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TELLUS

The H_2/CO ratio of emissions from combustion sources: comparison of top-down with bottom-up measurements in southwest Germany

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ABSTRACT

The hydrogen-to-carbon monoxide (H_2/CO) emission ratio of anthropogenic combustion sources was determined from more than two years of quasi-continuous atmospheric observations in Heidelberg (49°24′ N, 8°42′ E), located in the polluted Rhein-Neckar region. Evaluating concurrent mixing ratio changes of H_2 and CO during morning rush hours yielded mean molar H_2/CO ratios of 0.40 ± 0.06, while respective results inferred from synoptic pollution events gave a mean value of 0.31 ± 0.05 mole H_2/mole CO. After correction for the influence of the H_2 soil sink on the measured ratios, mean values of 0.46 ± 0.07 resp. 0.48 ± 0.07 mole H_2/mole CO were obtained, which are in excellent agreement with direct source studies of traffic emissions in the Heidelberg/Mannheim region (0.448 ± 0.003 mole H_2/mole CO). Including results from other European studies, our best estimate of the mean H_2/CO emission ratio from anthropogenic combustion sources (mainly traffic) ranges from 0.45 to 0.48 mole H_2/mole CO, which is about 20% smaller than the value of 0.59 mole H_2/mole CO which is frequently used as the basis to calculate global H_2 emissions from anthropogenic combustion sources.

1. Introduction

Atmospheric molecular hydrogen (H_2) today has an almost balanced budget, which is implied by its almost stable mixing ratios for more than one decade (Schmidt and Wetter, 2003; AGAGE, 2007). However it may largely increase in a future hydrogen energy economy due to anticipated leakages from extended gas distribution systems. Future scenarios postulate mixing ratios up to a factor of four larger than today with possible severe consequences for atmospheric chemistry, including stratospheric changes of the water vapour content and associated perturbations of the global climate system (Schultz et al., 2003; Tromp et al., 2003). The dominant ground-level sources of H_2 today are incomplete combustion of carbohydrates, either as biomass burning or associated to fossil fuel use (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Sanderson et al., 2003; Xiao et al., 2007). The latter anthropogenic H_2 source is estimated to contribute about 25% to the global emissions; in polluted areas its share may, however, be as large as almost 100%. Estimates of H_2 emissions from fossil fuel burning are generally based on available carbon monoxide (CO) emissions inventory data and mean H_2/CO ratios of respective emissions derived from source studies (Seiler and Zankl, 1975; Novelli et al., 1999; Vollmer et al., 2007). The accuracy of the global fossil fuel H_2 source estimate is, thus, also dependent on the accuracy of the H_2/CO ratio used for this extrapolation. As the range of H_2/CO emission ratios of various sources studied in the literature is rather large (0.15–1.0 moles H_2 per mole CO) global estimates of this anthropogenic source have a similarly large uncertainty. Sinks of H_2 are oxidation in the atmosphere by hydroxyl free radicals (ca. 20–30%), and, most importantly, destruction in soils (ca. 70–80%) (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002).

Here we present long-term measurements of the H_2/CO emission ratio of anthropogenic emissions inferred from atmospheric observations at a polluted monitoring site in the upper Rhine valley in Heidelberg. Mean H_2/CO ratios are derived from quasi-continuous observations during the morning rush hour, and thus, mainly represent traffic emissions, but they also contain domestic heating sources and other emissions. The top-down ratios are compared to bottom-up results from samples collected in the immediate vicinity of traffic emissions from the same area, and are discussed in view of earlier studies published in the literature.

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2. Sampling site and measurement technique

2.1. Sampling site

The Heidelberg observational site (49°24′N, 8°42′E, 116 m a.s.l., approximately 130 000 inhabitants) is located in the upper Rhine valley, a polluted region in southwest Germany. Air sampling is installed on the top of the Institut für Umweltphysik building located in the western outskirts of the city. The intake lines, one in the southeastern and one in the southwestern corner of the building, are mounted ca. 30 m above local ground. Two different intake lines are used in order to allow detection and elimination of very local contamination (e.g. from the building itself), which is indicated by large mixing ratio differences between the two lines. The Heidelberg sampling site is exposed to a number of local sources: (1) domestic households and traffic from the city, (2) traffic from two highways close by, (3) agricultural land use in the surroundings of the city and (4) densely forested areas further to the east of Heidelberg. An industrial region with sources of numerous trace gases is located about 20 km northwest of the sampling site (Mannheim–Ludwigshafen). Occasionally, direct ‘plumes’ of elevated trace gases from this area are captured in Heidelberg (Schmidt et al., 2001). Large-scale biogenic influence is from the crop- and grassland in the Rhine valley, but also from the Odenwald, a region of extended forests and grassland at the eastern boarder of the Rhine valley.

