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# High-frequency urban measurements of hydrogen and carbon monoxide in the UK

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High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## Abstract

High-frequency measurements of atmospheric hydrogen ( $H_2$ ) and carbon monoxide (CO) were made at an urban site in the UK from mid-December 2008 until early March 2009. Very few measurements of these trace gases exist in the urban environment, particularly within the United Kingdom, but are an essential component in the assessment of anthropogenic emissions of  $H_2$  and 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  $H_2$ /CO emission ratios of 0.50 and 0.53 were calculated, the scatter plot of which displayed an unusual two population pattern, the source of which could not be elucidated.  $H_2$  emissions from transport in the UK were estimated at 175 Gg/yr, with 7.8 Tg/yr of  $H_2$  produced from vehicle emissions 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  $H_2$ ,  $1.3 \times 10^{-3}$  and  $2.2 \times 10^{-4} \text{ m s}^{-1}$ , respectively, going against the law of molecular diffusivity. 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.

## 1 Introduction

Atmospheric mixing ratios of molecular hydrogen ( $H_2$ ), reported to be stable over the past 14-yr (Grant et al., 2009), 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 and distribution

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

of the fuel, thereby altering tropospheric chemistry. Major sources of  $\text{H}_2$  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  $\text{H}_2$  economy. Current estimates of  $\text{H}_2$  emission from transport and industry are based on inventories of carbon monoxide emissions combined with emission ratios of  $\text{H}_2/\text{CO}$  from transport, which have been found to vary with engine and vehicle type (Vollmer et al., 2007). Although numerous studies have reported  $\text{H}_2/\text{CO}$  ratios from road transport sources (Hammer et al., 2009 and references therein) there is a paucity of  $\text{H}_2/\text{CO}$  ratio measurements from other sources such as aviation, domestic heating and industry.

The major loss of  $\text{H}_2$  is from its poorly constrained biologically active soil sink, contributing 70–80% (Novelli et al., 1999; Sanderson et al., 2003; Price et al., 2007; Xiao et al., 2007) of its total loss, whilst reaction with the hydroxyl (OH) acts as a minor sink.  $\text{H}_2$  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 (Yonemura et al., 1999; Schmitt et al., 2009). 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 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  $\text{H}_2$  and CO were made in Bristol, UK from December 2008 to March 2009 at an urban city centre location. To our knowledge they represent the first set of continuous measurements of  $\text{H}_2$  in the UK. The presented

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



data and their analyses provide essential information on local sources and sinks of both H<sub>2</sub> and CO which may aid in the assessment of the impact of a future H<sub>2</sub> economy.

## 2 Experimental

### 2.1 Sampling location

5 Semi-continuous measurements of H<sub>2</sub> 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°27' N, 2°36' W; 62 m a.s.l.) located at the Atmospheric Chemistry Research Group in the University of Bristol is representative of urban conditions (Rivett et al., 2003; Khan  
10 et al., 2009). 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  
15 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<sub>2</sub> and CO. This instrument is fitted with a mercuric oxide bed and, following mercury's reduction by H<sub>2</sub> or CO, the ensuing vapour is measured by UV photometry. 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. Each sample was dried prior to separation using a permeation Nafion drier (Permapure, USA). All measured mole fractions were determined relative to a working standard also known as the quaternary standard. The  
25

High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



quaternary is filled by compressing background ambient air at Mace Head, California 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 working standards used in the Advanced Global Atmospheric Gases Experiment (AGAGE) network was used in the Bristol urban sampling campaign. H<sub>2</sub> 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 MPI scales where good agreement was found, with MPI values approximately 16 ppb H<sub>2</sub> higher than the CSIRO scale (Grant et al., 2009).

Due to the non-linear response of the RGA3 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 ( $1\sigma$ ) of 5 ppb and 1 ppb was found for H<sub>2</sub> and CO, respectively, assuming average concentrations of 500 ppb H<sub>2</sub> and 120 ppb CO determined from recurrent working standard analyses.

