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Atmospheric Chemistry and Physics Discussions

Interactive comment on "High-frequency urban measurements of hydrogen and carbon monoxide in the UK" *by* A. Grant et al.

Anonymous Referee #2

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General Comments: This is a useful contribution and suits very well within the scientific scopes of this jour-nal. In their study of atmospheric H2 and CO at an urban site, the authors find several results which chal-lenge some conclusions from similar studies published over the last years. In particular, the authors find some unexpected ratios of H2/CO in the atmosphere, which are difficult to interpret, and a CO soil deposition velocity which exceeds those found in similar studies. This study therefore presents some exciting new find-ings which merit publication here. The lack of proper explanations for these findings is by no means a deficit of this study, but the authors fail to develop some new ideas and threads, which could help in interpreting these findings. The manuscript is well structured and clearly written but some explanations need to be car-ried out in more detail and more precisely. In general, the abstract is clear and short and includes all most findings. Some of the summarizing sentences in the abstract seem to have no

related detailed connection in the main text.

There are three major and many minor comments on this manuscript 1) Some rather unusual observations are made by this group but the authors fail to find explanations for them. In my opinion it has not been tried hard enough to understand these results, and more efforts need to be put into this. The unusual observations are a) CO concentrations are low compared to other urban studies (e.g. Steinbacher et al., 2007), although these samples were taken very close to the sources of CO. b) An unusual branch of H2/CO ratio of $\sim$1 has been found in addition to the well-understood branch of $\sim$0.5. c) CO deposition velocities have been found to be very large compared to similar studies, and even larger than for H2. Some more thoughts need to be put into this. For example, these 3 phenomena may be related to each other. If, for whatever reason, CO consumption by soil is indeed unusually large for this study, this may be linked to the relatively low concentrations observed, and also to the large H2/CO ratio of 1. The current analysis is somewhat deceptive, it is not the 'airport' branch in Fig. 5 that is unusual, it is the upper branch. In that sense, the wind direction is irrelevant in this discussion because those data with the unusual ratio of 1 are not from a specific wind sector. These are about 30 samples. Could they be linked to the times of strong CO decline under stable atmospheric conditions? Have the authors e.g. tried to color-code these $\sim$30 sam-ples in their Fig. 2. Have they e.g. tried to correlate them with their temporal gradients to understand if the strong draw-down found could account for these ratios. It suggest to also make an additional plot in Figure 4 where the ratios are plotted for these hourly averaged data for Mon-Fri, Sat, Sunday. 2) My second major comment is concerned with the explanations of the diurnal variations. This section 3.1 is far too speculative in its interpretations. Most of the interpretations are not backed up with any firm supporting arguments. Although it is most likely that these diurnal patterns are mainly driven by traffic pat-tern, this causal relationship is not a-priori known. The authors need to e.g. support the following statements with independent information (e.g. statistical traffic results) or they need to revise their sentences such that it becomes clear that these are hypotheses or interpretations without firm supporting evidence. e.g. line 9: ‘due to nightlife associated transport’. How do you know that this is the cause?

e.g. line 22: ‘ due to commuter traffic emissions, with contributions later in the morning from school transport ..’ How do you know that school traffic is causing this?

e.g. line 25: ‘.. with the additional effect of stronger vertical mixing at this time.’ Have you measure vertical mixing, or how can you tell?

A clear over-interpretation is e.g. line 25 ‘much broader than the morning peak because of school transport’. First, this ‘broader’ evening peak is not really evident from Fig. 3, morning and evening peaks look similar (except for Friday, but for that, the authors come up with yet another speculation). If there is really a difference in the broadness of the peak, then there is probably also one seen in the data of the tunnel study by Vollmer et al (2007), but Switzerland does not have school traffic, so what the authors of this Bristol study believe to see is probably something else.

On a related matter, it does not become clear, on what data base the yellow highlighted bands were drawn in Fig. 3 indicating rush hour traffic. Is this based on traffic statistics, or have the authors blindly assumed some rush hour traffic periods and drawn vertical bands accordingly? Or have they even used the CO and H2 data to ‘define’ rush hour? That would be a circular interpretation. Please clarify. Also, why is there no rush hour on Fridays, there is no vertical band. In most countries, Friday evening rush hours are the worst and the longest.

3) The suggestion that aviation may produce lower H2/CO ratios than road transport cannot be drawn from this study. The unusual branch in Fig. 5 is branch A, not B. Also, the molar H2/CO ratio of branch B (0.39) may be somewhat lower than typical ratios found in urban/suburban studies, but the fact that the ‘aviation-sector’ tagged samples in this branch A are no different than the ‘non-aviation’ tagged samples in the same branch, suggest that aviation does per se not contribute significantly to these findings. The authors should focus more on branch A.

Minor Comments:

Title: Usage of the abbreviation ‘UK’: UK should not be abbreviated in the title. In the abstract and in the text body, UK should first be spelled out before using the abbreviation, not vice versa, see e.g. abstract lines 2 and 5. Check entire manuscript for consistency.