Bottom-up statistics imply that in Heidelberg and in the surrounding Rhein-Neckar district more than 90% of the anthropogenic CO emissions are caused by traffic (LUBW, 2006). Only minor CO emissions stem from residential heating and industry. Besides man-made combustion sources, natural carbon monoxide is produced by chemical oxidation of methane and other hydrocarbons in the atmosphere. No emission statistics for H_2 are available yet for Europe or elsewhere. However, since the production mechanisms for CO and H_2 during combustion processes, e.g. in motor vehicles (Auckenthaler, 2005), are very similar, it is generally assumed that the source distribution of anthropogenic H_2 is similar to that of CO (Hauglustaine and Ehhalt, 2002). Following this assumption, the major anthropogenic H_2 emissions in the Heidelberg catchment area originate from traffic, while natural H_2 production due to photolysis of HCHO in the troposphere probably plays only a minor role in the short-term variability of H_2.

2.2. Measurement techniques

The analysis techniques for atmospheric H_2, and CO observations are described in detail by Hammer (2008). Briefly, H_2 and CO mixing ratios are measured by gas chromatography with a Reduction Gas Analyser at a temporal resolution of 5 min. This allows analysis of one standard gas and one ambient air measurement from each of the two intake lines every 15 min. In the present study, mean values and standard deviations have been calculated from the up to four ambient air measurements from the two intake lines within half an hour. Measurements from the southeastern intake line are missing if external samples, such as flasks or calibration gases, are analysed (Hammer, 2008). The reproducibility of the individual measurements at typical ambient mixing ratios is about ±3 ppb for both gases.

Regular monthly non-linearity calibrations are performed for both gases and applied to the raw mixing ratios. For these non-linearity calibrations we use six calibration gases covering the range of 222–822 ppb for H_2 and 55–900 ppb for CO. In addition, regular monthly dilution experiments of a high concentration tank with zero air are performed. This is crucial, because in cases where the non-linearity of a system is not properly corrected for both gases, this could easily change the $\Delta C_{\mathrm{H_2}}/\Delta C_{\mathrm{CO}}$ ratios in different concentration ranges. CO values are reported on the MPI-Mainz scale (Brenninkmeijer et al., 2001) while H_2 values are linked to the EuroHydros 2007 scale (Jordan, 2006). Differences of the calibration scales used here compared to scales used in other studies, which can be on the order of 10 ppb for both gases, do, however, not affect the reported $\Delta C_{\mathrm{H_2}}/\Delta C_{\mathrm{CO}}$ ratios.

Radon-222 (^{222}Rn) is measured at a temporal resolution of half an hour with the static filter method via its daughter activity, assuming disequilibrium of 0.704 in the atmosphere. For details see Levin et al. (2002).

3. Data evaluation and results

Figure 1 shows the H_2 and CO records of half-hourly mixing ratios measured in Heidelberg from January 2005 to July 2007. For both, H_2 and CO the largest variability and highest mixing ratios are found during winter when vertical mixing of the boundary layer is often suppressed due to strong inversions in the Rhine valley. In these situations the observed H_2 and CO mixing ratio increases are very well in line, which is expected if both gases share the same sources and atmospheric transport processes.

In this study, we apply two different approaches to infer H_2/CO emission ratios from continuous atmospheric measurements: One is using synoptic events of elevated mixing ratios, which occur preferentially during winter and can last for several days. By correlating the H_2 and CO concentration surplus over some baseline concentration before and after the event, the average H_2/CO emission ratio of the sources can be derived. A second way is to use only the observed increase ΔC_i in both, CO and H_2 mixing ratios during the morning rush hours. In the early morning, when the boundary layer is still shallow, rush-hour traffic provides a strong anthropogenic source and leads to pronounced increases of CO and H_2 mixing ratios. In both approaches the concentration surplus ΔC_i of CO and H_2 originating from the net fluxes j_i^{net} over a selected time period are used to calculate atmospheric molar $\Delta C_{\mathrm{H_2}}/\Delta C_{\mathrm{CO}}$ ratios, which are then proportional to the ratios of the net fluxes according to

