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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric hydrogen variations and traffic emissions at an urban site in Finland" *by* T. Aalto et al.

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We thank the anonymous referees 1 and 2 for constructive comments and will modify the manuscript according to the guidelines given. Specifically, we will extend the introduction and add discussion on the seasonal variation. The seasonal variation of H2/CO slope was briefly discussed in p. 13926 and in discussion, but the role of winter was not emphasized. This was mainly because the winter 2007-2008 was warm in Helsinki (no snow cover lasting over winter etc.). The differences to more southern sites were mainly due to irradiance conditions. The winter/summer variation of the H2/CO slopes and annual averages were in good agreement with literature, so it should be noted that the influence of the northern latitude factors was relatively small at least during the time period examined.

Answers to Referee 1 specific comments:

Page 13921: Yes, they did use the same inlet. See text '. . .Sample air was taken as a side flow from a high flow stream (used by the radon instrument). . .'

Page 13921: No non-linearity correction was used, because the instrument was linear in the atmospheric concentration range. Text will be modified: 'The RGA5 instrument's response was studied against a range of mixing ratios created *from a high concentration (103 ppm H2 in synthetic air, Messer, Air Liquide) reference gas* using a gas blender (Peak Laboratories Peak Span Gas Blender). *First and higher order polynomials were fitted to the measurement series of concentration vs. sample peak area resulting in R2 of over 0.99 (the average standard deviation 3.5 %) over the atmospheric range (400-700 ppb). Use of higher order polynomials did not improve R2 suggesting that the response of the instrument was linear, and no non-linearity correction was applied. . .'*

Page 13922: Equation 3 for jEmiCO will be added to text.

Page 13923: Soil exhalation rate of radon comes from analysis of local measurements modeling, introduced in a companion article currently in ACPD. Text will be modified: ' . . .using the observed radon activity and soil exhalation rate of radon ( ),*estimated from local measurements (see Lallo et al., 2009).'*

Page 13923. Determination of background H2 and CO mixing ratios. The main reason for not using a harmonic fit as background condition was that the fitting might not be very reliable for current short time series. During periods of rapid concentration change (autumn), however, the monthly mean might not work well in the beginning and end of the month in e.g. deleting outliers. After comparison of methods, the harmonic fit was decided to adopt here and Figures 5-7 were redrawn relative to the new background. Shape of the diurnal curves remained the same, as expected, but some excess levels shifted downwards due to involving earlier, erroneously, only one month average in drawing the original figures.

Page 13924: The following sentence will be added to text '. . ..*The traffic intensities in Europe are higher than in Finland, and the lifetime of H2 is longer than that of CO supporting long range transport. . .'*

Figure 4: Mean mixing ratios of H2 and CO were plotted in panels 1 and 2 instead of difference. Last panel; It would be a good idea to plot slopes in different wind directions, but in practice the wind direction changes significantly in the few hours used for calculating the slope, so that the resulting figure is not very illustrative.

Page 19325 and page 19326: A sentence will be added to Fig 56 captions '. . .*The record is a combination of workday and weekend data.'* The summer and winter diurnal cycles of H2 look similar, but probably due to different reasons linked with emissions and meteorological conditions. It is noteworthy that radon had, in average, a strong diurnal cycle in summer but not in winter suggesting weak boundary layer development (also the soil exhalation rate of radon was lower during winter due to high soil water content). The winter case was not very well explained, and the following will be added to text. '. . .*In comparison to autumn, the winter increase in hydrogen and CO mixing ratios was modest during morning rush hour. The radon activity was low in average and showed no diurnal cycle contrary to autumn. It is possible, that the winter morning emissions were often trapped under temperature inversion below the inlet height, resulting in observations of more aged air masses obscuring the hour-to-hour variation. . .*' and '. . .*The winter slopes had no clear connection to observed radon levels, which showed no daytime decrease either. The summer slopes were rather variable and the scatter in hourly values was larger than in other seasons, probably due to reduced traffic and thermal convection causing efficient atmospheric mixing already early in the morning. '*

Page 13927: The answer is complex. Helsinki was the largest town in the 5-day backward trajectory path. Possible traffic pollutant sources include highways and other towns, but it is difficult to point a certain source. We should not cancel out the possibility that the case was a Helsinki regional episode. The text will be modified: 'It is

therefore tempting to suggest that at least part of the increase in mixing ratios could be due to distant sources, though the rate of increase was so fast that it could have occurred due to more local sources, *supported by the preceding low wind speeds and air mass transport close to ground. Helsinki was the largest town in the studied 5-day air mass path* , but the lifetime of CO is of the order of few months, and thus long-range transport from other Finnish or European sources is possible.'

