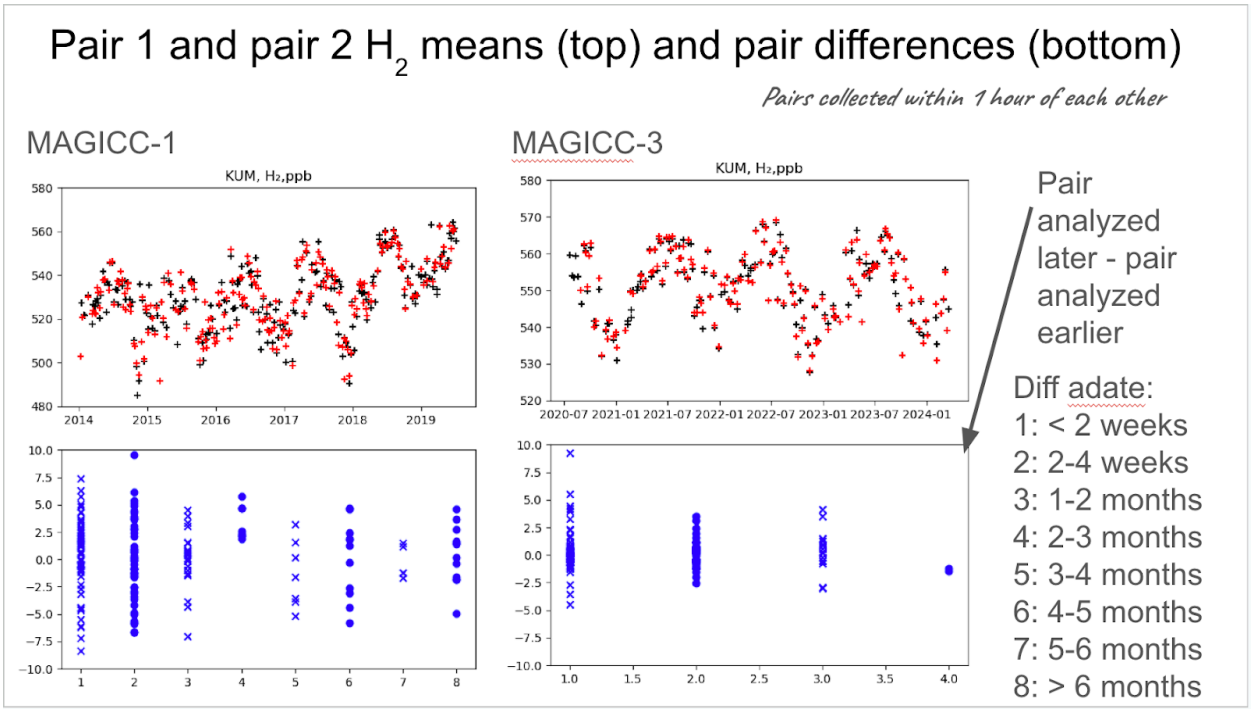
We have eliminated section 3.1 to reduce redundancy.

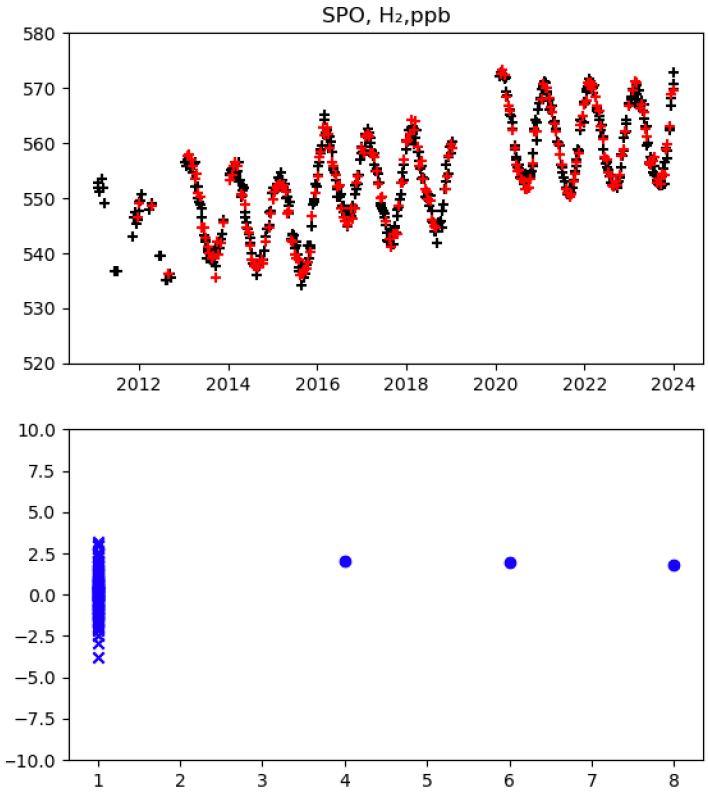
20. Is there any indication that H2 is stable/not stable in the glass flasks over time?