### 3 Results and discussion

The full record of high-frequency H<sub>2</sub> 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. Over the entire measurement period H<sub>2</sub> was found to range from a minimum of 494 ppb to a maximum of 1544 ppb with a mean ( $\pm$ standard deviation) mole fraction of  $601 \pm 92$  ppb, whilst CO showed a mean

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

### 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 Fig. 3 mole fractions of  $H_2$  and CO are seen to rise sharply during morning and evening rush hours (highlighted in yellow and green, respectively). The evening rush hour peak on Friday is obscured as concentrations rise sharply overnight due to nightlife associated transport. However, a corresponding peak due to nightlife activity is not seen overnight on Saturday, due to local meteorological conditions with high wind speeds diluting pollutants (e.g., Martin et al., 2008). The morning rush hour peak on Thursday was also affected by high wind speeds diluting pollutants (Fig. 3).

Figure 4 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 (7.30–10.00 a.m.) and evening (4.30–7.30 p.m.) rush hours, with mean mole fractions of 646 ppb  $H_2$ , 390 ppb CO for morning rush hours, and 630 ppb  $H_2$  and 341 ppb CO observed during evening rush hours. A clear pattern emerges from these plots where  $H_2$  mole fractions are seen to fall from midnight onwards, primarily 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 begin to increase from 6 a.m. onwards due to commuter traffic emissions, with contributions later in the morning from school transport, the accumulation of emissions resulting in peak  $H_2$  mole fractions at 10 a.m. 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 p.m. The evening rush hour peak which follows, is much broader than the morning peak because of school transport, which occurs earlier in evening and re-

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

duces peak commuter transport at classic rush hour times (4.30–6.30 p.m.). H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub> which falls to 555 ppb, near baseline levels. Interestingly a similar study by Steinbacher et al. (2007) saw much higher elevations of CO during rush hour periods but similar levels of H<sub>2</sub> elevation this work. The study by Steinbacher et al., was conducted at a suburban site in Switzerland and observed 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. Without prior knowledge the reverse scenario would be expected, since the Swiss suburban site is located further from direct sources. The difference cannot be accounted for by the seasonal cycle of CO since this is at a maximum in late winter early spring, the time at which urban Bristol measurements were taken. However, it is possible that the difference in the transport fleet between the two countries could account for this discrepancy. 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 and 32% diesel fuelled vehicles, whilst the Swiss fleet contains considerably larger fraction of petrol vehicles (76%) (Vollmer et al., 2007 and references therein). It is therefore possible that the higher fraction of petrol vehicles in Switzerland could account for the much higher elevation of CO.

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



### 3.2 H<sub>2</sub> to CO ratios

Figure 5 shows a scatter plot of H<sub>2</sub> and CO over the entire measurement period with background H<sub>2</sub> and CO mole fractions subtracted. It was proven to be essential to subtract baseline H<sub>2</sub> and CO values prior to plotting and assessment of the H<sub>2</sub> to CO ratio, as H<sub>2</sub> and CO show a seasonal cycle offset of two to four months thus it is vital to remove the effects of seasonality on the H<sub>2</sub>/CO ratio (Grant et al., 2009). A close correlation can be seen between H<sub>2</sub> 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<sub>2</sub> and CO show a single grouping around a central line with a small amount of scatter. However, Steinbacher et al. (2007) also displayed some unusual results where a linear relationship between H<sub>2</sub> and CO was observed up to 800 ppb H<sub>2</sub> and 1000 ppb CO with a clear shift to higher H<sub>2</sub>/CO ratios after this point. An explanation could not be given for this shift, however suggestions were made that it was a result of vehicle acceleration, which creates oxygen deficient conditions leading to higher H<sub>2</sub>/CO ratios (Vollmer et al., 2007). Analysis of branches A and B by time of day, air temperature and wind speed showed were inconclusive. The only significant difference found between the two branches was in the wind direction at which they occurred. Branch A was heavily dominated by winds from the northwest to west-southwest region, however many periods from branch B also occurred during this wind sector, as it is the prevailing regional wind. Possible sources from this wind sector are Bristol Airport, located 12 km to the south west of the measurement site with up to 170 flights/day and a busy motorway (the M5) 7 km to the northwest running southwest to northeast. These two major transport sources could have a large impact on H<sub>2</sub>/CO ratios, particularly aviation since its H<sub>2</sub>/CO emission ratio is yet to be defined. With this in mind, data were sorted more specifically according to wind sector only selecting data with direction of 220–230°, (Bristol airport), a clear pattern was seen to emerge showing a much lower H<sub>2</sub>/CO ratio of 0.39 from data within this sector (Fig. 3). This suggests that aviation emissions may produce a lower H<sub>2</sub>/CO ratio than road transport,

