

Interactive comment on “A 15 year record of high-frequency, in situ measurements of hydrogen at Mace Head, Ireland” by A. Grant et al.

A. Grant et al.

aoife.grant@bristol.ac.uk

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Reply to Referee #1 We thank reviewer #1 for their insightful comments. In response to referee comments modifications were made in accordance with suggestions, see below: Comments and responses

P 20196, line 4 {line 12 in revised manuscript}: ‘a wealth of’ was removed as suggested.

P20196, line 15-16 : ‘...the latitudinal gradient reflects the large photochemical source from southern latitudes...’ How was that proofed and extracted from the influence of a weaker soil sink in the southern hemisphere? Use better ‘low northern latitudes’ than southerly latitudes’ {line 23 in revised manuscript}: Wording changed as suggested. It was not possible to differentiate from these two sources (of H₂ elevation from low

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latitudes) thus it was assumed the elevated mixing ratios from this sector were due to both the influence of the inter-hemispheric gradient as well as increased production through photolysis.

P 20197, line 14 and line 23 {line 48 in revised manuscript}: Spelling of Ehhalt corrected as suggested.

P 20198, line 2-5: add paper by Lallo et al., 2008. Mention some numbers of the in-situ studies to stress the large site-to-site differences as well as the observed variability at specific sites. {line 76 and 66 in revised manuscript}: Paper by Lallo added. Text added to stress site-to-site variability: “Large variability in H₂ deposition has been observed at the same sites, Yonemura et al. (2000) reported a range of H₂ deposition velocities of 0.9×10^{-2} cm s⁻¹ from a year of chamber measurements taken in an arable field. The same soil types with differing vegetation also show large variation in deposition velocities, a recent study reported deposition velocities of 4.4 and 7.3×10^{-2} cm s⁻¹ over burned forest and mature forest sites (Rhan et al., (2002)).” P 20198, line 25, 29 {line 94, 99 in revised manuscript } : ‘on the West coast of Ireland’ removed as suggested

P20199, sampling location: The authors only refer to the AGAGE programme. What about all the other programmes that provide continuous data? Reactive gases, aerosols etc. What’s the height of the inlet above ground? {line 117 in revised manuscript } : Information added about GAW which also measures at Mace Head, however the majority of measurements made at the site are under the AGAGE programme. Sample inlet height added in Section 2.2 Analytical method and calibration {line 130}

P 20200, lines 5-7: add information on injections made every 20 mins and ambient air samples every 40 mins. Add some technical details. What is the size of the sample loop? Are there any other modifications made to the set-up of the RGA3? Did you use peak height or area for mixing ratio determination? {line 128 in revised manuscript } : Added “Injections made every 20 minutes alternated between analyses of air with a ref-

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erence gas to determine and correct for instrumental drift, resulting in 36 fully calibrated air samples per day. Samples collected at an inlet 25 m above seas level were flowed through a temperature and pressure controlled environment before collection in a 1 ml sample loop.” And {line 137 in revised manuscript } “H2 measurements, integrated by peak area, were referenced against a calibration scale”

P20200, line 15-18: The authors speak about good agreement but mention a difference of 16 ppb. Mention the known offset of the two different scales otherwise it is difficult to understand for the reader. {line 143 in revised manuscript }: We have include reported offset as well as measured offset “Reported differences between CSIRO and MPI2009 scales are 16 ppb at 460 ppb H2 rising to 17 ppb at 570 ppb H2 (A. Jordan, personal communication, 2009).”

P 20201, line 3-5: remove ‘of the possible 183,900 measurements’. Why not very simple: ‘Data coverage was 79%...’ Modified as suggested

P 20201, lines 22-24: ‘In Fig. 2 we plot the monthly mean H2 Northern Hemispheric baseline air, these data display both the seasonality and variability in mole fractions over the 15 year period’. To my mind, Fig.1 does show variability even better. Fig. 2 mainly reveals the inter-annual variability. I feel you may have misunderstood the point I was trying to make as Fig. 1 shows the whole dataset and I was trying to stress the differences in baseline air only which is shown in Fig. 2.

P 20201, line 24: How was data de-trended when there was no significant trend detected? No significant trend over all the years studied was observed however month to month differences were thus it was necessary to de-trend the data. Data was de-trended from month to month of different years so a spike in one month of one year would not throw off the seasonal cycle.