GML has not performed long storage tests on flask samples in a while, and it is something we know we need to do.

To try to answer your questions, I am looking at air samples collected close in time but not analyzed at the same time. Note that the 2 flasks from a pair (collected at the same time at a site) are always analyzed back to back on the flask analysis system in GML.

The GML team in Hawaii often collects 2 flask pairs back to back at KUM. Here we look at 2 pairs collected within 1 hour of each other and results from the H11 instrument . The second pair is typically used for various types of testing. Below we look at the mean H_2 for each pair (top plots) and plot the pair mean differences as a function of the length of time between the analysis times of both pairs. The difference plot shows the mean H_2 for the pair analyzed later minus the mean H_2 for the pair analyzed earlier. The scatter likely reflects both short term variability in the ambient level at the site and uncertainty in the measurement.





This is a similar plot as above for H2 in the South Pole S and P flasks.

We only have 3 sampling dates for SPO with pairs analyzed more than 2 months apart.

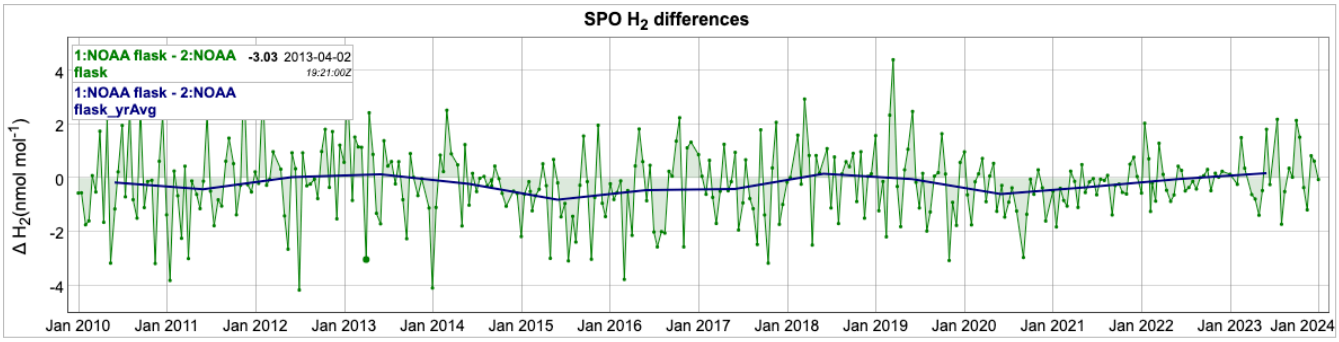
In those 3 pairs, the flask pair mean difference is about 2 ppb, which means H_2 in the flasks analyzed later (2 P pairs and 1 S pair) are about 2 ppb higher than the flasks analyzed earlier.

So with the data on hand there is no evidence of a flask storage effect on H_2 as the scatter of the mean pair differences is comparable for different storage times.

21. L677 to 678 and Figure 7. How are reliable results between S and P methods defined and tested? Visually from Figure 7, it looks like the S flask data are slightly below the P flask data (looking at the apex of the annual cycles in 2020 and 2021 for example)?

    Below is a plot of SPO H_2 S flask pair average minus P flask pair average at full resolution in green, with annual means of the differences shown in blue. Most of the time it looks noisy around zero and sometimes the differences are mostly positive. It is not clear what exactly causes these changes. We rotate the staff at the observatory and it may be due to slightly different sampling operations. The annual

mean difference ranges between -0.8 (2015) and 0.2 ppb and the standard deviation ranges between 0.6 (2021) and 1.7 (2010 and 2019) ppb.

