High-frequency urban measurements of molecular hydrogen and carbon monoxide in the United Kingdom

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Abstract

High-frequency measurements of atmospheric molecular hydrogen (H_2) and carbon monoxide (CO) were made at an urban site in the United Kingdom (UK) from mid-December, 2008 until early March, 2009. Very few measurements of H_2 exist in the urban environment, particularly within the UK, but are an essential component in the assessment of anthropogenic emissions of H_2 and to a certain extent CO. These data provide detailed information on urban time-series, diurnal cycles as well as sources and sinks of both H_2 and CO at urban locations. High-frequency data were found to be strongly influenced by local meteorological conditions of wind speed and temperature. Diurnal cycles were found to follow transport frequency very closely due to the sites proximity to major carriageways, consequently a strong correlation was found between H_2 and CO mole fractions. Background subtracted mean and rush hour molar H_2/CO emission ratios of 0.53 ± 0.08 and 0.57 ± 0.06 respectively, were calculated from linear fitting of data. The scatter plot of all H_2 and CO data displayed an unusual two population pattern, thought to be associated with a large industrial area 85 km to the west of the site. However, the definitive source of this two branch pattern could not be fully elucidated. H_2 emissions from transport in the UK were estimated to be 188 ± 39 Gg H_2/yr, with 8.1 ± 2.3 Tg/yr of H_2 produced from vehicle emissions globally. H_2 and CO deposition velocities were calculated during stable night-time inversion events when a clear decay of both species was observed. CO was found to have a much higher deposition velocity than H_2, $1.3 \pm 0.8 \times 10^{-3}$ and $2.2 \pm 1.5 \times 10^{-4}$ ms^{-1} (1σ) respectively, going against the law of molecular diffusivity. The source of this unusual result was investigated, however no conclusive explanation was found for increased loss of CO over H_2 during stable night time inversion events.

1 Introduction

Atmospheric mixing ratios of molecular hydrogen (H_2), reported to be stable over the past 14-years (Grant, et al., 2010), may be altered with the possible introduction of H_2 as an energy carrier. This has provoked increased interest in the H_2 budget as it may result in increased H_2 emissions due to leakages during transport, distribution and usage of the fuel, thereby altering tropospheric and stratospheric chemistry. Major sources of H_2 consist of VOC oxidation (~50%), biomass burning (~20%) and fossil fuel combustion in transport and industry (~25%) (Novelli, et al., 1999; Price, et al., 2007; Xiao, et al., 2007). The latter is thought to be the main emission source significantly altered with introduction of a H_2 economy. Current estimates of H_2 emission from transport and industry are based on inventories of carbon monoxide emissions combined with emission ratios of H_2/CO from transport, which have been found to vary with engine and vehicle type (Vollmer, et al., 2007). Although numerous studies have reported H_2/CO ratios from road transport sources (Hammer, et al., 2009 and references therein) there is a paucity of H_2/CO ratio measurements from other sources such as aviation, domestic heating and industry.

The major loss of H_2 is from its poorly constrained biologically active soil sink, contributing 70-80% (Novelli, et al., 1999; Price, et al., 2007; Sanderson, et al., 2003; Xiao, et al., 2007) of its total loss, whilst reaction with the hydroxyl (OH) acts as a minor sink. H_2 deposition to the soil is particularly difficult to quantify as it has been found to vary depending on a number of parameters such as soil moisture, temperature, porosity, diffusivity and type (Schmitt, et al., 2009; Yonemura, et al., 1999). It is thus vital to accurately quantify the magnitude of the soil sink in different areas and soil types to accurately estimate the magnitude of this loss process.

Carbon monoxide (CO) is one of the key components controlling the oxidative capacity of the troposphere by reacting with the OH radical, which is its primary loss route. Uptake by soil micro-organisms contributes up to 10% of its loss (Bergamaschi, et al., 2000). CO is also emitted by soils which results in a net global balance of uptake and production in soil (Conrad, 1988). However, soils in temperate environments have been found to primarily show CO uptake rather than emission (Moxley and Smith, 1998).

Continuous high-frequency measurements of H_2 and CO were made in Bristol, United Kingdom (UK) from December 2008 to March 2009 at an urban city centre location. To our

knowledge they represent the first published set of continuous measurements of H_2 in the UK. The presented data and their analyses provide essential information on local sources and sinks of both H_2 and CO which may aid in the assessment of the impact of a future H_2 economy.

2   Experimental

2.1   Sampling Location

Semi-continuous measurements of H_2 and CO in ambient air have been performed using an automated, high-frequency system sampling in the city centre of Bristol, UK (Fig. 1) from mid December 2008 to early March 2009. The sampling site [$51^o27'$N, $2^o36'$W; 62 m above sea level] located at the Atmospheric Chemistry Research Group in the University of Bristol is representative of urban conditions (Khan, et al., 2009; Rivett, et al., 2003). Air quality at this urban sampling site is dominated by traffic emissions as it sits close to a number of major carriageways, which act as busy and often congested commuter routes to and from the city centre. With a population of nearly 500,000 Bristol is the UK's sixth largest city. The city centre sits in a basin like depression surrounded by hills on each side. Two major motorways run nearby the city, with a high volume of local traffic. These combined effects often result in pollutant build-up during stable high pressure systems.

2.2   Analytical method and calibration

A commercial gas chromatograph (Peak Performer 1 (PP1), Trace Analytical, Inc., California, USA) was used to measure H_2 and CO. This instrument is fitted with a mercuric oxide bed and, following mercury's reduction by H_2 or CO, the ensuing vapour is measured by UV photometry. A customised sample introduction system was fitted to the PP1 very similar to that reported by Grant et al., (2010) which is used at one of the five Advanced Global Atmospheric Gases Experiment (AGAGE) measurement sites at Mace Head, Ireland. This customised sample introduction system enabled continuous, high frequency, and concurrent analysis of air and standard samples. The analysis sequence consisted of an air sample followed by a standard to determine and correct for instrumental drift, resulting in 72 fully calibrated air samples per day. A carrier gas flow of 20 ml/min of synthetic air is passed through a Sofnocat cleanup trap to remove any trace CO impurities prior to use. Each sample

is dried prior to separation using a permeation Nafion drier (Permapure, USA). Once dried the sample is flushed through the 1 ml sample loop and allowed to decay to ambient pressure, before injection onto two isothermal packed columns. The pre-column, used to protect the main column from contamination by gases which adsorb to the surface, is held a 105°C, as is the main column, both using standard PP1 column combination with Unibeads 1S, 60/80 mesh and molecular sieve 5 Å, 60/80 mesh, respectively. Once H_2 and CO have been separated on the main column they are analysed by the mercury detector. All H_2 and CO peaks were integrated by height using customised software (GCWerks) developed for instruments in the AGAGE network, mole fractions were determined relative to a working standard also known as the quaternary standard. Quaternarys are filled by compressing background ambient air at Mace Head, Ireland into 35 L electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3, RIX California, USA). The internal surfaces of the cylinder are electropolished to remove active sites on the surface of the stainless steel. One of these calibrated quaternary standards used in the AGAGE network was used in the Bristol urban sampling campaign. H_2 and CO measurements were referenced against a calibration scale developed at CSIRO (Commonwealth Scientific and Industrial Research Organisation). Inter-calibrations have been carried out between CSIRO and a scale developed at the Max Plank Institute (MPI) in Jena (Jordan and Steinberg, Submitted). This scale was developed for the Eurohydros project to enable a network of calibrated measurements across Europe. Good agreement was found, with MPI values approximately 16 ppb H_2 higher than the CSIRO scale (Grant, et al., 2010).