### High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

### 3.3 H<sub>2</sub> emissions from transport

Recently there has been increased interest in H<sub>2</sub>/CO emission ratios from transport (Barnes et al., 2003; Vollmer et al., 2007; Hammer et al., 2009; Steinbacher et al., 2007) as it enables the estimation of large-scale H<sub>2</sub> emissions by scaling from CO, which has well constrained regional and global emission inventories. In this study only 5 morning rush hours (7–9 a.m.) were used to calculate H<sub>2</sub> emissions from transport, as this period when transport emissions are highest best represents the  $\Delta H_2/\Delta CO$  transport emission ratio. An overall H<sub>2</sub>/CO ratio of  $0.50 \pm 0.07$  was observed for the 10 week 10 measurement period, with a ratio of  $0.53 \pm 0.05$  observed during morning rush hours (7–9 a.m.). This rush hour ratio agrees well with other urban studies (Table 1) and represents vehicle emissions with lowest impact from background H<sub>2</sub>/CO mole fractions. Variations of our H<sub>2</sub>/CO ratio of 0.53 from those observed by other studies could occur 15 for a number of reasons: If ambient air was not sampled adjacent to the emission location mixing and dilution of the direct emission ratio may occur prior to sampling (Hammer et al., 2009; Steinbacher et al., 2007); Due to different fractions of petrol and diesel vehicles used in each countries vehicle fleet, for example a study carried out in Switzerland in a busy tunnel measured a lower mean ratio of 0.48 (Vollmer et al., 2007), whilst 20 a study in Boulder, Colorado in the US measured a ratio of 0.6 over a busy intersection (Novelli et al., 1999); If there are large industrial emissions close to the measurement location  $\Delta H_2/\Delta CO$  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<sub>2</sub>/CO ratios have been found to display a higher correlation coefficient 25 than summer ratios, as increased mixing and dilution during summer months caused by thermal convection alters the direct emission ratio (Steinbacher et al., 2007). Thus H<sub>2</sub>/CO ratios derived solely from winter data (as used in this study) are thought to be more accurate in predicting H<sub>2</sub> emissions from transport sources.

High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



$\text{H}_2$  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  $\text{H}_2$  emissions was 5 calculated using a simple approach incorporating annual CO emissions and the measured  $\text{H}_2/\text{CO}$  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, 2006b; NAEI, 2006a). Applying a rush hour  $\text{H}_2/\text{CO}$  ratio of 0.53, Bristol's  $\text{H}_2$  source 10 can be estimated as  $302 \pm 78 \text{ Mg H}_2/\text{yr}$ , this is considered an upper estimate of overall  $\text{H}_2$  emissions in the area as it has been suggested that a  $\text{H}_2/\text{CO}$  ratio of much less than 0.5 may be more appropriate for non-transport sources of  $\text{H}_2$  (Grant et al., 2009). UK 15 vehicle transport emissions of  $175 \pm 9 \text{ Gg H}_2/\text{yr}$  were also estimated using a transport emissions ratio of 0.53.

Since diesel vehicles are known to produce significantly less  $\text{H}_2$  than their petrol 15 counterparts (Vollmer et al., 2007), to accurately predict global  $\text{H}_2$  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; Vollmer et al., 2007). We can thus scale up our  $\text{H}_2/\text{CO}$  emissions ratio 20 of 0.53, measured in a fleet of 68% petrol vehicles (Anderson, 2008) to a ratio of 0.58, to account for the difference between the UK transport fleet (68% petrol vehicles) and global transport fleet (92% petrol vehicles). Global CO emissions from road transport 25 have been taken from the EDGAR v3.2 database with 186 Tg CO/yr for 2000 (Olivier et al., 2002). We thus estimate  $7.8 \pm 2.3 \text{ Tg H}_2/\text{yr}$  is produced from road transport globally, with uncertainties in the scaling of an emissions ratio based on percentage of vehicle types and the error associated with the CO emissions estimate.