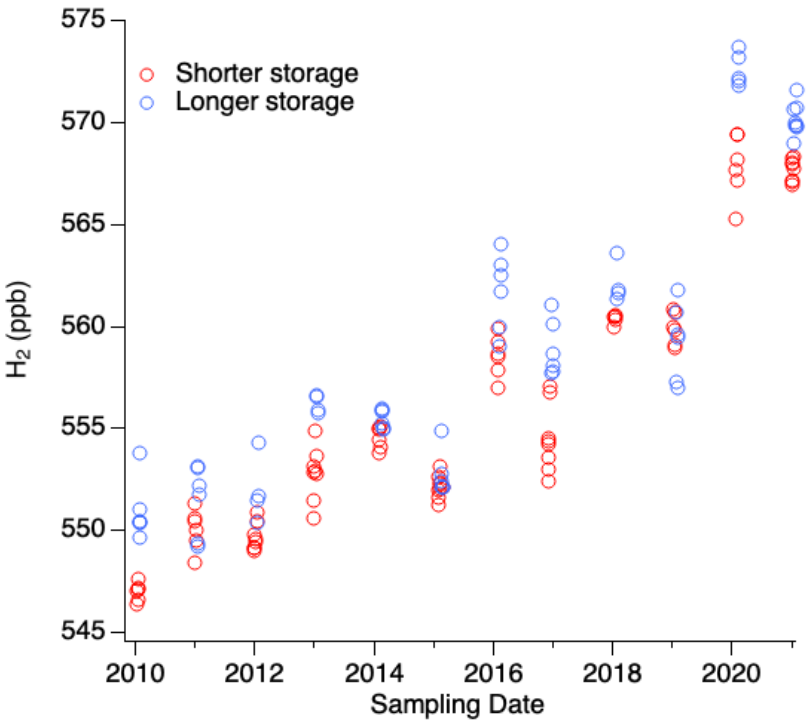


22. How do you define “reliable”, this is a bit non-specific.

This sentence has been removed.

23. What metrics have you used to determine that there are no biases?

The plot below shows H_2 at the times of transition between SPO flask shipments. The shorter storage samples (red symbols) were collected typically in late December or early January and were analyzed in the next 1.5 to 3 months. The longer storage samples (blue symbols) were collected in mid January to mid February and were analyzed 11 to 12 months later. We chose to limit the transition to 3 weeks of sampling dates, centered on the first sampling date with the longer storage time. The transition occurs when H_2 is increasing before peaking in February. There is no systematic offset for H_2 from the longer storage samples.



24. L779-781. It is clear that the Mauna Loa data show more short-term variability that Samoa and South Pole, but not necessarily Barrow

    Yes, this is correct.

25. L779 to 787. It is not clear how the maxima and minima for each site have been determined, and wouldn't these vary year to year given that there is a growth trend in the data?

    Thank you for your question. We used the smooth curve fit to the data and here we are talking about absolute min/max for each year so yes it includes the "trend". We have switched the order of sections 4.1 and 4.2 to introduce the curve fit and smooth curve concept before using it for the observatories extrema discussion. We have also switched the order for Figures 9 and 10.

26. What does ASC stand for?

    Sorry, this is the code for Ascension Island, and this has been clarified in the main text.

27. L 816 and Figure 10. Given all the sites are defined at the top of the plot, why do you need to use the x-axis to number the sites. Surely you should use it to illustrate the latitudinal gradient.

    The index labels on the x axis in this figure (Figure 9 now) have been removed.

    A sentence Line 728-729 mentions the interhemispheric gradient:

"The interhemispheric gradient of H_2, with higher levels in the SH, is apparent in the annual means

distribution across sites in Figure 9 (green circles)."

28. L 817 to 834. I can't find any information in the manuscript of SI defining the site acronyms or detailing their lat/longs (useful). Can this be contained in a Table? Also, in the text you define some sites described in the text e.g., TPI site, on Taiping Island, but don't define others e.g., TAP, AMY, LLN, CPT, KUM, WIS.

    SI Table S4 has been added with this information in the Supplementary material. Thank you for the suggestion.

    The paragraph about the sampling location change at KUM and WIS was removed.

    We have added the country for the other sites in L 733.

"A few sites (for ex. TAP (Taiwan), AMY (Republic of Korea), LLN (Taiwan), CPT (South Africa)) show higher smooth curve annual maxima (Figure 9, red crosses), likely reflecting upwind local or regional emissions."

29. L828 to 834. Is this short description of moving sites required? There is no supporting evidence to explain why the mean level of H2 or seasonal cycle have changed since the move. Just the assumption that increased soil uptake is responsible – is the new location more inland? Can you use ozone deposition or radon measurements to confirm this?