Due to the non-linear response of the PP1 detector, linearity testing was carried out during the reported measurement period. This was completed using a high concentration reference gas (BOC Speciality gases Ltd., Surrey, UK) which was dynamically diluted with zero air to the range of atmospheric concentrations by means of a custom made dynamic dilution unit. Results provided measurements for the non-linearity correction thus producing an equation to correct data for non-linearity. A maximum internal reproducibility (1σ) of 5 ppb and 1 ppb was found for H_2 and CO respectively, assuming average concentrations of 500 ppb H_2 and 120 ppb CO determined from recurrent working standard analyses.

3   Results and discussion

The full record of high-frequency H_2 and CO observations taken at an urban site in Bristol from mid-December 2008 to early March 2009 are shown in Fig. 2. This dataset contains ~80% of the possible measurements taken over this period with segments of missing data due to instrumental problems. Overall accuracy on measurements is within ± 2%, this takes into account standard to standard reproducibility, uncertainties in non-linearity corrections and scale propagation. Over the entire measurement period H_2 was found to range from a minimum of 494 ppb to a maximum of 1544 ppb with a mean (± 1σ) mole fraction of 601 ± 92 ppb, whilst CO showed a mean of 291 ± 151 ppb with a range of 96-1214 ppb.

3.1   Diurnal variations

Anthropogenic emissions, particularly from the transport sector were found to have a significant effect on the short-term variability of H_2 and CO, evident in Fig. 3, a plot of a six day period of high-resolution H_2 and CO mole fractions where nearly every peak in H_2 coincides with elevated levels of CO. In this plot mole fractions of H_2 and CO are also seen to vary with wind conditions. In Fig. 3 mole fractions of H_2 and CO are seen to rise sharply during morning and evening rush hours, approximate times of which are highlighted in yellow and green, respectively. The diurnal variation is however severely affected by meteorology. A rise in wind speed on Wednesday evening and Thursday morning leads to lower H_2 and CO mole fractions than expected. High wind speeds at midday on Friday also reduce the amplitude of the evening rush hour peak. Overnight on Friday a large elevation of H_2 and CO is observed. Low wind speeds overnight combined with the expected emissions from Friday evening related transport both contribute to this large elevation. Overnight on Saturday the expected traffic peak due to night life associated traffic is not observed due to high wind speeds (e.g. Martin, et al., 2008). The effects of both wind speed and temperature on H_2 and CO observations are shown in Figure 4. Low temperatures in winter act to reduce the height of boundary layer. Pollutants are then trapped in a smaller volume resulting in the observation of elevated H_2 and CO mole fractions. As Bristol is located in a bowl shaped depression pollutants can easily build up. High wind speeds which increase turbulence act to dilute pollutants by bringing clean air for rural areas which mixes with polluted urban air.

Figure 5 illustrates hourly mean H_2 and CO mole fractions separated into weekdays, Saturdays and Sundays shown in local winter time (GMT). Highest mole fractions for both H_2

and CO were observed during morning and evening rush hours. Rush hour time periods were verified by statistical traffic count data provided by Bristol City council (2009). These are produced by a combination of manual traffic counts, carried out across central Bristol during the same week every year on mid-week days, and through the use of automatic traffic counters. Traffic flow data shows morning rush hour beginning at 07:00, peaking from 07:30 to 08:45 and dropping to baseline levels by 09:30. Evening rush hour is evident from traffic count data by a slow increase in traffic from 15:00, with traffic flow peaking at 17:30 and dropping off at 18:30. Mean mole fractions of 646 ppb H_2, 390 ppb CO for morning rush hours, and 630 ppb H_2 and 341 ppb CO were observed during evening rush hours. H_2 mole fractions are seen to fall from midnight onwards, due to uptake by soil enzymes but also due to dilution caused by dispersion within the boundary layer (Steinbacher, et al., 2007). H_2 mole fractions are seen to rise in a delayed pattern in comparison with traffic flow data. Morning peaks in H_2 and CO reach their highest from 09:00 to 10:00, an hour and a half later than peak morning traffic flow. After this time, transport emissions decrease and with the additional effect of stronger vertical mixing at this time, dilution with background air and H_2 deposition, resulting weekday and weekend minimum is seen from 1-3 pm. Evening rush hour peaks of H_2 are wider than those observed during the morning, also verified by traffic flow data. Peak evening levels of H_2 are also observed later than peak traffic flow, delayed by ~1 hour. This delay between vehicle emission and measurement of elevated mole fractions of H_2 can be attributed to the mixing time required for emissions to rise from average emission source height to the measurement point, elevated by a few hundred metres from major carriageways. H_2 levels drop off more slowly after the evening rush hour as the boundary layer height decreases with more stable nocturnal inversion conditions concentrating pollutants. A very similar pattern is seen for CO, with identical morning and evening rush hour peaks. However, differences can be seen in the amplitude of rush hour peaks and overnight depletion of CO. It is well known that transport emits a much larger mole fraction of CO than H_2 which results in the larger amplitude seen for rush hour peaks of CO (Colls, 1997; Vollmer, et al., 2007). Dry deposition of CO is reported to be much lower than that of H_2 (Yonemura, et al., 2000), thus dispersion and mixing is thought to be the primary parameter controlling the CO decrease seen overnight with concentrations only dropping to 225 ppb compared with H_2 which falls to 555 ppb, near background levels. Interestingly a similar study by Steinbacher et al., (2007) saw much higher mole fractions of CO during rush hour periods but similar levels of H_2 compared with this work. The study by Steinbacher et al., was conducted at a suburban site in

Switzerland and observed average morning and evening rush hour peaks of ~520 ppb and ~500 ppb CO respectively, compared with our study in an urban environment, in which morning and evening rush hour peaks of 370 ppb and 325 ppb CO were observed. However, CO elevation from early morning minimum was found to be very similar (~150 ppb CO) in both studies. Therefore we believe that the higher CO mole fractions observed during rush hour in the Swiss study was an artefact of the higher background levels observed at the suburban site. One would initially expect the site to have lower background mole factions due to its location further from direct emission sources however local conditions such as meteorology or unknown emission sources may bias this. The difference in transport fleets between the two countries may also contribute to higher background mole fractions of CO. Petrol vehicles are known to emit over twice the amount of CO per km compared with diesel vehicles (Colls, 1997). The UK vehicle fleet is known to consist of approximately 68% petrol fuelled vehicles, whilst the Swiss fleet contains considerably larger fraction of petrol vehicles (76%) (Vollmer, et al., 2007 and references therein). This may contribute to elevated background levels of CO but is not likely to be the main cause for the higher mole fractions observed.