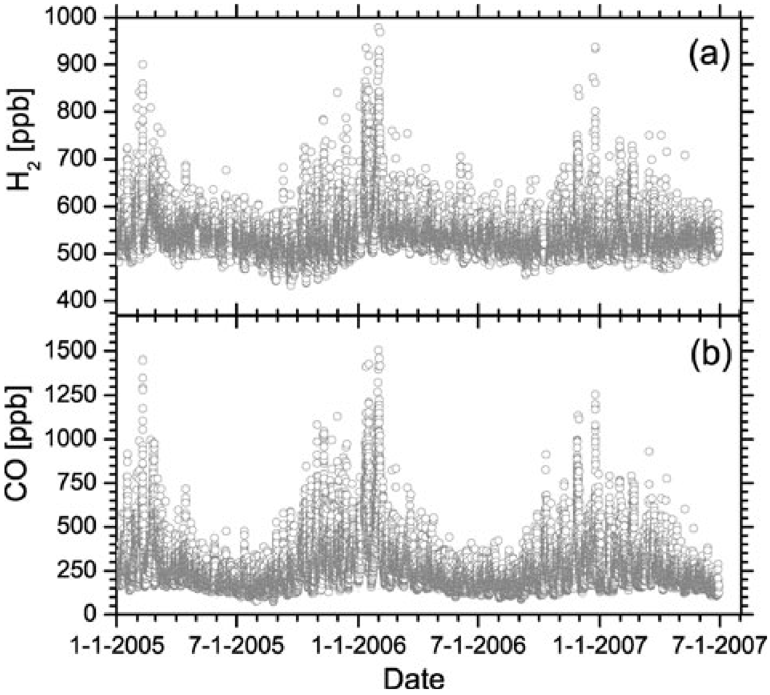

Fig. 1. Half-hourly mixing ratios of (a) H_2 and (b) CO measured in Heidelberg from January 2005 to July 2007. Both trace gases show very similar variations pointing to similar sources but also similar modulation by atmospheric mixing conditions.

Eq. (1)

$$\frac{\Delta C_{H_2}}{\Delta C_{CO}} \cong \frac{j^{net}_{H_2}}{j^{net}_{CO}}. \qquad (1)$$

3.1. Data selection for the rush-hour based $\Delta C_{H_2}/\Delta C_{CO}$ ratio

Mornings with distinct rush-hour peaks were selected from the data set in Fig. 1 by visual inspection to estimate a H_2/CO ratio of emissions from the regional area of influence of our measurement site. This selection is important since concentration changes caused by changing synoptic conditions are not only driven by local sources but also influenced by emissions from a catchment area, which may be as large as several hundred kilometres around the sampling site. Furthermore, only those rush hours were selected where the nocturnal inversion situation was still well developed (compare Section 3.3). Accordingly, we selected only rush-hour situations where the accumulated ^{222}Rn concentration was not declining before 8:30 AM local time. For each selected rush-hour period, a linear regression of half hourly H_2 and CO mixing ratios was calculated for the time span from 6:00 to 8:00 AM, using a weighted least-squares algorithm proposed by Krystek and Anton (2007). The uncertainty of each half-hourly mean mixing ratio (calculated as the standard deviation of the individual measurements from the two intake lines falling into this half hour) was taken into account in the linear regression. Half-hourly mean mixing ratios with standard deviations larger than 10% of the absolute value were rejected from the fit, to exclude data potentially influenced by very local sources (see above). In Fig. 2 a linear regression of half hourly H_2 and CO mixing ratios measured on July 19, 2006, between 6:00 and 8:00 AM is shown. Error bars denote the standard deviation of the half-hourly mean values. For the present example a $\Delta H_2/\Delta CO$ slope of 0.35 ± 0.07 ppb ppb^{-1} was retrieved with a correlation coefficient of $R^2 = 0.99$.

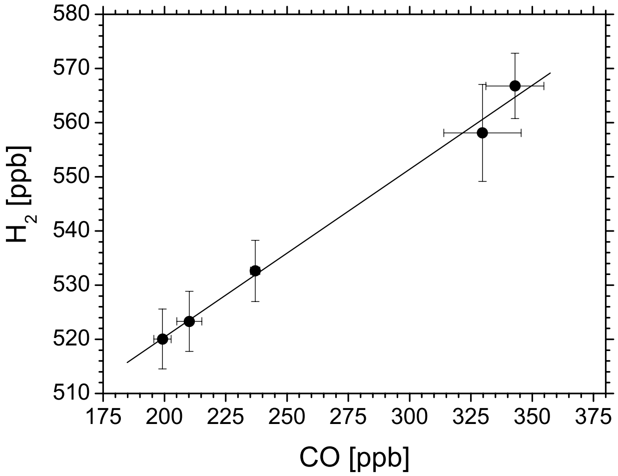

Fig. 2. Correlation of rush-hour H_2 and CO concentrations for July 19, 2006 (6:00–8:00 local time). The slope of the regression line in this example is $\Delta C_{H_2}/\Delta C_{CO} = 0.35 \pm 0.07$ ppb H_2 per ppb CO with $R^2 = 0.99$.

