

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

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We thank reviewers for their comments. We disagree with referee #3 and in keeping with referees #1 and #2 believe this work is within the scientific scope of Atmospheric Chemistry and Physics and worthy of publication. In response to referee comments modifications were made in accordance with suggestions and guidelines, with specific descriptions of changes below.

Reviewer #1: Suggested that rapidly depositing species can have a deposition velocity as large as 10-2 m/s so these lower deposition velocities are clearly not limited by molecular diffusion, rather by kinetics of the uptake process whatever it is. Since uptake is almost certainly biological it is not unlikely that different locations have different CO removing flora and fauna and thus show differing deposition velocities.

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We thank the reviewer for this comment and have taken it into account and modified the text accordingly (see page 12)

Reviewer #2 brought up three general comments and various specific suggestions/comments. We have addressed all specific comments, many of which do not need a response. All modifications made in accordance with these suggestions have been highlighted in the revised manuscript in blue. However, we detail a few responses to the more detailed of these suggestions.

Firstly in response to major comments.

#1) H₂/CO ratio split was not investigated thoroughly enough. The reviewer suggested investigating various sources for this split. Are large CO deposition velocities related to the H₂/CO split? Does the split have relation to temporal gradients? Investigate wind speed, temperature, time of day as source of split? Calculate the H₂/CO ratio of the upper branch

All of these sources were investigated and a more detailed analysis of the split is given in Section 3.2 (pages 7 and 8).

#2) Section 3.1 describing Diurnal variations is far too speculative. Need to support statements with independent information or need to revise sentences so it's obvious that these are hypotheses or interpretations. Need to explain small scale changes in variation e.g. no Friday night peak due to high wind speeds.

Independent verification of statistics related to traffic data has been included in the manuscript and any speculative statements have been removed or backed up with statistical data. Extensive detail has now also been added explaining small scale changes in data shown in Figure 3 as requested. Extra information has been added on the effects of temperature and wind speeds on measured mole fractions to support these statements (Figure 4)

#3) The suggestion that aviation may produce a lower H₂/CO ratio than road transport

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cannot be drawn from this study. . . . The authors should focus more on branch A.

We thank the reviewer for this comment and have removed this suggestion that aviation may produce lower H₂/CO ratios. As detailed previously we have focussed analyses on Branch A in Section 3.2 of the revised manuscript

Minor Comments: Changes have been made in accordance to suggestions to all minor comments. Large sections of text which have been changed are highlighted in blue to aid the editor in assessment of the manuscript.

In response to specific comments:

P1168, line 8/9 The authors don't show any of this analysis of wind speed and temperature in the text. Included it or remove the sentence from the abstract.

Analysis of H₂ and CO mole fractions with wind speed and temperature has now been included on page 5 with an additional Figure detailing this.

P1171, line 9. Define MPI Check the exact name of the scale. Check for publication updates with the producers of the primary scale at MPI Jena. A Publication has been submitted on this new scale and details of the scale development have now been included (page 4)

P1174, l3-4: Are background and baseline used synonymously? If yes use only one expression. Explain how background was calculated. Also make it clear to the reader that the time dependant values were subtracted and not mean baseline values. The authors are correct that baseline values need to be subtracted. However, it is hard to believe it is vital for this study. How big are the amplitudes in seasonal cycles for this dataset?

We have changed wording as suggested (page 7). Background values were calculated as monthly mean values by visual inspection of data and use of seasonal cycle curve from a background northern hemispheric station to account for monthly changes in amplitude. We do believe it is 'important' but possibly not 'vital' for this study to subtract

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background values and have changed the wording of this sentence accordingly. The amplitudes of seasonal cycles cannot be fully observed due to the length of the record but we believe failure to subtract baseline values could bias results by lowering the observed ratio (Grant et al., 2010).

P1174, 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. It also needs to become clear that these are molar ratios. Explain how the linear fits were calculated. Have the authors used a least-square fitting technique? Have they fitted with respect to x and y? Were different weighting functions used for x and y to account for different uncertainties in H₂ CO values?

Full details of the linear fitting have now been included (page 7). Linear fits were applied using reduced major axis regression which takes into account error in both the x and y axes. Uncertainties in measurements are small (<2%) and were not found to have a significant effect on ratios obtained from linear fitting.

P1176, l 19. Scaling up from 0.53 and 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.

Details on scaling have been described on page 10.

P1179, l 20 ff These conclusions are simply a summary of the text and appear unnecessary. This manuscript could be strengthened by exploring some aspects beyond summarizing the results, discussing the 3 unusual observations and their potential links, some broader views on these results. Here (and not in Section 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 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

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what time frames these may be applicable.

We thank the reviewer for their insightful comments and have changed the conclusion sections to incorporate these suggestions removing summarizing aspects and adding our thoughts on potential improvements that could be made in future studies to improve knowledge on hydrogen.