3.2 H_2 to CO ratios

Figure 6 shows a scatter plot of H_2 and CO over the entire measurement period with background H_2 and CO mole fractions subtracted. It was proven to be essential to subtract background H_2 and CO values prior to plotting and assessment of the molar H_2 to CO ratio, as H_2 and CO show a seasonal cycle offset of two to four months thus it is important to remove the effects of seasonality on the H_2/CO ratio (Grant, et al., 2010). A close correlation can be seen between H_2 and CO with an interesting two branch pattern emerging at higher mole fractions. This is the first study to display such a pattern. Ordinarily, scatter plots of H_2 and CO show a single grouping around a central line with a small amount of scatter. A linear fit was applied to all data, a molar H_2/CO ratio of 0.53 ± 0.08 with an R^2 value of 0.84 was calculated using reduced major axis regression taking into account the error in both x and y axes. Branch A displayed a molar H_2/CO ratio of 1.34 ± 0.12 (R^2 = 0.95) from linear fitting. Error from linear fitting was taken into account by use of the regression coefficient (or R^2 value). Branch A was separated from the rest of the dataset according to points highlighted in Figure 2 and Figure 6 (75 points in total) to enable assessment of its source. The highlighted points accounted for 2% of the entire dataset. Branch A was analysed by time of day, day of

week, weeks during the months, wind speed and wind direction. Points were found to be evenly scattered throughout the day with an equal number of points overnight and during the day. No points in branch A fell between 14:00 and 16:00 local time. And we do not believe this to be significant. No significant pattern was observed with day of week, 25% of points were found to fall at weekend however this is close to the percentage of points which fell at the weekend over the entire dataset (26%). A large proportion (43%) of the points which made up branch A were found to occur between the 15th and 17th of February which accounted for 15% of the entire dataset over this period. Points in branch A mainly (88%) occurred from the 7th of February until the 2nd of March, 2009. Points in branch A were found to occur at a large range of wind speeds from 3 – 15 m s^{-1}. No correlation was found between nocturnal inversion events (Section 3.4) and the source of Branch A. Wind direction was the only condition where a clear relationship could be demonstrated. Points from branch A were found only to occur between a wind angle of 240° and 330°, 70% of which were from a westerly direction ($\pm 10^{o}$). However, all data arriving from this broad westerly region (240°-330°) showed data points which encompassed branches A and B. A possible source of elevated H_2 compared with CO in this region is the town of Port Talbot. Situated 85 km to the west of Bristol, Port Talbot contains a high density of heavy industry including a large industrial gases plant (British Oxygen Company), a steelworks, and a gas fired power plant. Given the very consistent H_2/CO ratio of branch A, its appearance without an obvious bias for time of day and its onset at a threshold of 3 ms^{-1} suggests a continuous point source some distance away. We believe emissions from some of this industry, possibly the industrial gases plant or the gas turbine engines in the power plant may be the cause for branch A where higher H_2/CO ratios are observed. Gas turbine engines which use liquid fuels which have a high hydrogen content have been shown to emit high levels of CO under low firing temperatures due to incomplete combustion (Pavri and Moore, 2003). It is possible that unburnt H_2 could also be emitted in similar or higher quantities. This would give rise to a much higher H_2/CO ratio as seen in Branch A.

3.3 H_2 emissions from transport

Recently there has been increased interest in H_2/CO emission ratios from transport (Barnes, et al., 2003; Hammer, et al., 2009; Steinbacher, et al., 2007; Vollmer, et al., 2007) as it enables the estimation of large-scale H_2 emissions by scaling from CO, which has well constrained regional and global emission inventories. In this study only weekday morning rush hours (7-9

am) were used to calculate H_2 emissions from transport, as this period when transport emissions are highest best represents the molar H_2/CO transport emission ratio. An overall molar H_2/CO ratio of 0.53 ± 0.08 from linear fitting using a reduced major axis regression method of calculation with regression coefficients providing a measure of the uncertainly in the slope. A molar H_2/CO ratio of 0.57 ± 0.06 was calculated using the same method for weekday morning rush hours (7-9 am). This rush hour ratio agrees well with other urban studies (Table 1) and primarily represents the H_2/CO emission ratio from transport. Variation of our molar H_2/CO ratio of 0.53 (and 0.57 for rush hour) from those observed by other urban studies is statistically insignificant with respect to the errors involved in this and other studies. Molar H_2/CO ratios reported by Steinbacher et al., (2007) are lower (0.33 ± 0.01) due to the suburban nature of this site. Barnes et al., (2003) reported a molar ratio of 0.34 from a rural location downwind of high pollution where much dilution of pollution plumes would have occurred prior to sampling. Hammer et al., (2009) reported a molar ratio of 0.40 ± 0.06 from an urban site. This molar ratio, lower than that calculated in this study could be attributed to differing local conditions such as location of industry, incinerators and reduced traffic levels which may alter the H_2/CO ratio. If there are large industrial emissions close to the measurement location H_2/CO ratios may be altered, as a recent study found chimney stack emissions from incinerators and domestic heating to produce a significantly reduced ratio compared with emissions from vehicle exhaust (Vollmer M.K. personal communication). Winter H_2/CO ratios have been found to display a higher correlation coefficient than summer ratios, as increased mixing and dilution during summer months caused by thermal convection alters the direct emission ratio (Steinbacher, et al., 2007). Increased depletion of H_2 due to dry deposition to the soil has also been found to alter H_2/CO ratios less in winter than summer (Grant, et al., 2010). Therefore we believe H_2/CO ratios derived solely from winter data (as used in this study) are thought to be more accurate in predicting H_2 emissions from transport sources.

H_2 emissions from transport and other anthropogenic sources are very poorly constrained, with a scarcity of bottom up emissions estimates. Thus top down estimates are produced as a best guess constrained by bottom up emission estimates for CO, a much more widely studied tropospheric pollutant. The mass of H_2 emissions was calculated using a simple approach incorporating annual CO emissions and the measured H_2/CO emissions ratio (Dunse, et al.,

2005). Annual CO emissions for Bristol are estimated to be 7.9 Gg/yr, with 4578 Gg CO/yr from UK transport emissions (NAEI, 2006a; NAEI, 2006b). Applying a rush hour H_2/CO ratio of 0.57 ± 0.06, Bristol's H_2 source can be estimated as 325 ± 67 Mg H_2/yr, this is considered an upper estimate of overall H_2 emissions in the area as it has been suggested that a H_2/CO ratio of much less than 0.5 may be more appropriate for non-transport sources of H_2 (Grant, et al., 2010). UK vehicle transport emissions of 188 ± 39 Gg H_2/yr were also estimated using a transport emissions ratio of 0.57 ± 0.06.