Page 13929: Niemi et al reports CO emissions based on number and type of vehicles in an administrative district. This is difficult to convert to ground area basis because the result may vary considerably inside Helsinki in the busy center vs. in the quiet suburb. Furthermore, we were studying only the rush hour data. However, if our ground area based result is just multiplied with the non-forested land area of Helsinki and assumed constant over the year, we get CO emissions of about 13 t in 2007, while Niemi et al. reports about 9 t. The uncertainty comes mainly from the CO/Rn slope fitting procedure (geometric mean regression), which had >20% error limits, and from radon exhalation rate uncertainty, which was about 5% according to Lallo et al 2009. These uncertainties were added together, and the same was done for jEmiCO, jsoilH2 and H2/CO when estimating the uncertainty for the corrected H2/CO slope.

Chapter 4: Discussion will be added on winter meteorological conditions and H2/CO slopes. '. . ..*In winter the boundary layer development starts later and is not as strong as in summer due to less heating by radiation. However, surface temperature inversions may occur, trapping the pollutants below the observation height and causing delay and mixing of the observed air parcels. The diurnal variations of H2, CO, radon and traffic were most consistent during autumn and spring, suggesting that the slopes obtained during these seasons were most reliable. '*

Page 13930: The number is the mean of individual selected (R2 > 0.8) morning slopes. The regression coefficient (geometric mean regression) for all autumn workday morning data presented in Figures 5 and 6 was 0.44 ppb (H2) / ppb (CO), as discussed in Section 3.2.2.

References: Solomon Tignor et al are editors of IPCC 2007 report and listed alphabetically according to 'IPCC' (referred as IPCC, 2007 in the text).

Figure 2, Figure 3: Changes will be made according to referee's suggestions. In addition, a line describing the harmonic fit will be added to Figure 2.

Figure 7: The idea was to compare to Fig. 5, where two-month diurnal averages are shown for data not separated between weekend and workdays. If year-round data were gathered to one figure, the long (summer) holiday periods with different traffic flow timing would blur the result.

Figure 8: Corrections will be made according to referee's suggestions. For visibility a sentence will be added to the caption *'Visibility is expressed as fraction of the maximum of the observation range, which is about 50 km.'*

Yver et al will be added to discussion; their results were very similar to ours.

The rest of the minor corrections will be made according to referee's suggestions.

Answers to Referee 2 specific comments:

Introduction: General considerations about H2 variation and budget will be added to the text together with he high northern latitude aspect: ' . . . *The annual mean hydrogen background is lower in the Northern Hemisphere than in the Southern Hemisphere, and the northernmost continental sites have the largest annual cycles (Novelli et al, 1999).* Variations in the observed mixing ratio are due to different removal mechanisms in addition to changes in emissions. The chemical removal of hydrogen from tropospheric air occurs through reaction with OH radical. Thus, hydrogen is indirectly affected by numerous air chemical cycles. Soil deposition is even more important removal route, the mechanism and extent of which is due to large uncertainties (e.g. Smith-Downey et al., 2006, Xiao et al., 2007, Lallo et al., 2008, Schmitt et al., 2008). *The difference between Southern and Northern Hemisphere hydrogen levels has been attributed to asymmetry of soil uptake, because the majority of global land area is located in North-*

ern Hemisphere (Novelli et al, 1999). The low annual autumn - early winter minimum in northern continental high latitudes is also due to dominance of the soil sink together with weakening of the photochemical sources and formation of a stable boundary layer which prevents vertical mixing (Price et al., 2007). However, the soil sink weakens in persistent freezing temperatures when soil freezes and snow cover becomes thick hindering diffusion (Lallo et al., 2008).

The most important sources of hydrogen include photochemical methane and other hydrocarbon (mainly isoprene) oxidation, biomass burning and combustion from technological processes (e.g. Novelli et al., 1999, Rhee et al., 2006, Ehhalt and Rohrer, 2009). *The influences of the hydrogen source from fuel combustion are largest in the Northern Hemisphere and can be seen as high short-term variability in the continuous urban hydrogen observations (e.g. Steinbacher et al., 2007, Yver et al., 2009).* Urban emissions of hydrogen, such as sources from traffic-related combustion processes, can be estimated by using simultaneous observations of CO, whose sources are similar and emission inventories are well established. The H2/CO slopes have been observed at relatively polluted and unpolluted sites (Simmonds et al., 2000, Barnes et al., 2003, Steinbacher et al., 2007, Hammer et al., 2009) as well as in a traffic tunnel (Vollmer et al., 2007). The value of the slope depends on e.g. the vehicle types, chemical transformation, and deposition on the way to the measurement site. This makes the slope dependent on the local emission structure and environmental conditions. *The value of the slope may be influenced by the seasonal variation of the meteorological conditions. During the high northern latitude winter the photochemical reactions and vertical mixing are suppressed, while in summer the radiation may enhance vertical mixing and photochemical reactions already before the morning rush hour, '*

Page 13920 line 3: The sentences will be corrected for English language.

Page 13920 line 20-22: The sentences will be corrected according to referee's suggestion.

Page 13921 line 23: See reply to comment by Ref 1.

Page 13922 line 7: These measurements were targeted for urban high CO conditions, and close to the background level they are not as accurate as our measurements. However, the lower detection limit for the instrument is around 0.05 ppm (2 sigma), which should be satisfactory. The repeatability and linearity are typically around 1%. Specific error sources include zero drift and span drift, which are checked regularly.