P 20202, lines 1-2: To my mind, it is not correct to compare the observed annual cycles with the cycles reported with the cycles reported by Simmonds et al. (2000) since the Simmonds data are also part of the present data set. Please reword sentence that it

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becomes obvious to the reader that the present paper at the extended data set only confirms the findings of Simmonds et al. for the first four years of the 15 year record. I agree with this comment and have reworded the sentence as suggested to “This study extends the four year dataset of Simmonds et al. (2000) at the same site, Simmonds et al. observed highest mole fractions in spring and lowest mole fractions in late autumn.”

P 20202. Lines 15-17: Replace ‘(Fig. 3)’ by ‘See Fig. 3 for comparison of the H2 and CO seasonal cycles.’ Please elaborate why the 3-month offset in spring maximum can be explained by the dominant soil sink. Reworded as suggested. Extra sentence included to elaborate on the seasonal cycle offset “Both shifts are due to the dominant influence of the H2 soil sink, though as the soil sink is weaker in late winter the spring maximum is delayed by only one to two months, whilst the late summer minima is delayed by two to three months, since the soil sink has a much stronger influence at this time of year.” P 20205: The authors are investigating the H2 to CO ratio during pollution events. I do agree that it is necessary to de-seasonalise both the H2 and CO data. The authors did that by subtracting baseline values. How was this exactly done? Daily mean baseline values were subtracted from the European data, this has been included in the text. After subtraction of the baseline values, why did the authors use all data (Fig. 7B also shows negative values) and not only data above baseline as they are interested in H2 to CO ratios from emissions? The slope might not be strongly affected as it is mainly determined by very high data. However, the authors should consider determining the slope with only data above baseline. How was the slope calculated? Most of the common spreadsheet programmes (like excel) do only consider error for the y-component and thus retrieves slightly incorrect slopes. The correct approach is an orthogonal or reduced major axis regression analysis. This is a valid point which had not been considered. Reported ratios were calculated using excel and thus only consider error in the y-component. As suggested slopes have now been calculated using only values above baseline (i.e. greater than zero) and using orthogonal or reduced major axis regression. Orthogonal regression produced slightly higher slopes by approximately 0.03, however when below baseline or negative values

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were removed slopes with differences of less than 0.01 were found. We have now replaced values in text with those calculated from orthogonal regression with below baseline values removed.

P 20205, line 13: What are 'raw H2 mole fractions'? 'raw H2 and CO mole fractions' has been reworded to 'raw H2 and CO mole fractions without baseline data subtracted' to further explain this expression.

P 20205, line 13-15: An extrapolation to CO=0 makes no sense. The intercept can be dominated by the seasonal cycle of the different trace gases. This is my point that it is essential to subtract baseline values since the intercept (and slope) can be dominated by the seasonal cycle effects.

P 20205, line 20-23: 'Winter data cover a broader range and show a higher correlation coefficient due to lower H2 deposition.' I do not agree with this statement. A higher correlation coefficient might be most likely a result of the broader range of data. If there is no variability at all, the correlation coefficient might be very low. If there is a steady soil sink that is just stronger in summer, the data are simply shifted or even not shifted in this case here because the seasonal variation is subtracted. Higher concentrations in winter can also be caused by less vertical dilution and thus a smaller buffer volume that let emissions appear more pronounced close to the ground and lead to an accumulation of freshly emitted trace gases in the lowermost levels. Comment: Fig. 7 A and B show that the consideration of the seasonality of the background concentrations leads to better H2 to CO correlation. I agree with this statement and have changed this sentence to "the winter data covers a broader concentration range. This is thought to be a combination of the reduction in soil sink due to increased rainfall and soil moisture content, and reduced vertical dilution resulting in accumulation of pollutants in a more shallow winter boundary layer."

P 20207, line 16 and P 20208, line 5: 'The conversion value for non-transport emissions... a range of values from 0.07 to 0.57 has been used...'. 'The best match is

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for a non-transport emissions scenario of 0.06...'. It is hard to understand what these numbers mean without having a look at Fig. 8. Is it 'The best match is for a non-transport molar H2 to CO ratio of 0.06...'? {line 395 in revised manuscript} I agree line 5 on page 20208 may have been worded a little unclearly. I have reworded this sentence to "The best match between this and the model-derived ratios is for a non-transport molar H2:CO emission ratio of ~ 0.06 ..."

P 20209: The authors discuss if the observed H2 to CO ratio has to be corrected for H2 soil deposition? What about the CO soil deposition? The best guesses of soil deposition velocities in the literature are pretty similar for H2 and CO. CO deposition was not considered to be a major loss process for CO as modelling studies suggest loss of CO through deposition accounts for $\sim 10\%$ (Bergamaschi et al. 2000) of the CO sink, it's major sink reaction with the OH radical (90%) loss has been accounted for. Also unlike H2 a detailed soil sink parameterisation was not available for implementation in the NAME model.