Since diesel vehicles are known to produce significantly less H_2 than their petrol counterparts (Vollmer, et al., 2007), to predict global H_2 emissions from transport, one must consider the proportion of diesel and petrol fuelled vehicles worldwide. The world fleet has been estimated to consist of ~ 92% petrol vehicles (Fulton and Eads, 2004). However, as our molar H_2/CO emissions ratio was measured in a fleet of 68% petrol vehicles we must assume our ratio of 0.57 is at the lower end of the emissions ratio (Anderson, 2008) which would produce an emission of 7.7 ± 2.2 Tg H_2/yr. Assuming global CO emissions from road transport of 186 Tg CO/yr for 2000 taken from the EDGAR v3.2 database (Olivier, et al., 2002). We can also scale up our molar H_2/CO emissions ratio in the same manner as Vollmer et al., (2007) to produce an estimate for the world fleet of 92% petrol vehicles. Our emission ratio of 0.57 can be scaled up to 0.63 assuming a pure petrol fleet which is then reduced to 0.61 to account for the 8% of diesel vehicles globally. This scaled ratio estimates 8.1 ± 2.3 Tg H_2/yr is produced from road transport globally, with uncertainties in scaling of an emissions ratio based on the percentage of vehicle types and the error associated with the CO emissions estimate. This is within the wide range quoted by Novelli et al., (1999) of 5 – 20 Tg H_2/yr. It is at the upper end of the range of 4.2 – 8.1 Tg H_2/yr quoted by Vollmer et al., (2007). Differences between our study and that of Vollmer and co-workers are due to the lower molar H_2/CO emission ratio measured in that study but also due to the range of different methods of calculation used in the study by Vollmer and co-workers. The lower estimate of 4.2 Tg H_2/yr produced by Vollmer was formed by use of the H_2/CO_2 emissions ratio from vehicles and a global road vehicles CO_2 emissions estimate.

3.4 Nocturnal depletions of H_2 and CO

Over several nights during the measurement period strong nocturnal depletions of H_2 and CO were observed, thought to occur due to a combination of mixing and dry deposition for CO and dry deposition for H_2. The deposition velocity can be calculated if the height of the

boundary layer is known. The boundary layer height (h) in meters can be calculated according to the equation:

$$h = \sqrt[3]{\frac{\gamma^2 . T . u_*^4}{f . \kappa . g}\left(-dT/dt\right)}$$ (1)

where $\gamma = 0.4$ is the Zilitinkevich constant, T is the mean temperature in Kelvin, f is the coriolis parameter for Bristol, g is the acceleration of gravity, dT/dt is the mean cooling rate and u_* is the friction velocity (Garland and Derwent, 1979; Moxley and Cape, 1997). Friction velocity was calculated according to the equation:

$$u(z) = \frac{u_*}{\kappa} . \ln \frac{z}{z_0}$$ (2)

where u is wind speed at height z = 10 m, the von Karman constant $\kappa = 0.4$ and the roughness length (z_o) for an urban area of 0.4 m (Stull, 1988), which resulted in a mean friction velocity of 1.05 ms^{-1} for the Bristol area. Although this is a rough estimate of the boundary layer height making many assumptions, such as a constant cooling rate and average friction velocity for each event, it is preferable to using a constant boundary layer height of 100m for instance (suitable for winter nighttime). This method allows variation of boundary layer height with wind speed and turbulence therefore results in a more refined estimation of deposition velocities.

Calculation of the boundary layer height enables estimation of the deposition velocity, υ_d (m s^{-1}) according to the equation:

$$\upsilon_d = k_1 h$$ (3)

where k_1 is the first-order decay constant for the decrease in X (s^{-1}) (where X=H$_2$ or CO mole fractions, assuming no mixing or dilution occurs). The decrease in X follows first order kinetics and can be written as:

$$-\frac{d[X]}{dt} = k_1[X] \qquad \text{or} \qquad [X]_t = [X]_0 e^{-k_1 t}$$ (4)

Where [X]$_0$ is the mole fraction at approximately 11pm local time depending on the night-time event and [X]$_t$ is the mole fraction at time t after 11pm. Decay rate constants (k_1) for H$_2$ and CO ranged from 2.26×10^{-6} to 1.19×10^{-5} s^{-1} and 1.84×10^{-5} to 6.31×10^{-5} s^{-1}, respectively.

The boundary layer height was calculated for each night time event and displayed a range of 18 to 100 m, well within reported ranges of 20-30 m (Mahrt and Vickers, 2002), 50-150 m (Salmond and McKendry, 2002) and 100-500 m before sunrise (Stull, 1988). H_2 deposition velocities were calculated with individual boundary layer heights for each nocturnal event. A range of 0.9 ± 0.2 -$5.7 \pm 1.1 \times 10^{-4}$ m s^{-1}, with a mean of $2.2 \pm 1.5 \times 10^{-4}$ m s^{-1} (1σ) and a median of 1.8×10^{-4} m s^{-1} were found over the fourteen nocturnal events studied. This mean value agrees well with that of $2.4 \pm 1.3 \times 10^{-4}$ m s^{-1} (Yver, et al., 2009) and 3.0×10^{-4} m s^{-1} (Hammer and Levin, 2009) both measured in urban environments but using a different method. However our value is slightly higher than another urban estimate of 0.5-1.0×10^{-4} m s^{-1} (Steinbacher, et al., 2007). Our estimate is smaller than $4.8 \pm 1.3 \times 10^{-4}$ m s^{-1} (Gerst and Quay, 2001) and a recent modelling estimate of 5.3×10^{-4} m s^{-1} (Sanderson, et al., 2003) but within the wide range reported 0-10×10^{-4} m s^{-1} from flux chamber measurements (Yonemura, et al., 1999).

CO deposition velocities displayed a range of 4.2 ± 0.8 - $31 \pm 6.2 \times 10^{-4}$ m s^{-1}, with a mean of $13 \pm 8 \times 10^{-4}$ m s^{-1} (1σ) and a median of 8.8×10^{-4} m s^{-1} over the fourteen nocturnal events. Two other studies using similar methods have estimated deposition velocities. A study in a semi-rural area approximately 4 km outside Edinburgh a CO deposition velocity of 11×10^{-4} m s^{-1} was estimated (Moxley and Cape, 1997), which agrees well with our work. However a value of 0.4×10^{-4} m s^{-1} was calculated at a costal background site (Simmonds, et al., 2000), significantly lower than our estimate which is unexpected as with a larger soil area exposed at this rural area one would conversely expect higher deposition velocities. Other estimates range from 0.56 - 7.6×10^{-4} m s^{-1} mainly from chamber studies in the field (Table 2), significantly lower than the mean CO deposition velocity but close to the median CO deposition calculated in this study.