The calculated atmospheric morning rush-hour molar $\Delta C_{H_2}/\Delta C_{CO}$ ratios were additionally selected using the

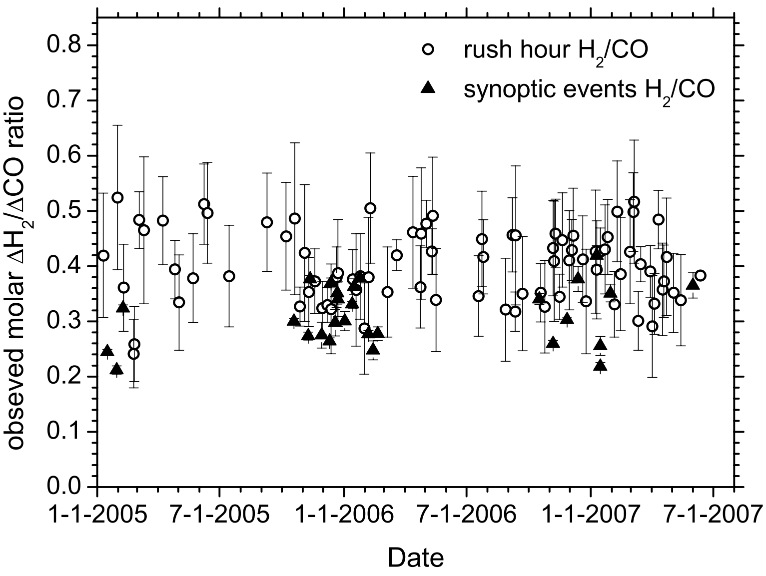

Fig. 3. Molar $\Delta C_{H_2}/\Delta C_{CO}$ ratios obtained from morning rush-hour data, derived from the slopes of the regression lines of H_2 and CO according to Fig. 2 (open circles). Molar $\Delta C_{H_2}/\Delta C_{CO}$ ratios derived from synoptic events are shown as filled triangles.

following criteria: (1) the squared correlation coefficient (R^2) had to be larger than 0.60, (2) the overall concentration change ΔCO during the selected period had to be larger than 70 ppb and (3) the uncertainty of the $\Delta C_{H_2}/\Delta C_{CO}$ ratio (regression slope) had to be smaller than 33%. In total 83 rush-hour situations fulfil all three criteria. The individual $\Delta H_2/\Delta CO$ ratios are shown in Fig. 3 as open circles. Averaging all situations yields a mean $\Delta C_{H_2}/\Delta C_{CO}$ ratio of 0.40 ± 0.06 (1σ) ppb ppb^{-1}.

3.2. *Data selection for the synoptic event based $\Delta C_{H_2}/\Delta C_{CO}$ ratio*

Emission ratios from synoptic events have been evaluated in addition to the rush-hour peaks. Those situations were selected from the record visually using the following criterion: The synoptic event had to last for at least one day and affect all trace gases concentrations measured (i.e. H_2, CO, CO_2, CH_4, N_2O and ^{222}Rn). A weighted linear regression was performed on all H_2 and CO values within a synoptic event. The mean molar $\Delta C_{H_2}/\Delta C_{CO}$ ratio resulting from the synoptic events is 0.31 ± 0.05 (1σ); note, however, that synoptic events occur mainly during winter, i.e. not all seasons are covered in Fig. 3.

3.3. *Soil sink correction of the observed $\Delta C_{H_2}/\Delta C_{CO}$ ratios*

From atmospheric measurements, only the ratio of the net H_2 and CO flux densities (Eq. 1) can be derived. (Note that the correct term here is *flux density* (given in moles m^{-2} s^{-1}), and not *flux* (which would be in moles s^{-1}). However, both terms are used here synonymously although we are always dealing with flux densities (in moles m^{-2} s^{-1}). The net H_2 source flux $j_{H_2}^{net}$ during the morning rush hour, however, consists of at least three components, (1) the flux caused by the H_2 emissions $j_{H_2}^{emi}$, (2) the soil sink flux $j_{H_2}^{sink}$ and (3) the flux $j_{H_2}^{mix}$ due to the entrainment of air from the residual layer above the boundary layer

$$j_{H_2}^{net} = j_{H_2}^{emi} - j_{H_2}^{sink} + j_{H_2}^{mix}. \tag{2}$$

The air in the residual layer, which supplies the morning entrainment flux destroying the boundary layer inversion, has not been in contact with the ground during the night; contrary to the boundary layer air it is, therefore, not depleted in H_2. Free tropospheric and boundary layer air have, thus, different H_2 mixing ratios and the entrainment flux $j_{H_2}^{mix}$ has, in principle, to be accounted for when estimating pure ground level emission flux ratios. We addressed this problem by selecting only those rush-hour situations where the ^{222}Rn concentration was not yet declining during the period of investigation. The flux $j_{H_2}^{mix}$ caused by the entrainment of free tropospheric air should thus, as a first approximation, be negligible in the selected time periods (6:00–8:00 AM). Especially during summer this ^{222}Rn criterion is a strong restriction to the number of selected rush hours since the soil-borne trace gas ^{222}Rn declines on average already at about 7:00 AM during summer.