### 3.4 Nocturnal depletions of $\text{H}_2$ and CO

Over several nights during the measurement period strong nocturnal depletions of  $\text{H}_2$  and CO were observed, thought to occur due to a combination of mixing and dry depo-

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

sition 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 can be calculated according to the equation:

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

5 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:

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

10 where  $u$  is wind speed at height  $z=10$  m, the von Karman constant  $\kappa=0.4$  and the roughness length ( $z_0$ ) for an urban area of 0.4 (Stull, 1988), which resulted in a mean friction velocity of  $1.05 \text{ m s}^{-1}$  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 15 layer height of 100 m 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,  $v_d$  ( $\text{m s}^{-1}$ ) according to the equation:

$$20 v_d = k_1 h \quad (3)$$

where  $k_1$  is the first-order decay constant for the decrease in  $X$  ( $\text{s}^{-1}$ ) (where  $X=H_2$  or CO, assuming no mixing or dilution occurs) and  $h$  as the boundary layer height (m). The decrease in  $X$  follows first order kinetics and can be written as:

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

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Where  $[X]_0$  is the mole fraction at approximately 11 p.m. local time depending on the night-time event;  $[X]_t$  is the mole fraction time  $t$  after 11 p.m., and  $k_1$  is the first order rate coefficient ( $\text{time}^{-1}$ ). This equation assumes the concentration of X would be zero after an infinite time. Decay rate constants ( $k_1$ ) for  $\text{H}_2$  and CO ranged from  $2.26 \times 10^{-6}$  to  $1.19 \times 10^{-5} \text{ s}^{-1}$  and  $1.84 \times 10^{-5}$  to  $6.31 \times 10^{-5} \text{ s}^{-1}$ , 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).  $\text{H}_2$  deposition velocities were calculated with individual boundary layer heights for each nocturnal event displayed a range of  $0.9$ – $5.7 \times 10^{-4} \text{ m s}^{-1}$ , with an overall mean of  $2.2 \times 10^{-4} \text{ m s}^{-1}$ . This mean value agrees well with that of  $2.4 \pm 1.3 \times 10^{-4} \text{ m s}^{-1}$  (Yver et al., 2009) and  $3.0 \times 10^{-4} \text{ m s}^{-1}$  (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  $0.5$ – $1.0 \times 10^{-4} \text{ m s}^{-1}$  (Steinbacher et al., 2007). Our estimate is smaller than  $4.8 \pm 1.3 \times 10^{-4} \text{ m s}^{-1}$  (Gerst and Quay, 2001) and a recent modelling estimate of  $5.3 \times 10^{-4} \text{ m s}^{-1}$  (Sanderson et al., 2003) but within the wide range reported  $0$ – $10 \times 10^{-4} \text{ m s}^{-1}$  from flux chamber measurements (Yonemura et al., 1999).

CO deposition velocities displayed a range of  $4.2$ – $31 \times 10^{-4} \text{ m s}^{-1}$ , with a mean of  $13 \times 10^{-4} \text{ m s}^{-1}$ . 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  $11 \times 10^{-4} \text{ m s}^{-1}$  was estimated (Moxley and Cape, 1997), which agrees well with our work. However a value of  $0.4 \times 10^{-4} \text{ m s}^{-1}$  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  $0.56$ – $7.6 \times 10^{-4} \text{ m s}^{-1}$  mainly from chamber studies in the field (Table 2), significantly lower than the mean CO deposition velocity calculated in this study.

As expected the deposition velocities of  $\text{H}_2$  and CO were closely correlated ( $R^2 = 0.61$ ), however the mean ratio of  $\text{H}_2/\text{CO}$  deposition velocities (0.19) was signifi-

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



cantly lower than previously reported. Yonemura et al. (1999) reported a ratio of  $\text{H}_2/\text{CO}$  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  $\text{H}_2/\text{CO}$  correlation coefficient of 0.88 in an arable field, with a  $\text{H}_2/\text{CO}$  deposition velocity ratio of 1.79, however the forested site in this study showed much lower correlation ( $R^2=0.41$ ) with a  $\text{H}_2/\text{CO}$  deposition velocity ratio of 2.33. In light reported ratios of  $\text{H}_2/\text{CO}$  deposition in literature, our  $\text{H}_2/\text{CO}$  deposition velocity ratio is unusually small (<1), showing much larger CO deposition velocities than  $\text{H}_2$ . This goes against the law of molecular diffusivity which states that as  $\text{H}_2$  is a lighter gas it must diffuse into the soil much faster than CO and consequently have a higher deposition velocity, as diffusion into the soil surface is the primary parameter controlling deposition of both  $\text{H}_2$  and CO. Loss of CO by reaction with the OH radical can also be ruled out, as CO loss of  $3.3 \times 10^{-5} \text{ s}^{-1}$  (mean loss from night-time events) would require a night-time OH radical concentration of  $1.6 \times 10^8 \text{ molecules cm}^{-3}$  which is not possible under night-time conditions. Night-time OH radical concentrations in the range of  $2 \pm 1.5 \times 10^5 \text{ molecules cm}^{-3}$  have been measured and modelled in recent studies (Geyer et al., 2003; Emmerson and Carslaw, 2009) whilst daytime average OH is thought to be  $1 \times 10^6 \text{ molecules cm}^{-3}$  (Prinn et al., 2005; Khan et al., 2008). Reaction of CO with the nitrate radical ( $\text{NO}_3$ ) is too slow to account for any significant loss.