As expected the deposition velocities of H_2 and CO were closely correlated ($R^2 = 0.61$), however, the mean ratio of H_2/CO deposition velocities during individual events (0.19) was significantly lower than previously reported. Yonemura et al. (1999) reported a ratio of H_2/CO deposition of 1.55, whilst Simmonds et al. (2000) reported an extremely large ratio of 6.5. Another study by Yonemura et al. (2000b) displayed a high H_2/CO correlation coefficient of 0.88 in an arable field, with a H_2/CO deposition velocity ratio of 1.79, however the forested site in this study showed much lower correlation ($R^2 = 0.41$) with a H_2/CO deposition velocity ratio of 2.33. In light reported ratios of H_2/CO deposition in literature, our H_2/CO deposition

velocity ratio is unusually small (<1), showing much larger CO deposition velocities than H_2. This is surprising as the law of molecular diffusivity states that lighter gases diffuse into the soil much faster than heavier gases. One may therefore expect H_2 to have a higher deposition velocity than CO as diffusion into the soil surface was found to be the primary parameter controlling deposition of H_2 (Schmitt, et al., 2009). However, CO deposition may be controlled by kinetics of the biological uptake process as well as diffusion which results in this unusual uptake ratio. Loss of CO by reaction with the OH radical can be ruled out, as CO loss of 3.3×10^{-5} s^{-1} (mean loss from night-time events) would require a night-time OH radical concentration of 1.6×10^8 molecules cm^{-3} which is not possible under night-time conditions. Night-time OH radical concentrations in the range of $2 \pm 1.5 \times 10^5$ molecules cm^{-3} have been measured and modelled in recent studies (Emmerson and Carslaw, 2009; Geyer, et al., 2003) whilst daytime average OH is thought to be 1×10^6 molecules cm^{-3} (Khan, et al., 2008; Prinn, et al., 2005). Reaction of CO with the nitrate radical (NO_3) is too slow to account for any significant loss (Boyd, et al., 1991).

4   Conclusions

High-frequency measurements of H_2 and CO were performed at an urban site in the UK from December 2008 to March 2009. To our knowledge these are the first published measurements from an urban UK site, influenced predominantly by vehicle emissions. The site was found to be heavily influenced by transport emissions, where a clear transport related diurnal cycle was observed. However, local meteorological conditions of temperature, wind speed and direction were also found to influence the high-frequency measurements taken at the site, which may have implications for future analysis of measurements taken in an urban environment. Future studies should consider placing urban measurement stations in areas less prone to strong winds which disrupt urban emission patterns. A scatter plot of H_2 versus CO revealed an unexpected two population pattern which has not been observed in any previous studies and whose origin proved difficult to elucidate. An industrial gases plant and power plant were suggested as the possible source of the higher H_2/CO ratio, a higher ratio than observed in any previous studies. However, measurements of specific sources such as this must be carried out for this hypothesis to be verified. We suggest that further investigation into the H_2/CO emission ratios from poorly constrained sources of H_2 such as chimney stack emissions from industry, incinerator and aviation emissions would aid the assessment of future studies,

particularly in the analysis of H_2/CO ratio anomalies. This would enable more accurate estimates of H_2 emissions from combustion sources globally.

H_2 and CO deposition velocities were calculated over stable periods when a clear decay of both species was observed. CO was found to have a much higher deposition velocity than H_2 (1.3×10^{-3} and 2.2×10^{-4} ms^{-1} respectively). The source of this unusual result was investigated, however no conclusive evidence was found for increased loss of CO over H_2 during stable night time inversion events.

Acknowledgments

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Table 1: Literature comparisons of molar H_2/CO ratios calculated from linear fitting.

Source	Location	Year of study	H_2/CO ratio
Novelli et al. (1999)	Urban, Busy intersection, Colorado	1989	0.6 ± 0.1
Barnes et al. (2003)	Rural but downwind of pollution Harvard Forest, US	1996-1998	0.34
Steinbacher et al. (2007)	Suburban, Switzerland	11/2002-02/2005	0.33 ± 0.01[a]
Vollmer et al., (2007)	Urban, Highway tunnel, Switzerland	Nov/Dec 2004	0.48 ± 0.12[b,c] 0.51 ± 0.11[b,d]
Hammer et al., (2009)	Urban Heidelberg, Germany	01/2005-07/2007	0.40 ± 0.06[a]
This study	Urban, Bristol, UK	12/2008-03/2009	0.57 ± 0.06[a] 0.53 ± 0.08[b]

[a]:weekday morning rush hour; [b]: all data; [c]: mean ratio; [d]: vehicle weighted ratio;