In Fig. 4 the mean diurnal ^{222}Rn cycle for all days during the summer months is shown in comparison to that of selected days in summer and winter. Although mixing ratios in selected rush hours on average do no longer increase after 6:30 AM, which implies some entrainment flux after 6:30 AM (open circles in Fig. 4), the selection is at least capable to exclude the more common situations with strong influence of air entrainment from the residual layer (strong decrease of ^{222}Rn after about 06:30 AM, compare solid line in Fig. 4).

In order to estimate the pure H_2/CO emission ratio from the observed $\Delta C_{H_2}/\Delta C_{CO}$ slopes also the influence of the soil sink

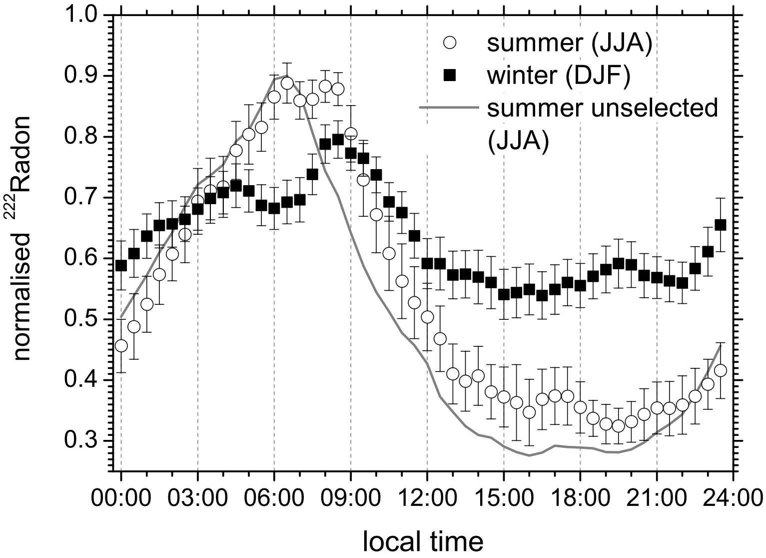

Fig. 4. Mean diurnal ^{222}Rn cycle for the selected rush-hour periods pooled by season. The individual diurnal cycles have been normalized to their maximum activity. Open symbols summer (JJA), closed symbols winter (DJF). The diurnal ^{222}Rn cycle of unselected data during summer is plotted as solid line.

for H_2 and CO needs to be accounted for

$$\frac{\Delta C_{H_2}}{\Delta C_{CO}} \cong \frac{j_{H_2}^{emi} - j_{H_2}^{sink}}{j_{CO}^{emi} - j_{CO}^{sink}} \approx \frac{j_{H_2}^{emi} - j_{H_2}^{sink}}{j_{CO}^{emi}}. \quad (3)$$

Since the relative influence of the CO soil sink is much smaller compared to that of the H_2 soil sink [ca. (2.8 ± 1.4) × 10^{-8} g CO m^{-2} s^{-1} (Hammer and Levin, 2009)] which corresponds to about 1% of the rush-hour emission flux and about 3% of the emission flux during synoptic events, see below), we assume that the net CO flux density j_{CO}^{net} equals the CO emission flux density j_{CO}^{emi}, and we rewrite Eq. (3), now showing an explicit H_2 soil sink correction term:

$$\frac{j_{H_2}^{emi}}{j_{CO}^{emi}} \cong \frac{\Delta C_{H_2}}{\Delta C_{CO}} + \frac{j_{H_2}^{sink}}{j_{CO}^{emi}}. \quad (4)$$