## 20 4 Conclusions

High-frequency measurements of  $\text{H}_2$  and CO were performed at an urban site in the UK from December 2008 to March 2009. To our knowledge these are the first reported measurements from such a site in Europe, influenced predominantly by vehicle emissions but also by industrial and aviation 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

### High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



the site, which may have implications for future analysis of measurements taken in an urban environment. A scatter plot of H<sub>2</sub> versus CO revealed an unexpected two population pattern which has not been observed in any previous studies and whose origin proved difficult to elucidate. Aviation emissions may account for this split as their

5 H<sub>2</sub>/CO emissions ratio is currently poorly defined and may be much lower than vehicle emissions. This ratio split may also have been caused by industrial and/or chimney stack emissions in the region, which have recently been found to produce a significantly lower ratio than transport sources. However, the definitive source of this split in H<sub>2</sub>/CO ratios remains unexplained and merits further investigation. An overall H<sub>2</sub>/CO ratio of

10 0.50 was found, however this is thought to be strongly influenced by dilution and mixing with background air, thus a weekday morning rush hour ratio of 0.53, assumed to most accurately represent transport emissions, was used for “bottom-up” H<sub>2</sub> estimates. H<sub>2</sub> emissions from transport in the UK were estimated at 175 Gg/yr, with 7.8 Tg/yr of H<sub>2</sub> produced from vehicle emissions globally.

15 H<sub>2</sub> 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<sub>2</sub> ( $1.3 \times 10^{-3}$  and  $2.2 \times 10^{-4} \text{ m s}^{-1}$ , respectively). The source of this unusual result was investigated, however no conclusive evidence was found for increased loss of CO over H<sub>2</sub> during stable night time inversion events.

20 **Acknowledgements.** AG thanks “EuroHydros – A European Network for Atmospheric Hydrogen Observations and studies”, a part of the 6th EU framework program ~ FP6-2005-Global-4 and Bristol ChemLabS for funding.

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## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

**Table 1.** Literature comparisons of H<sub>2</sub>/CO ratios.

Source	Location	Year of study	H <sub>2</sub> /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 <sup>a</sup>
Vollmer et al. (2007)	Urban, Highway tunnel, Switzerland	Nov/Dec 2004	0.48±0.12 <sup>b,c</sup> 0.51±0.11 <sup>b,d</sup>
Hammer et al. (2009)	Urban Heidelberg, Germany	01/2005– 07/2007	0.40±0.06 <sup>a</sup>
This study	Urban, Bristol, UK	12/2008– 03/2009	0.53±0.05 <sup>a</sup> 0.50±0.07 <sup>b</sup>

<sup>a</sup> weekday morning rush hour, <sup>b</sup> all data, <sup>c</sup> mean ratio, <sup>d</sup> vehicle weighted ratio