Page 13922: Reference to Eurohydros will be removed.

Page 13922, line 13: I am afraid I don't quite understand this comment (is the line/page correct?). Analyses was made using Matlab, and it is quite common to give information about the analysis tool used.

Page 13924, line 1: Price et al estimates 500-520 ppb for Helsinki latitude during March-May, while our result was 503 ppb and 450-475 for September-November (465 ppb). Text will be modified accordingly.

Page 13924, line 4: Information from nearby sites tells us what is the variation of CO inside Helsinki. It gives us an indication of what is the typical range of CO in Helsinki close to the high traffic road in the city center and further away. Looking at other CO results we can put our results on a scale, similarly than when comparing hydrogen levels to literature. Furthermore, seeing that the lower envelopes of CO exhibit similar behaviour indicates that we occasionally observe air masses that are representative at least for the Helsinki region.

Page 1394 line 21: H2 was much more evenly distributed among the wind sectors and the difference between high and low concentrations was smaller than in CO, as said in the text. Therefore the maximum was also broader and not as well distinguishable as with CO. Looking at closely, one could discover three maximums inside the broad maximum between 60 and 300 degrees. Some of these may be due to local traffic, but since the general behavior of H2 and CO is so different, their source/sink patterns

should also be somewhat different. Text will be modified '..*The high mixing ratio sectors coinciding with those of CO may indicate influences from traffic sources close by, but the notable difference with CO in southwest sectors may refer to different source/sink patterns. . .'*

Page 13925: Text will be modified '..*sink processes'.*

Page 13925, line 13: Will change mixing layer to stable boundary layer. The observation here was that H2 and CO increased during morning hours (due to traffic). The visible decrease (due to soil deposition) occurred earlier during night and was overridden by the traffic emissions in the morning. During the morning hours the mixing ratios may further increase due to entrainment flux as already discussed on p. 13929: . . . 'Hammer et al. (2009), who found more seasonal variation when the late morning hours where included in the slope calculation. They attributed this to the entrainment flux, which amplifies after the sunrise and brings hydrogen rich air from higher altitudes close to the ground, where the stable nocturnal air layer has been depleted with hydrogen over the night due to soil deposition. . .' The night time decrease due to soil deposition is discussed in more detail in the companion article by Lallo et al. (ACPD 2009)

Page 13925 line 1-26: Explanation about single seasons added + clarification about data to fig. 56 captions, see answers to referee 1 comments.

Page 13926, line 10-12: LT 05:00 - 08:00 was used. There was no wind speed limit, because the intention was *not* to specifically examine background data. Instead, goodness of the fit (R2 > 0.8, uncertainty of the slope < 0.09 ppb (H2) / ppb (CO)) and radon levels were monitored, as explained in the text (see also e.g Yver et al, 2009). Text will be modified 'The mean slope of H2/CO was calculated from the increase in H2 and CO mixing ratios during morning hours *(LT 05:00 - 08:00).* Individual episodes were hand-picked from the data resulting in 81 events, mainly occurring during fall, winter and spring. The *slope derived by geometric functional regression* was calculated for

each episode with a squared correlation coefficient (R2) > 0.8 and *uncertainty of the slope < 0.09 ppb (H2) / ppb (CO)...'*

Page 13926, line 1-20: New figure 7 will be added for seasonal changes in the H2/CO slope. The slope values are not yet corrected for the soil sink. The simple error of the mean slope is given by the GMR fitting, while sensitivity analysis, I think, is being performed as we proceed forward. Firstly, the result from individual slopes is compared to result from mean hourly values. Secondly, the effect of soil deposition is investigated. Instrumental errors might bring an additional <2% uncertainty on the slope values, and text will be modified accordingly '. . .The mean of all slopes was 0.43 $\pm$ 0.03 ppb (H2) / ppb (CO). *The uncertainty is given by the fitting procedure. Instrumental reasons (reproducilibility, non-linearity) might cause an additional uncertainty of max. 0.01 ppb (H2) / ppb (CO). At this point the value of the slope was not corrected due to influence by soil deposition. . . ..'*

Page 13927: The slope of the highest event recorded was 0.40 $\pm$ 0.01 ppb (H2) / ppb (CO). It is at the lower end of our current range, however a very typical result. The slope value will be added to text. For long range transport see answer to Ref 1. comment.

Page 13930: Errors in H2 emissions arise most importantly from ground based CO emissions, which were difficult to estimate as explained in Ref 1. answer, and from radon exhalation rate uncertainty, which is estimated together with H2 deposition rate uncertainty in the companion article by Lallo et al 2009. Text will be modified '. . .*The other sources of uncertainties include e.g. instrumental accuracy and, more importantly, variation in radon exhalation from ground and hydrogen deposition to soil. The last two were estimated in the companion article by Lallo et al., (2009). Together all the uncertainties mentioned above might lead to about 9% change on the total H2 emissions.. . ..'*

Figures: Changes will be made according to referee's suggestions. Figure 3 will be changed to logarithmic scale.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13917, 2009.