In an accompanying study Hammer and Levin (2009) have estimated the H_2 soil sink strengths for the respective catchment area from atmospheric night-time measurements in Heidelberg for the same period we evaluate here (January 2005 to July 2007) using the Radon-Tracer Method. The annual mean H_2 soil flux density was estimated to -1.28 10^{-8} g H_2 m^{-2} s^{-1} with a standard deviation (1σ) of 0.31 × 10^{-8} g H_2 m^{-2} s^{-1} and a seasonality of 25% (higher uptake rates in summer than in winter). With the same method as used by Hammer and Levin (2009) we here estimate ^{222}Rn-based CO_{emi} flux densities from parallel measurements of ^{222}Rn and CO during the morning rush hours. The Radon-Tracer Method applied to the core morning rush hours from 7:00 to 8:00 AM yields a mean CO emission flux density of (291 ± 35) × 10^{-8} g CO m^{-2} s^{-1} for the whole period. The scatter of individual values is large, and no significant seasonal variation is observed, which is why we used this mean value for the correction term. Converting the mass flux densities of $j_{H_2}^{sink}$ and j_{CO}^{emi} to molar flux densities, and using this ratio for the correction term in Eq. (4), results in a corrected molar H_2 to CO emission ratio of 0.46 ± 0.07, which is 15% larger than the measured $\Delta C_{H_2}/\Delta C_{CO}$ concentration ratio of 0.40 ± 0.06 ppb ppb^{-1}.

An equivalent correction method can be applied to the observed synoptic $\Delta C_{H_2}/\Delta C_{CO}$ ratios. However, the catchment areas of the synoptic events are much larger than for the rush hours, and the ground-level source mix may be different with other H_2/CO emission ratios than in the local Heidelberg area. With smaller flux densities from combustion sources the relative contribution of the soil sink in the correction term of Eq. (4) increases, leading to smaller observed $\Delta C_{H_2}/\Delta C_{CO}$ ratios. For the synoptic events the mean ^{222}Rn-based net CO flux density is only (106 ± 13) × 10^{-8} g CO m^{-2} s^{-1} which, assuming the same H_2 soil uptake rate as for the Heidelberg area, leads to a correction of the observed ratios (0.31 ± 0.05 ppb ppb^{-1}) by more than 50%, yielding a corrected molar emission ratio of 0.48 ± 0.07. Note that after the contribution of the soil sink is considered both approaches, the rush-hour evaluation and the evaluation of synoptic events are in excellent agreement.

3.4. *Emission ratios derived from direct source studies*

A more direct way to determine emission ratios of trace gases from various sources in the catchment area of our sampling site is to collect highly polluted air in the close vicinity of the sources. A mobile sampling device was, therefore, developed to collect air samples in the field. The sample containers (1 l two-stopcock glass flasks) were flushed and pressurized to 2 bar absolute pressure during sampling, and the air was subsequently analysed on the Heidelberg GC system. In 2006 and 2007, four sampling campaigns were conducted in the Heidelberg and the Mannheim–Ludwigshafen area. During all campaigns samples

Table 1. Locations and H_2 resp. CO background mixing ratios used to calculate the mixing ratio offsets for the four sampling campaigns in Mannheim and Heidelberg

Date	Location	Background location	H_2 (ppb)	CO (ppb)
March 2006	Heidelberg	Königstuhl	536	267
March 2006	Mannheim	Telecommunication tower	525	153
June 2007	Mannheim	Roof of Maritime Hotel	530	145
November 2007	Heidelberg	Roof of Institute building	480	167

with a strong traffic influence were collected, including locations like road tunnels, parking garages and intersections, and including situations with congested traffic. The maximum CO and H_2 mixing ratios were observed in a tunnel sample with 1870 ppb H_2 and 3350 ppb CO. To derive the H_2 and CO concentration surplus $\Delta C_g = C_g^{meas} - C_g^{BG}$ in individual samples, the background mixing ratios C_g^{BG} of H_2 and CO had to be subtracted from the measured concentration C_g^{meas}. Especially for small ΔC_{H_2} and ΔC_{CO} offsets the choice of the background mixing ratio is crucial and can lead to systematic errors of inferred emission ratios. Therefore, wherever possible, a background location in the vicinity of the polluted sites, which was only moderately influenced by local sources, was sampled in addition. In Table 1, the background locations and the respective background mixing ratios for all campaigns are listed.

Figure 5 shows the ΔC_{H_2} versus ΔC_{CO} offsets from background mixing ratios (Table 1) of all source samples collected during the four campaigns. The mean H_2/CO emission ratio can be approximated by the slope of the linear regression line:

$$\frac{j_{H_2}^{emi}}{j_{CO}^{emi}} = \frac{\Delta C_{H_2}}{\Delta C_{CO}}. \qquad (5)$$

Linear regression yields a mean traffic H_2/CO molar emission ratio of 0.448 ± 0.003 with a correlation coefficient $R^2 = 0.996$. Only one of the source samples has to be considered as an outlier, shown in Fig. 5 as an open symbol. This sample was taken during a traffic jam on the highway from Mannheim to Heidelberg. So far, no rational can be given to explain this outlier. The H_2 offset of the fit line is (-4.8 ± 2.9) ppb, confirming that the assumed background mixing ratios for all campaigns were appropriate. During the first sampling campaign in Mannheim–Ludwigshafen, additional samples were taken in the vicinity of the BASF premises. These samples are also plotted in Fig. 5 as open stars. Both samples show significant H_2 enhancement but are only slightly elevated in CO. In the plume of this chemical factory the source mix (also of other trace gases such as N_2O) is completely different to emissions from traffic, which is why we also rejected these two samples from the regression.