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

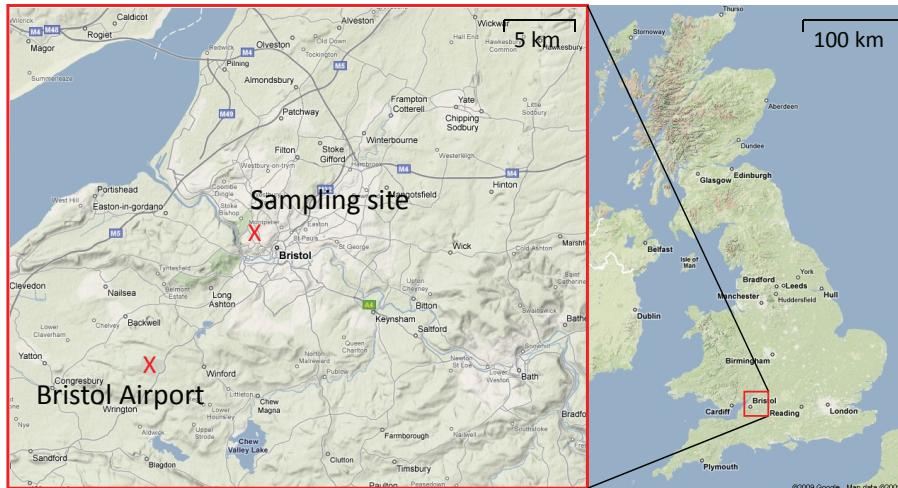


**Table 2.** Comparison of CO deposition velocities.

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 <sub>2</sub> 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	13 (4.2–31)	Our work

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.



**Fig. 1.** Sampling site location in Bristol's city centre, UK.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

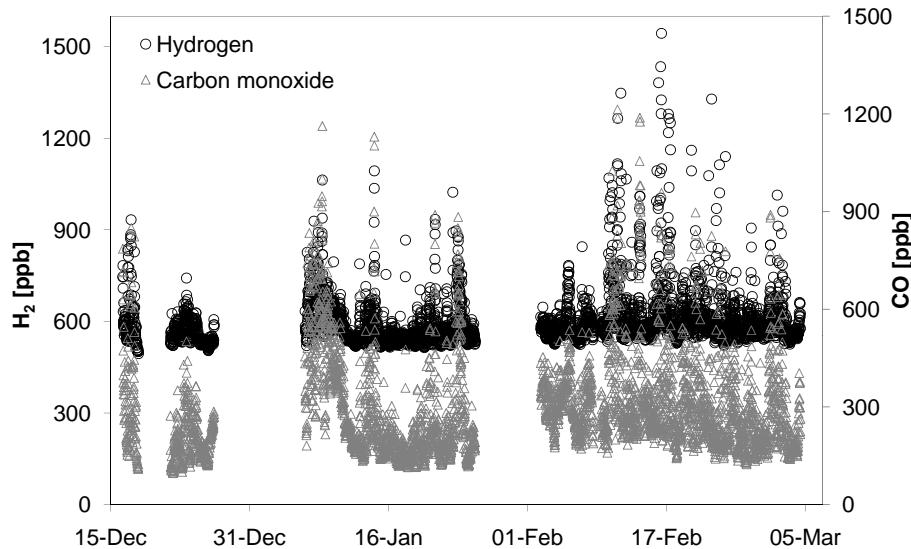
[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

**High-frequency urban measurements of hydrogen and carbon monoxide**

A. Grant et al.



**Fig. 2.** Urban air measurements for  $\text{H}_2$  and CO from 15 December 2008 until 4 March 2009.

[Title Page](#) [Abstract](#) [Introduction](#)  
[Conclusions](#) [References](#)  
[Tables](#) [Figures](#)

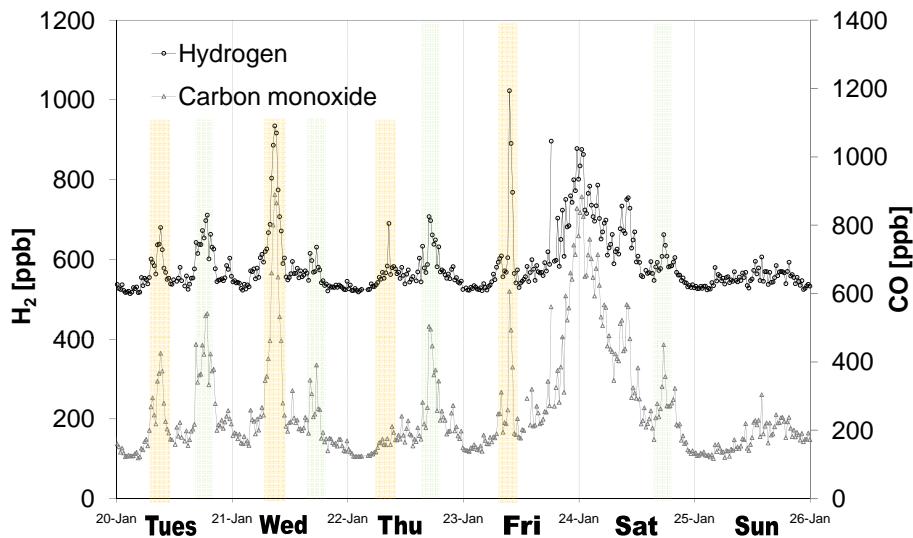
[◀◀](#) [▶▶](#)  
[◀](#) [▶](#)  
[Back](#) [Close](#)  
[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.