Table 2: Comparison of CO deposition velocities

Method	Vegetation	CO v_d ($\times 10^4$ m s^{-1})	Reference
Decay rate	Mixed	11 (2.6-33)	Moxley and Cape (1997)
Open flow chamber	Andisol field	0 - 6	Yonemura et al. (1999)
CO_2 tracer method	Grass field	3.4	Yonemura et al. (2000a)
Flux chamber	Arable field	2.4±1.6 (0-7)	Yonemura et al. (2000b)
	Forest	2.7±0.6 (1.5-4.5)	
Closed flux chamber	Pine forest	0.85	Zepp et al. (1997)
	Spruce forest	1.5	
Ozone tracer method	Rural mixed	0.4	Simmonds et al. (2000)
Static chamber	Agricultural	0.14	Moxley and Smith (1998)
	Forest	0.23	
Decay rate	Urban mixed	12.7 ± 8.4 (1σ) mean	Our work
		8.79 median	
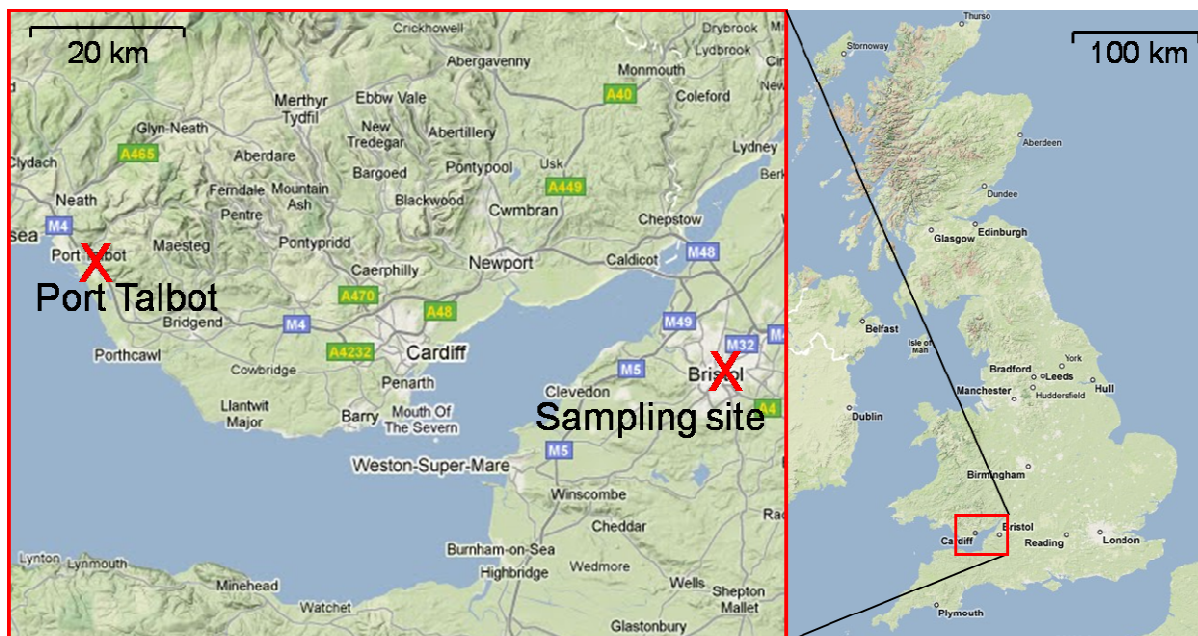