Conclusions: The authors mention at the very end of the introduction that 'this 15 year dataset may provide essential information to improve assessments of the effect of a possible future H2 economy on atmospheric composition'. No reference is made to this statement in the conclusions. The authors should refer to that and should discuss how the assessment of the effects of a future H2 economy on the environment can profit from the present study.

{line 529 in revised manuscript} Information was added on how this study could improve assessments on the effect of a future H2 economy. "Overall this 15 year dataset provides essential information on the long term trends of atmospheric H2 in the northern hemisphere. This record illustrates the timescale required to observe elevated mole fractions of H2 at a background site, resulting from increased emissions due to biomass burning episodes. These observations also illustrate the timescale in which the atmosphere responds to lower elevated background levels of H2. Results ultimately lead to increased understanding of atmospheric H2 which will improve assessments of

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the effect of a possible future H₂ economy on atmospheric composition.”

References: Simmonds (2009) is it published? No not yet.

Fig. 1: Add a curve that represents mean baseline values Yes will do

Fig. 4: Add a horizontal line at $y=0$ Yes will do

Fig. 5: Are these the baseline data that are subtracted from the dataset? No daily baseline values were used to subtract from the polluted European dataset.

Fig. 6: Shift the two time series a bit to improve readability. Okay.

Fig. 7: Improve quality of Fig. 7. The inset is hard to read. Why not three Figs A, B and C? Have been split into three figures as suggested

Fig.7A: Mark the episode mentioned on p20204-5 with an arrow. Add a second arrow that indicates the circular direction with time (counter clockwise)? Use colours, the different symbols are hard to distinguish. What is really shown in Fig. 7A? Are these daily averages? Please clarify. Fig. 7B: add regression coefficients. All suggestions included

Fig. 9: The authors state that episodes with southerly advection are pretty seldom at Mace Head (250 in total). I would be curious to see the number of data points that are considered from the three seasonal cycles for each month (eg. On the top of the graph?). This can give valuable information to the reader about the representativeness of the mean values. Error bars illustrating standard deviations of the mean might also be helpful. The graph has been modified to include a plot with the number of measurements contributing to each monthly mean. Error bars were added but obscured the plot so were not included.

Response to Referee #2 In response to referee comments modifications were made in accordance with suggestions, see below:

Section 3.1 Baseline air-masses {P 20201, line 24} How was data de-trended for
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monthly baseline means? {line 180 in revised manuscript }An explanation on data detrending has been added.

{P 20202, line 19} The authors state that no significant trend over 15 years is observed, as from Figure 2. However, once again no details on the statistical procedure used to assess the trend are given. No statistical method was used to assess the lack of trend here merely visual analysis of Fig. 2 and Fig. 4 with show no overall upward or downward trend.

{line 214 in revised manuscript } In contrast to previous literature no overall upward or downward trend in H₂ mole fractions in baseline air masses was observed over the fifteen year period from visual inspection of both Figures 2 and 4.

Section 3.1.1 Biomass Burning Figure 4 reporting monthly growth rates needs to be redrawn because in the x axis there are no tick marks, so that it is difficult to assign years to the peak s and troughs. This graph has been modified as suggested to include x-axis ticks and labels

P20203, line 6 The authors should clarify what they mean by “smoother correlative behaviour” This has been reworded as follows:

{line 225 in revised manuscript } Smoother correlative behaviour was observed in 1997-98 between the gases, with concentrations of CO₂, CO, CH₄, H₂, O₃ and CH₃Cl rising and falling simultaneously, whilst during the 2002-03 period a more complex pattern with slightly lower correlation between species was observed.

P20203, Line 15/16 How can the authors be confident that the deviation observed in 1996 can be attributed to long range transport events rather than measurement uncertainties? It is very unlikely that this elevation is due to measurement uncertainties as over this year long period relative standard deviation of 0.2 % or 1 ppb, if one assumes an average concentration of 500 ppb. However we are just suggesting this as a possible cause for the elevation, to reflect this the sentence has been reworded from:

“Elevations in 1996 have been linked to long range transport from Siberian fires...” To: “Elevations in 1996 may be linked to long range transport from Siberian fires...”

Section 3.2 European Pollution Events P20203, line 27 Authors state that a strong correlation is observed between H₂ and CO peaks, as shown in Figure 6. However, it would be useful to clarify if they refer to non-local pollution episodes or to the whole period shown in Figure 6?

{line 251 in revised manuscript} It has now been clarified in the text that Figure 6 displays only periods of “non-local” pollution which show high correlation.