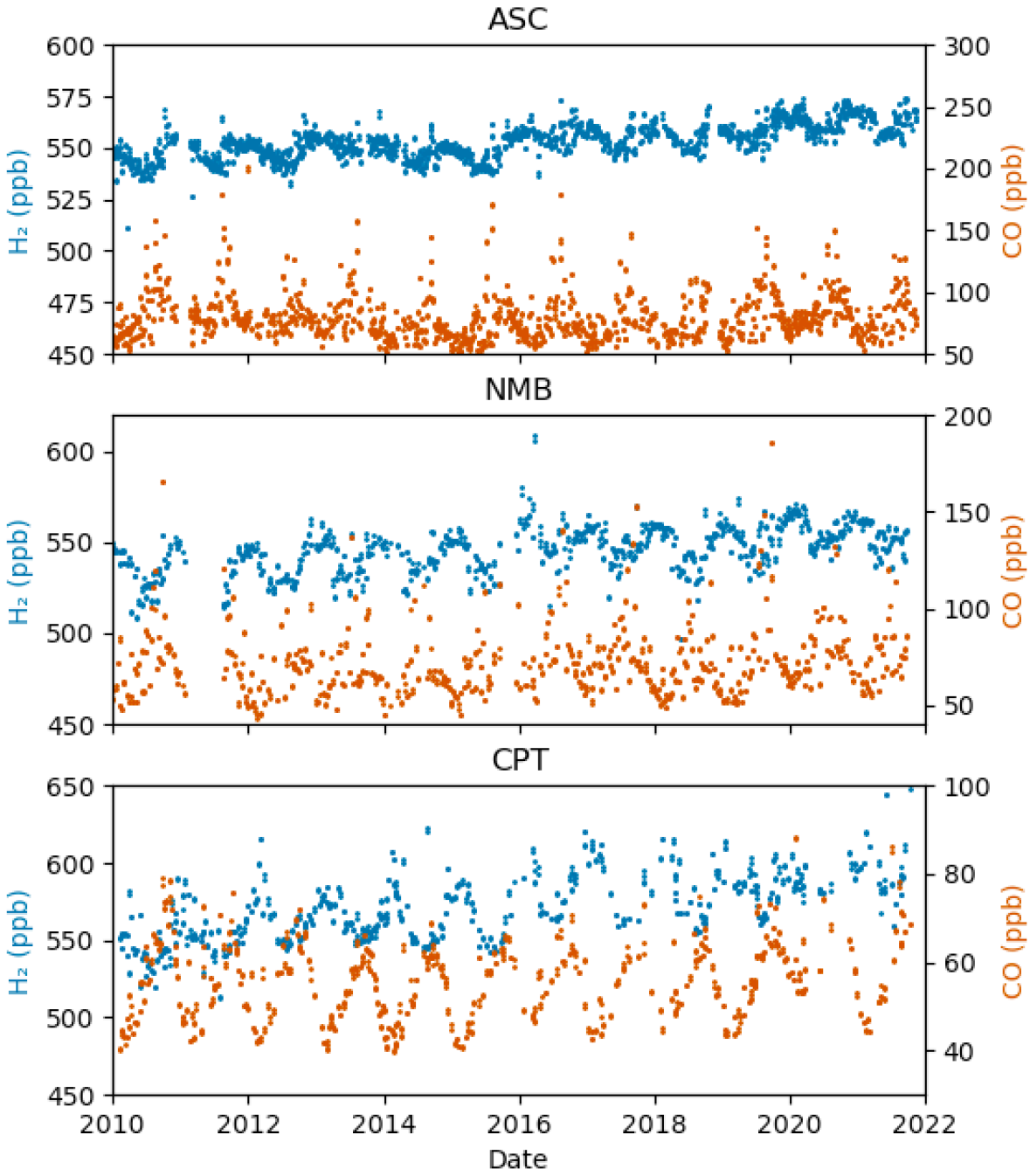
    We have removed this section discussing the change in sampling site locations.

    We do not have colocated ozone or radon measurements at these sites to investigate the assumption of the soil sink impacting the measurements. Field studies are needed to advance the parameterization and estimation of the soil sink in various ecosystems and regions.

30. L844. A large proportion of Africa (and fires) are in the NH. The flask sites at ASC, NMB & CPT look well located to sample SH fires from the Peoples Republic of Congo, Angola and Zambia?

    The plot below shows the H_2 and CO records at the 3 sites ASC, NMB and CPT. There are several samples at ASC and NMB in June-October months with elevated CO which may be related to biomass burning in South African countries. We do not see clear H_2 enhancements at the 3 sites during the region's fire season. Further analysis using atmospheric transport models and biomass burning products is

needed to study the observed variability.



31. Table 2. The time of use and Fill date time formats are different, less confusing if you use the same format.

The inconsistency has been fixed in Tables 1 and 2. Thank you for bringing it up.