**Fig. 3.** H<sub>2</sub> and CO mole fractions for over a six day period in January 2009, with rush hours highlighted in yellow for morning and green for evening.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

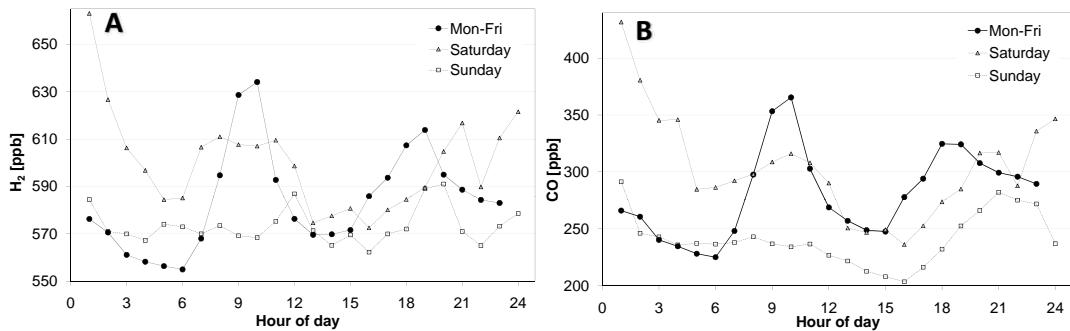
[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

## High-frequency urban measurements of hydrogen and carbon monoxide

A. Grant et al.



**Fig. 4.** Hourly averaged (A) H<sub>2</sub> and (B) CO data for weekdays (solid circles) and Saturday (grey triangles) and Sundays (empty squares) for the entire measurement period.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

[Back](#)

[Close](#)

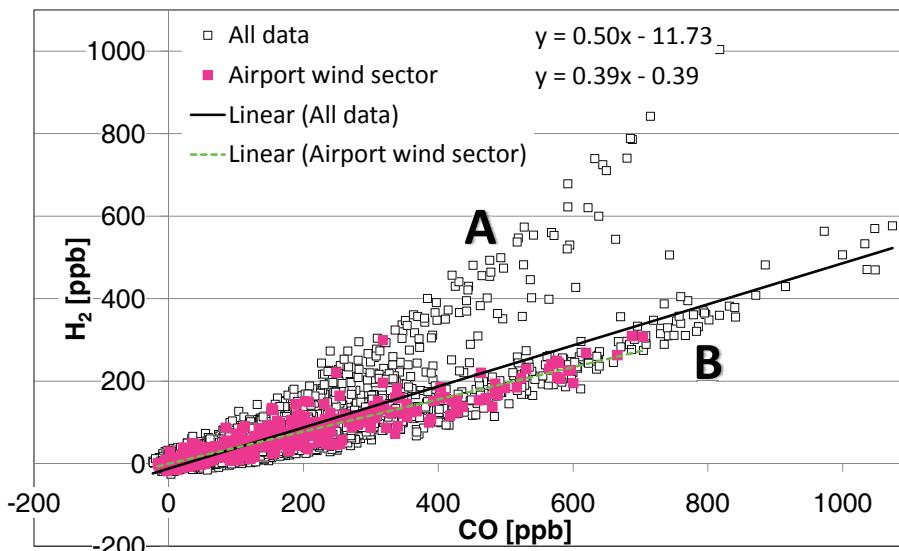
[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

**High-frequency  
urban measurements  
of hydrogen and  
carbon monoxide**

A. Grant et al.



**Fig. 5.** A scatter plot of baseline subtracted  $\text{H}_2$  and CO mole fractions over entire measurement period.

[Title Page](#)  
[Abstract](#) [Introduction](#)  
[Conclusions](#) [References](#)  
[Tables](#) [Figures](#)

[◀](#) [▶](#)  
[◀](#) [▶](#)  
[Back](#) [Close](#)  
[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)