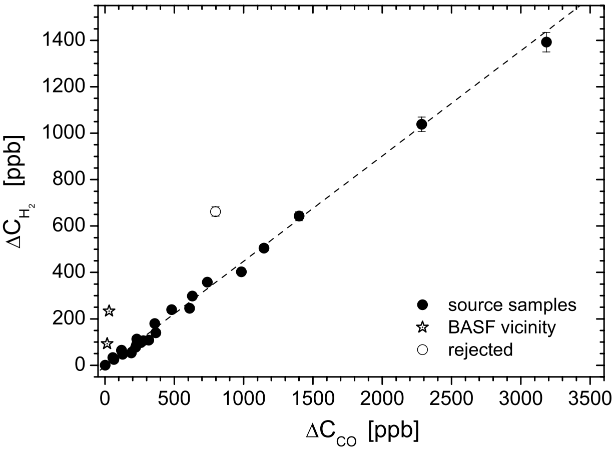

Fig. 5. $\Delta C_{H_2}/\Delta C_{CO}$ ratios derived from source samples: H_2 and CO offsets of the traffic source samples are shown as filled circles. The two outliers at low CO offsets (open stars) are samples collected in the vicinity of the chemical factory BASF in Ludwigshafen and are not accounted for in the linear regression. One outlier (open circle) corresponds to a sample taken during a traffic jam on the highway Mannheim–Heidelberg.

4. Discussion

4.1. Possible data selection artefacts

Selecting the proper time span for the evaluation of rush-hour data is crucial. On one hand the main rush hour in the Heidelberg catchment area takes place between 7:00 and 9:00 AM local time, but on the other hand stable nocturnal inversion situations disintegrate in the early morning after sunrise. It is outlined in Section 3.3 that the break up of the stable boundary layer leads to intense mixing and thus to an H_2 and CO entrainment flux, which is hard to quantify. Generally, one can assume that the entrainment flux increases the observed $\Delta C_{H_2}/\Delta C_{CO}$ ratio, since the residual layer is not directly affected by the night-time H_2 soil sink fluxes. In our dataset we observed that by extending the time span of rush-hour data from 8:00 to 9:00 AM introduces a seasonal cycle in the observed $\Delta C_{H_2}/\Delta C_{CO}$ ratio with larger values during summer (more entrainment flux) than during winter (Hammer, 2008). A similar seasonal variation was also found by Barnes et al. (2003) but not discussed. Our strict selection of rush-hour situations with minimum entrainment flux using concurrent ^{222}Rn observations eliminates this problem, but reduces the number of evaluated rush-hour situations drastically.

It should be noted, however, that the molar ratios presented here all stem from evaluation of morning rush-hour measurements. It is, thus, possible that the reported ratios do not represent daily mean values, e.g. if the mix of combustion sources changes over the day. Unfortunately, however, evaluation of evening rush hours could not be achieved, as the respective atmospheric signals were too small to obtain reliable H_2/CO ratios.

Another problem emerges when selecting a suitable period to estimate the ^{222}Rn-based CO emission flux density for the rush-hour period. From 6:00 to 8:00 AM we observe peak increases of CO mixing ratios while the corresponding ^{222}Rn concentration converges towards its maximum value at that time. Thus correlating radon and CO for the whole rush-hour interval underestimates the real CO flux during the peak rush hour. We addressed this problem by reducing the investigated period for the CO flux estimate to 7:00–8:00 AM.

4.2. *Comparison of the mean H_2/CO emission ratios with other studies*

Our results inferred from the atmospheric top-down approach evaluating morning rush-hour situations and synoptic events in Heidelberg, and showing a mean molar H_2/CO ratio of 0.47 ± 0.07, compare very well with the mean molar H_2/CO emission ratio found in bottom-up source studies from the same area of 0.448 ± 0.003. In Table 2 these H_2/CO emission ratios are further compared to values reported in the literature. If we disregard the measurement by Seiler and Zankl (1975), which is only based on one aircraft measurement in an urban plume, the other values based on continuous atmospheric data cover a range from 0.15 to 0.4 mole H_2/moles CO. However none of the earlier studies estimating the H_2/CO emission ratio have made a correction for a catchment area-dependent soil sink influence at the sites investigated. The very low ratio measured by Simmonds et al. (2000) was obtained from continental, polluted air masses arriving at the background station Mace Head. Simmonds et al. (2000) did not apply a correction for the contribution of the H_2 soil sink, but the authors already mentioned that their ratio might be too small, and attributed this to the presence of the soil sink.