Title: The authors may want to be more precise about hydrogen and specify ‘molecular’ hydrogen.

p. 1168, line 8/9. The authors don’t show any of this analysis of wind speed and temperature in the text. Have they done it? Include it or remove the sentence from the abstract. The abstract should only contain in-formation that is also worked on in the main text.

p. 1168, l. 13: replace ‘calculated’ by ‘calculated, respectively’.

p. 1168, l. 13: ‘of which’. There is no scatter-plot of the background subtracted mean, so maybe replace ‘of which’ by ‘the latter’

p. 1168, l. 16: ‘stable periods’. What is stable? Revise. E.g. ‘periods of stably stratified air’ or similar.

p. 1168, l. 18: deposition velocities: add uncertainties.

p. 1168, l. 20: replace ‘evidence’ by ‘explanation’.

p. 1168, l. 26: may want to add ‘usage’ as a source of loss also. E.g. H2-powered vehicles may have large H2 loss rates.

p. 1169, l. 1: The stratospheric chemistry is also believed to be altered (H2O content, link to PSC).

p. 1169, l. 29: Is it possible that these are not the first H2 measurements in the UK, aren’t there measure-ments from the Weybourne site? The authors may want to change ‘first set’ to ‘first published set’.

p. 1170: Write a sentence explaining the column lengths, filling materials, the sample loop size and any modifications. As far as I know, alternating samples (air/standards) is not possible with the original design of a PP1, so possibly, some alterations of the instruments were performed. Was integration by height or area. Was a specific software used?

As a general remark: Potential readers of this manuscript may tend to waive the unusual findings with skepticism about the data quality. The authors may want to provide all possible strong evidences for their high data quality.

p. 1171, l. 1: Change ‘California’ to ‘Ireland’

p. 1171, l. 1: Use either plural (‘quaternaries are filled’) or singular (‘stainless steel canister’).

p. 1171, l. 5: Change ‘working’ to ‘quaternary’

p. 1171, l. 9: Define ‘MPI’. Check the exact name of the scale. Check for publication updates with the pro-ducers of the primary scale at MPI Jena.

p. 1171, l. 25. Add a sentence or two explaining the overall accuracy of the field measurements, by including the accuracy of the scale, uncertainties in transferring the primary scale, uncertainties from the nonlinearity corrections, and measurement repeatability. It is important to know the overall accuracy of the results be-cause of the emission estimates. These uncertainties will also be later used to infer the overall uncertainties on the emission estimates later in the manuscript.

p. 1173, l. 13: change ‘elevation this work’ to ‘elevation compared to this work’ or similar.

p. 1173, l. 15 and l. 17: Are these CO values by Steinbacher et al, and from this study averaged values? Are these absolute values or ‘above baseline’? For this comparison,

the increase above baseline is important.

p. 1173, l. 21 ff. If the effect of a lower fraction of petrol vehicles in the UK compared to Switzerland was a possible explanation than a ‘conversion’ of the UK fleet to a Swiss fleet would enhance the above-baseline CO in Bristol by a factor of approx. 76/68 = 1.1 assuming no CO emissions from diesel. This demonstrates that the differences in the vehicle fleet cannot be the major cause for these observed differences, and that other factors must be more important (meteorology?).

p. 1174, l. 3, l. 4: Are ‘background’ and ‘baseline’ used synonymously? If yes, it might be less confusing to use only one expression. If no, then explain the difference. Use these expressions consistently throughout the entire manuscript. Explain how the baseline (or background) was calculated. Also, make clear to the reader here and in the caption of Figure 5, that the time-dependent baseline values were subtracted, and not a mean baseline value.

The authors are correct in their statement that the baseline values need to be subtracted. However, it is hard to be believe that this is ‘vital’ for this study. How big are the amplitudes in the seasonal cycles derived for this data set?

p. 1174, l. 10 ff. The ‘unusual’ results displayed by Steinbacher are very different to what is observed in this study, and the comparison to Steinbacher et al, and the word ‘also’ are miss-leading. I suggest omitting this comparison here.

p. 1174, l. 16, or nearby. Somewhere, the ratios of both branch A and B should be mentioned as numerical values. The ratio of branch B is listed later, but should be listed here as a result. The H_2/CO ratio of branch A, which is actually far more interesting, does not seem to be mentioned anywhere in this manuscript.

p. 1174, l. 16: Change ‘showed were’ to ‘were’ or ‘showed’.

p. 1174, l. 21: ‘south west’, hyphenate or spell as one word.

p. 1174, l. 24: ‘since’. If the word ‘since’ is used synonymously to ‘because’, than this sentence does not make sense, the reason why aviation could have a large impact is not ‘because’ it is yet to be defined.

p. 1174, l. 27, or whenever numerical values are first mentioned. It needs to become clear also in the text that these ratios are from linear fitting (and not e.g. calculated as a mean H2 / mean CO). It also needs to become clear that these are molar ratios, so the expression ‘molar’ needs to be at all necessary places where numerical values are first introduced, i.e. in the abstract, in the main text, in the figure and table cap-tions.