Figure 1: Sampling site location in Bristol's city centre in the United Kingdom and the location of Port Talbot to the west of the site.
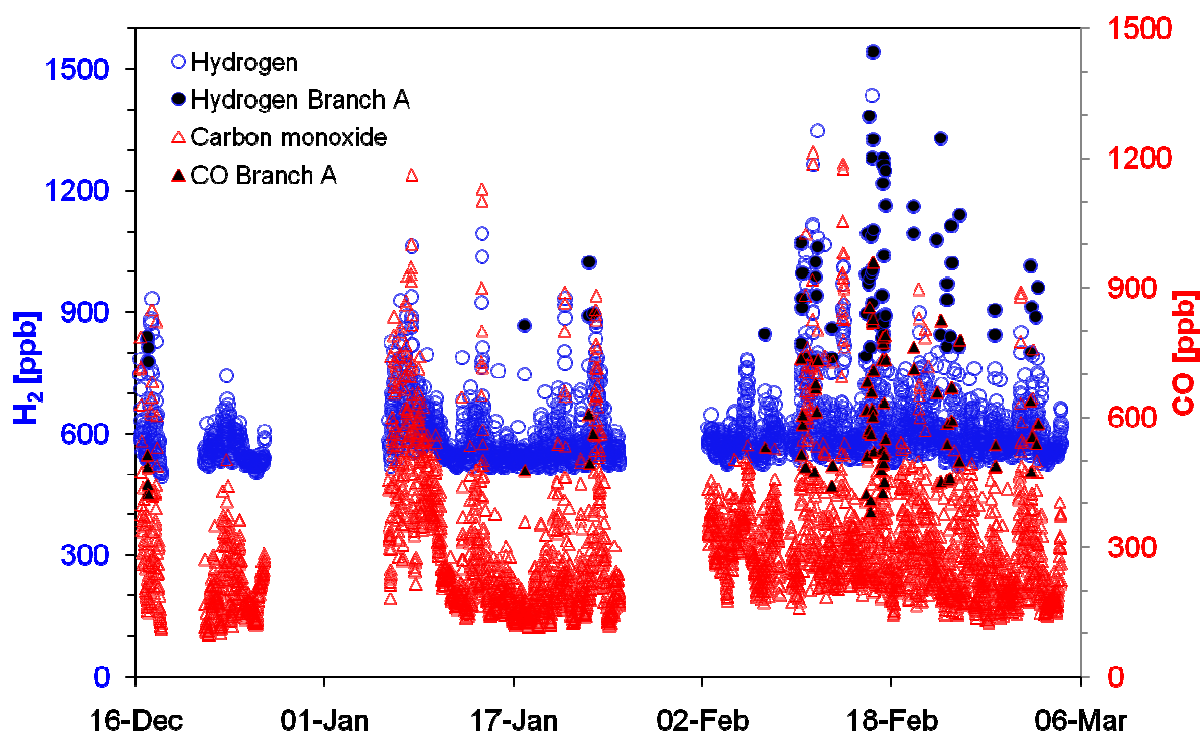
Figure 2: Urban air measurements for H_2 and CO from the 15th of December 2008 until the 4th of March 2009 measured at Bristol in the United Kingdom.
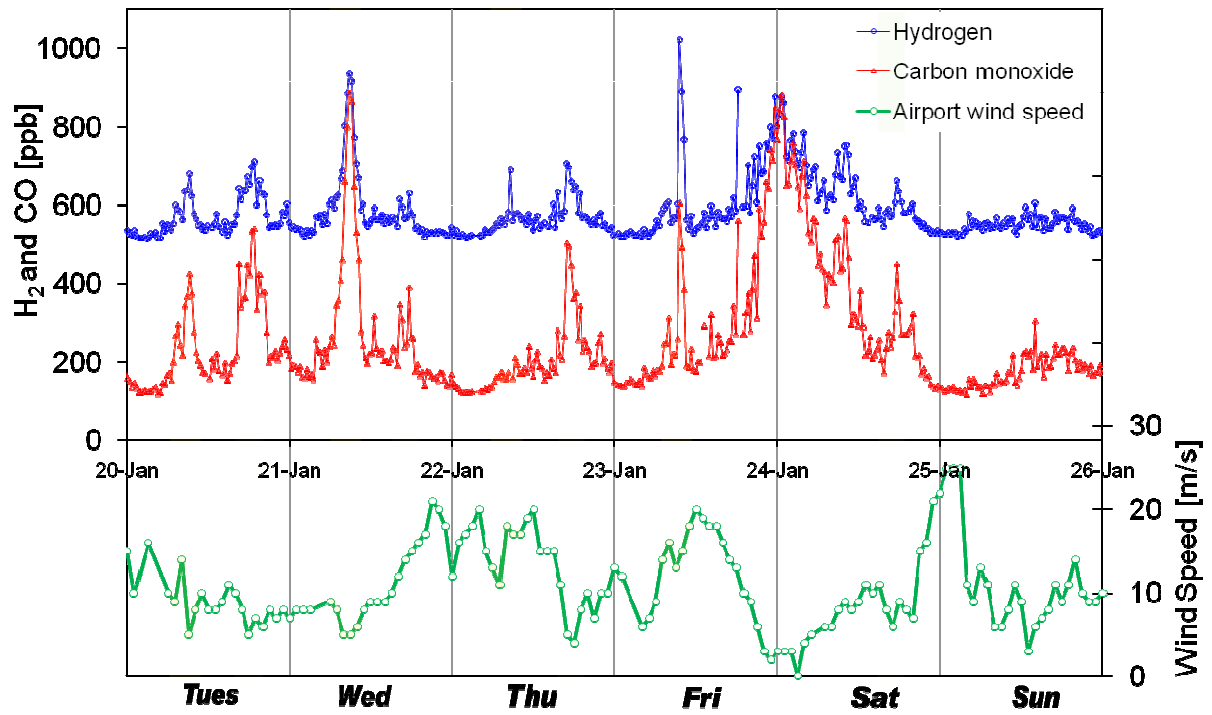
Figure 3: H_2 and CO mole fractions and wind speed over a six day period in January 2009, with rush hours highlighted in yellow for morning and green for evening.
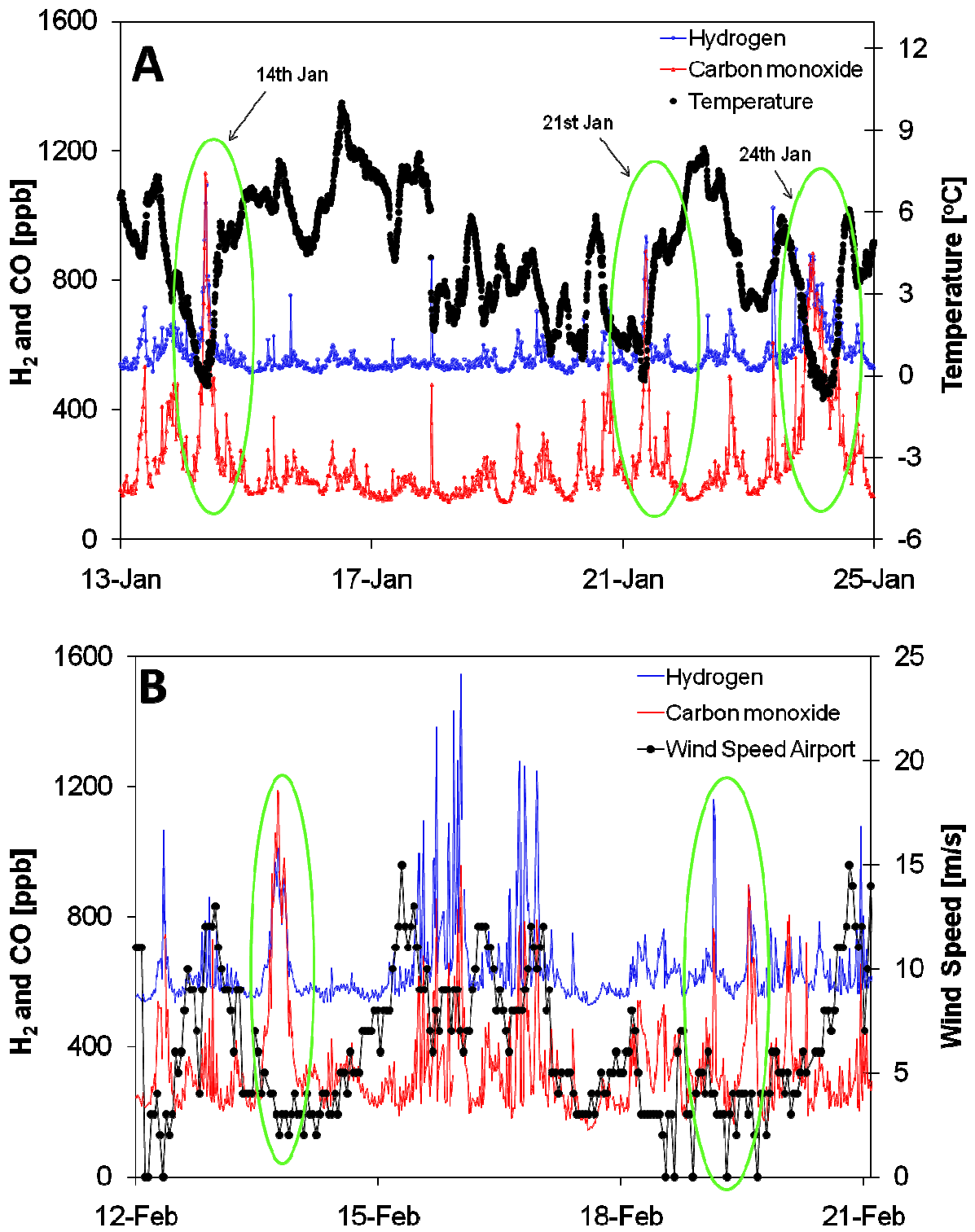
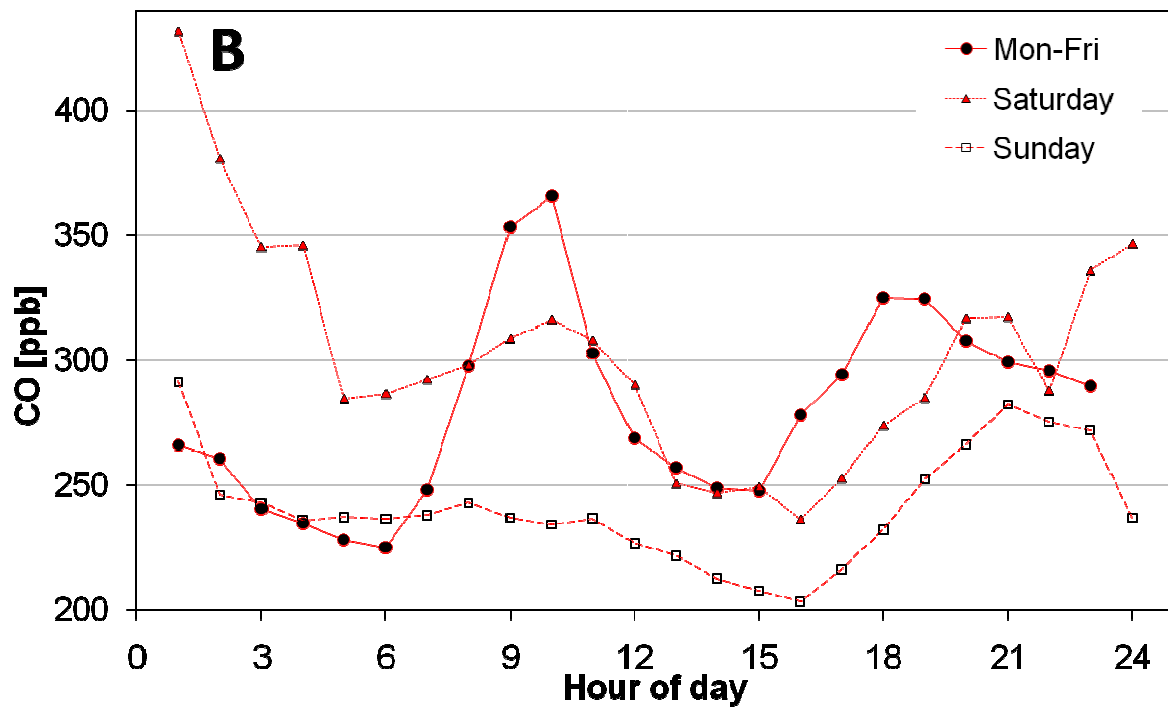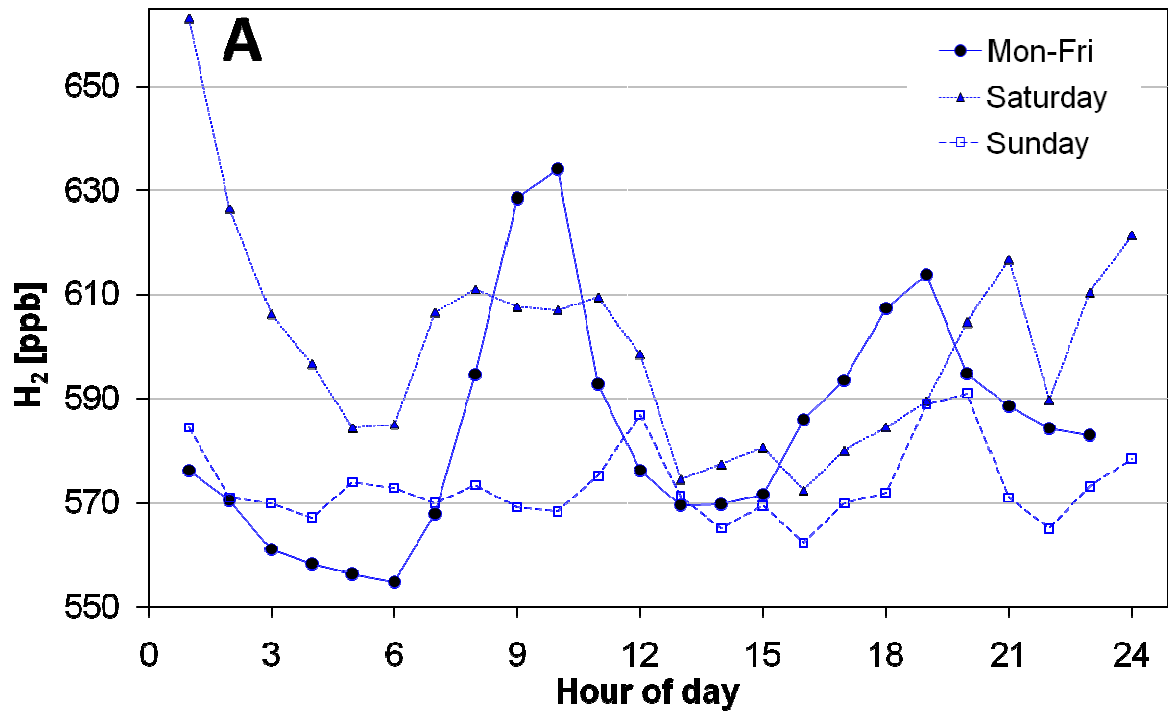Figure 4: H$_2$ and CO mole fractions plotted with a) temperature and b) wind speed.