P20204, line 10 The authors make reference to a procedure to calculate deposition velocity from a manuscript in preparation. I would be useful if they could describe even briefly, how they calculated deposition velocities.

{line 260 in revised manuscript } More detail has been added on the method of calculation used with reference to a paper that used the same method.

P20204, line 12 The authors state that in order to derive deposition velocities they need calm still conditions. However, it is not clear how during summer months it is possible to have long term records of stable boundary layer conditions that are necessary to calculate deposition velocity. It is correct that very few stable inversion events occur even during summer months at a coastal Atlantic site such as Mace Head. This resulted in only 225 events over the thirteen year record of deposition however we believe this is sufficient to calculate a robust set of deposition velocities.

Section 3.3 Observed H₂ to CO ratios In general, the discussion of the winter and summer correlation is not very clear. Moreover, at page 20205, line 21, the authors state that winter data show a higher correlation coefficient, that is not shown. How much is it higher than the summer one? In response to both reviewers' comments this discussion has been reworded to improve clarity and coefficients have been added to the scatter plots of data.

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Section 3.4 Modelled H₂ to CO ratios P20207, in the second paragraph from line 20-28, the approach used to model H₂ to CO ratio is briefly described. However, being this is the heart of the method, the authors must explain more clearly the procedure used. Extra information on the method used to calculate modelled H₂ to CO ratios has been added as suggested.

P20208, line 16 authors use the conversion scenarios of 0.47 for both transport and non transport emissions. Could they explain why they used the 0.47 ratio for both? A value of 0.47 was the initial best estimate for all emission sources (not just transport) when modelling work commenced. A non-transport emission scenario of 0.47 was used only as a test value and allow for maximum loss to occur thus providing an upper limit to the ratio of the effects of deposition and OH loss on the observed ratio.

P20208, line 23 when authors mention uncertainty in modelling, do they refer to the modelling in general or to the modelling of the ratio? This comment refers to uncertainty in the modelling of a H₂ to CO ratio.

{line 378 in revised manuscript }The text has been modified to reflect this changing “uncertainty in modelling” to uncertainty in the modelling process”

P20208, line 27 authors state that this “observation based value is the ratio calculated prior to correction for soil deposition”. Could they explain what they mean by a correction of observations for soil deposition?

{line 414 in revised manuscript} The text has been modified to reflect the meaning of a soil deposition correction “This observation based value is the ratio prior to correction for soil deposition, after such a correction was applied a much higher ‘corrected’ ratio of 0.48 was quoted. (In their work Hammer et al., (2009) correct their ratio for the assumed effects of soil deposition by assuming radon-222 exhalation from the soil is constant and related to CO emission from combustion sources. As these are two unrelated sources this may not be an entirely robust method by which to correct the H₂:CO ratio.)

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P20209, line 19/20 authors discuss the relative production of CO and H₂ for each VOC carbon atom. In the light of the following discussion, it would be useful to discuss/consider also the relative chemical loss rates of CO and H₂.

{line 438 in revised manuscript} The text has been modified to reflect the influence chemical loss rates may have on observed H₂:CO ratios. In essence chemical loss rates have been ruled out as a possible source of the difference in ratio between Mace Head and Heidelberg as the atmospheric lifetime of H₂ and CO with respect to OH reaction is 5.9 years and 2 months, with medium OH of 1×10^6 molecules cm⁻³. With maximum transport times of four to five days from Europe we believe even CO loss by OH is too small to affect the observed ratio at Mace Head or Heidelberg.

Section 3.5 Southerly Transport Events P20210, Figure 9 is discussed. Concerning this figure, the authors should add error bars. This was tried but was found to severely obscure the graph. The number of measurement contributing to each data point has been added in suggestion to Review #1s comment.

P20210, line 19/20 the authors state that varying synoptic conditions increase boundary layer ventilation. A deeper low would suggest an enhanced vertical mixing of the boundary layer more than a meridional mixing. Could authors better explain why baseline air would contain a larger southerly component?

We agree with the reviewers comments that a deeper low would suggest enhanced vertical mixing but also pulls air from further afield, thus this may not be the cause of higher H₂ mole fractions in baseline air in late winter and early spring. We believe seasonal variability in the Atlantic storm track, which has been found to track further south to lower latitudes in winter, may be the cause of the rise in baseline H₂ mole fractions in late winter early spring. However as this plot represents 15 years of data interannual variability in the NAO which alters the storm track, further complicates analysis. The source of this seasonal variability cannot therefore be attributed to a sole factor because of the long term nature of these records. Text has been modified to reflect

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this. {line 478 in revised manuscript}

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20195, 2009.

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