Figure 2: This figure could be 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 x-axis and major and minor tick marks for x, by colour coding those values that are defined as baseline, or by colour-coding those values that lead to Branch A in Fig. 5 Mention the location in the legend.

All these aspects have now been changed (see revised manuscript).

Figure 4: explain what horizontal lines mean.

Horizontal lines merely aid visual inspection of diagrams from y-axis.

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

In response to Reviewer #3

In response to specific comments:

a) "When discussing the observed diurnal features, the authors neglect the influence of atmospheric mixing. This leads to doubtful speculation that nightlife traffic on Fridays (but not on Saturdays) is a huge source of H₂ and CO or that school transport is a substantial source in the urban H₂ and CO budget without backing up their assumptions by independent datasets.

Section 3.1 which discusses diurnal features has been revised. Any speculations have now been removed or hypotheses for observations of specific features. Statistical data on traffic flow has now been included to substantiate diurnal variations." Atmospheric mixing is included in discussion of diurnal features (page 6).

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b) "One aspect of this manuscript is the investigation of the urban H₂/CO concentrations ratio. However, the most unusual feature in the data, two distinct regimes of H₂/CO ratios, is hardly discussed at all. Not enough effort is made to elucidate this finding; instead they focus on aviation emissions which do not significantly differ from the well understood H₂/CO ratio of combustion processes. Moreover, the discussion of the transport emission ratio lacks any statement (or estimates) concerning the influence of the H₂ and CO soil sink (the latter being further down estimates as considerably larger than found in other studies). In fact, several recent publications have pointed out that the influence of the regional soil sink must not be neglected when estimating reliable H₂/CO emission ratios."

The revised manuscript now includes extensive discussion of the source of the H₂/CO ratio split. To our knowledge it is not well known that aviation emissions do not significantly differ for the well understood ratio from combustion processes as the reviewer has stated. However, we have removed the statement regarding aviations contribution to the H₂/CO ratio as suggested by Reviewer #2 for reasons discussed previously. No correction was applied to H₂/CO ratios for the soil sink as emission ratios for rush hours were used in estimating H₂ emission from transport. These rush hour ratios have a minimal influence from deposition because of the measurement sites location in the centre of an area of very high transport emissions which therefore provide measurements almost immediately after emission has occurred thus not influenced by deposition. This is contrary to other 'urban' studies mentioned by reviewer #3 where measurements were made a distance away from emissions enabling effect of the soil sink to influence the H₂/CO ratio. This study was also conducted during the winter when H₂ deposition is known to be at a minimum. A recent study (Grant et al., 2010) also found that the correction of H₂/CO ratios for deposition has been overestimated by studies from Hammer and others. We do not therefore believe it is essential to correct for H₂/CO ratios in this particular study.

c) "When attempting to estimate the soil sink, the authors again attribute the evaluated

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concentration changes (decrease during the night) to the sinks only, i.e. by evaluating the evening CO and H₂ decrease during times when CO is still largely perturbed by traffic emissions during evening rush hour. The decrease of the rush hour peak by atmospheric dilution is complexly neglected and this decrease instead is solely attributed to the soil sink. A sensitivity study to investigate the effect of the time window used to calculate the CO sink strength would be the appropriate way to go.”

Soils sinks of H₂ and CO were calculated only after 11.30 pm when emissions from night time traffic were very low (verified by traffic count data). Atmospheric dilution was not completely neglected as soil sink estimated were only made during nocturnal inversion events with a wind speed of <4 m/s therefore ensuring a stable nocturnal boundary layer under which minimal dilution occurred.

“Besides these scientific omissions/errors, the manuscript is also flawed concerning technical details, and often lack scientific diligence. Handling uncertainties is only one example, i.e. the authors do not report any uncertainties of their key findings (e.g. mean soil sinks) nor do they show any error bars in the figures.”

As suggested by reviewer #2 uncertainties in all estimates have now been included and their sources detailed explicitly. Inclusion of error bars was found to obscure certain graphs and it was therefore decided not to include these as errors are included in the values quoted in the text.

“Moreover, at those rare occasions when error propagation is performed, the results are more than doubtful and not replicable. Basic information on the numbers calculated is not given (e.g. for regressions). The lack of care is apparent by the disagreement between values stated in the text and figure.”

Full details of the error propagation has now been included (see areas highlighted in blue) for regression, emission estimates and soil sink calculations. We apologise for the typing error where values stated in the text were different from that shown in a Figure. This has now been rectified.

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“Copying whole sections from other papers (e.g. analytical methods) should be carried out with great care.”

Analytical methods by nature are often very similar, particularly for publications on hydrogen as the same instrumental set-up is used in most studies. We do not therefore believe this statement is fully justified.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C2158/2010/acpd-10-C2158-2010-supplement.pdf>

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

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