Figure 5: Hourly averaged (a) H_2 and (b) CO data for weekdays (circles) and Saturday (triangles) and Sundays (squares) for the entire measurement period.
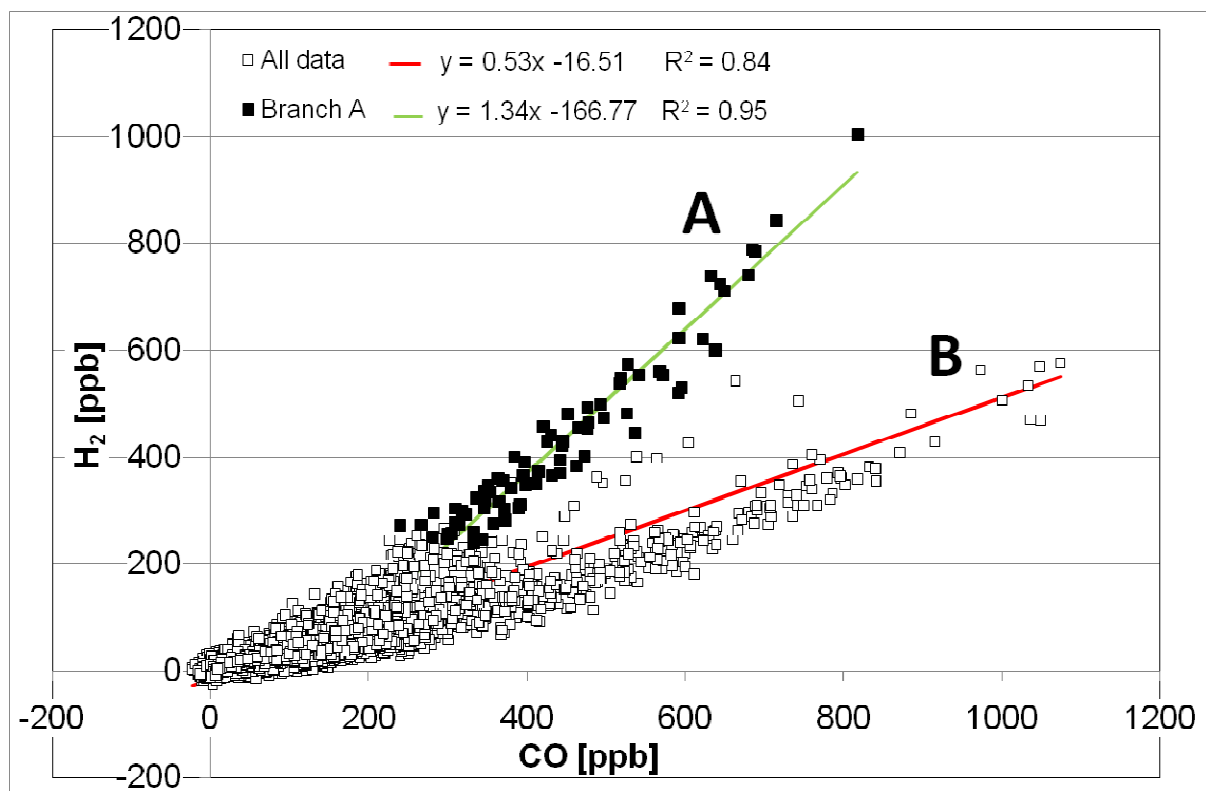
Figure 6: A scatter plot of individually background subtracted H_2 and CO mole fractions over entire measurement period. Molar H_2/CO ratios are displayed in the form of a linear fit through the scatter plot in the top of the plot.