Explain how the linear fits were calculated. Have the authors used a least-square fitting technique? Have they fitted with respect to x (CO) AND y (H2)? Were different weighing functions used for x and y to account for differing uncertainties in H2 and CO values? Can the authors assign some uncertainties to these calcu-lated slopes?

p. 1175: l. 7: You may want to clarify about including/excluding Saturdays and Sundays when mentioning the use of ‘morning rush hour’.

p. 1175, l. 8: Now the Delta notation appears. Define what you mean by Delta.

p. 1175, l. 9: The overall ratio of 0.50 +-0.07: Here it becomes very important to understand how this slope was calculated. By looking at Fig. 5, it is surprising that this slope is not higher. It is even more surprising that the uncertainty of that slope (0.07) is very small, considering the split into the two-branches. Please clarify.

p. 1175, l. 11: Not only the rush hour ratio agrees well with other studies, also the ‘overall’ ratio, and statistically they don’t seem to be any different.

p. 1175, l. 12: ‘with lowest impact from background H2/CO mole fractions’. Could this be re-worded, it is difficult to understand what the authors mean by this.

p. 1175, 17: The example of the Swiss tunnel and Boulder intersection studies to illustrate the petrol/diesel differences, is misleading. The different ratios found in these two studies don’t seem to have anything to do with diesel and petrol. I suggest to omit this example.

p. 1176, l. 12: The emissions of 175 +- 9 Gg H2/yr. How were these uncertainties calculated, they seem very low. Do they include the uncertainties in the H2/CO ratio and the uncertainties in the CO emissions?

p. 1176, l. 19: Scaling up from 0.53 to 0.58. Explain in more detail how this was done and what assumptions were used in terms of H2 and CO emissions from diesel vs petrol.

p. 1176, l. 20. The text in parentheses seems unnecessary as the 68% are mentioned one line before al-ready.

p. 1176, l. 23 ff: How does this global emission estimate compare to other global estimates (Novelli, Vollmer) and interpret the differences.

p. 1177, l. 3: Change ‘boundary layer’ to ‘boundary layer height (h) in m’.

p. 1177, l. 10, 11. Make sure you list all necessary units, e.g. ‘wind speed (m/s)’, does the roughness length zo have units?

p. 1177, l. 22: The definition of h is now not necessary anymore, it should be done earlier, as e.g. suggested on l. 3.

p. 1177, l. 21: ‘where X=H2 or CO mole fractions’.

p. 1178, l. 2: ‘change ‘mole fraction time t’ to ‘mole fraction at time t’.

p. 1178, l. 3: k1 is already defined, so omit this definition here.

p. 1178, l. 3: It is obvious from the exponential decay that X is zero after infinitesimal time. Why is this sentence here, what is its relevance. I don’t understand what the authors want to say with this.

p. 1178, l. 9 ff. It would be useful for the reader to know how many nocturnal events were calculated, which then become part of the indicated ranges. Also, how robust is this mean? Would the authors get very different answers if they took the median instead of the mean, particularly for CO, where the range is very large.

p. 1178, l. 20: sentence seems incomplete. p. 1178, l. 27: here or earlier or in the conclusions: The authors could take their CO deposition velocities from sect 3.4 and estimate, how much CO would draw down at night. E.g. for h=50m and v=13x10ˆ-4 m sˆ-1, and dT = 6 hours, dCO would approximately be 0.5x CO. Doing the same for H2 the authors could esti-mate if this would potentially lead to some of the large H2/CO ratios of approx 1 as found in their study. In other words, is this large deposition velocity compatible with the unusual branch A ratio?

p. 1179, l. 11: possibly add a reference for the statement that diffusion is the primary parameter controlling removal of H2 and CO.

p. 1179, l. 19: possibly add a reference for the statement about NO3 reaction.

p. 1179, l. 20 ff. These conclusions are simply a summary of the text and appear unnecessary. This manu-script could be strengthened by exploring some aspects beyond summarizing the results, discussing the 3 unusual observations and their potential links, some broader view on these results. Here (and not in sect 3.1) the authors could be more speculative in their thoughts and arguments and also point out deficiencies and potential improvements in subsequent studies. They could also make suggestions on what could be done in a future study to resolve the issues of unexplained observations. The authors could also discuss for which years the calculated H2/CO ratios in Bristol, UK, and world may be applicable, so if other people use these results, they know to what time frames these may be applicable. The suggestion for p. 1178, l. 27 could al-ternatively be applied here.

p. 1179, l. 22: 'To our knowledge . . . first reported . . . site in Europe'. This sentence is miss-leading and suggests that this is the first study in Europe of a kind. However there are several others (e.g. Aalto 2009, Stein-bacher 2007, Hammer et al., 2009). The mentioning of the influence by aviation is purely speculative.

Figure 2: This figure could be strongly improved by e.g. making it the width of 2 journal columns, by adding minor tick marks to the y-axes, by choosing a more meaningful date-labeling (x axis) and major and minor tick marks for x, by color-coding those values that are defined as baseline, or by color-coding those values that lead to the branch A data (not B) in Fig 5. etc. Mention in the legend the location (Bristol, United King-dom).

Figure 4: explain what horizontal lines mean.

Figure 5: legend: mention that these values were base-line subtracted (on each point).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1167, 2010.