The ratio reported by Barnes et al. (2003) from measurements at Harvard forest compares very well with the uncorrected $\Delta C_{H_2} / \Delta C_{CO}$ ratio determined for Heidelberg. Also Barnes et al. (2003) did not account for the H_2 soil sink. The ratio reported by Steinbacher et al. (2007) was also derived from measurements during morning rush hours, 150 m away from a busy street. Steinbacher et al. pooled all rush hours from November to February and applied one linear fit. Their H_2/CO emission ratio is significantly lower than the ratio found in our study, although the experimental setting is very similar, but also Steinbacher et al. (2007) did not correct for the influence of the soil sink. Our corrected result is, however, in very good agreement with the H_2/CO emission ratio derived in a highway tunnel study in Zürich, Switzerland, by Vollmer et al. (2007). One can assume that this study is not biased by the soil sink and that it reflects the pure H_2/CO traffic emission ratio. It should be mentioned that in the study by Vollmer et al. (2007) H_2/CO ratios were measured on the exhaust of a very similar car fleet as in the Heidelberg area where CO emissions in 2006 stem from about 85% passenger cars with approximately 25% diesel engines (LUBW, 2006). Therefore, keeping in mind that the H_2/CO emission ratio of Simmonds et al. (2000), Barnes et al. (2003) and Steinbacher et al. (2007) are probably biased towards

Table 2. Summary of H_2/CO emission ratios from combustion sources in mole H_2/mole CO

Authors	Location	Molar H_2/CO emission ratio (uncorrected)	Molar H_2/CO emission ratio (corrected)
Seiler and Zankl (1975)[a]	Aircraft; Munich	1	n.d.
Novelli et al. (1999)[b]	Boulder, Colorado	0.6 ± 0.1	n.d.
Simmonds et al. (2000)[c]	Mace Head, Ireland	0.15	n.d.
Barnes et al. (2003)[d]	Harvard forest	0.396	n.d.
Steinbacher et al. (2007)[e]	Dübendorf, Zürich	0.33 ± 0.01	n.d.
Vollmer et al. (2007)	Highway tunnel, Zürich	0.48 ± 0.12	0.48 ± 0.12
This study	Source samples, Heidelberg	0.448 ± 0.003	0.448 ± 0.003
This study	Heidelberg urban setting, rush hours	0.40 ± 0.06	0.46 ± 0.07
This study	Heidelberg urban setting, pollution events	0.31 ± 0.05	0.48 ± 0.07

[a] One estimate from an urban plume.

[b] 30 m above traffic intersection.

[c] European polluted air masses travelled to the background station.

[d] Pollution events from New York City, Washington.

[e] Morning rush hours.

smaller values due to neglecting the influence of the soil sink, the estimates of Vollmer et al. (2007) and the results from our study of the molar H_2/CO emission ratio all fall into a narrow range around 0.47 ± 0.03. This value is, however, 20% smaller than the value of Novelli et al. (1999) which is widely used in global H_2 budgets (e.g. Hauglustaine and Ehhalt, 2002). This may imply a respective over-estimation of the global H_2 source from fossil fuels by 20%.

5. Conclusions

Our study shows that it is possible to determine reliable mean H_2 to CO emission ratios of combustion sources from continuous observations in a polluted region. This ratio, however, can not simply be determined by ratioing measured atmospheric mixing ratio changes of H_2 and CO during rush hours or synoptic pollution events, but care has to be taken of processes modifying observed concentration ratios in the boundary layer: During morning rush hours, entrainment of air from the residual layer into the boundary layer can modify the observed molar ratio of $\Delta C_{H_2}/\Delta C_{CO}$. Different entrainment flux intensity during summer and winter may indeed lead to an apparent seasonality of the inferred H_2/CO emission ratio. Respective results were reported by Barnes et al. (2003) and Hammer (2008).

Another bias introduced in reported data of emission ratios is caused by the strong influence of the H_2 soil sink during nighttime inversions. Even in polluted areas, a respective correction needs to be applied, which, at first approximation, corresponds to the ratio of the molar H_2 uptake flux and the net molar CO emission flux in the catchment area of the site. For Heidelberg a correction of 15% for local scale rush-hour events and of more than 50% for large-scale winter time pollution events was determined. The large differences in inferred H_2/CO ratios found in the literature is most probably due to missing respective corrections in earlier studies.

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