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# London atmospheric Hydrogen and Carbon Monoxide: 12 year record, fluxes, and diurnal studies.

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Atmospheric hydrogen ($H_2$) and carbon monoxide (CO) have been measured at the Royal Holloway site, 30km WSW of London, for 12 years. This site receives air that has passed over London when there are easterly winds and cleaner, background air when the wind comes from the SW.

$H_2$ and CO mixing ratios are measured continuously at 30 minute intervals on a Trace Analytical Reduction Gas Detector coupled to a HP5890 GC since September 1996, and on a Peak Performer I (or PP1) since July 2007 at 5 minute intervals. Both instruments use 2 1/8" packed columns in series: a Unibeads 1S and a Molecular Sieve 5A. The PP1 detector (Reduced Compound Photometer) is an updated version of the old RGD2, and both use zero air as the carrier gas.

CO is calibrated twice a month against NOAA-CMDL standards (mixing ratios range: 186 to 300 ppb). $H_2$ was uncalibrated until 2006, but is now calibrated monthly against internal standards (range 530 to 750 ppb) measured at MPI-Jena as part of the Eurohydros project. A linearity correction is applied to each instrument, based on the standard measurements. A secondary standard is measured before each sample on the GC-RGD and another one is measured 4 to 6 times in a row twice a day on the PP1. A target gas is measured daily on both instruments since September 2008. The secondary standards and the target gas are dry ambient air in 70L stainless steel tanks filled to a pressure of 8 bars.

Comparison of results from the two instruments suggests that for the most part the data are in good agreement, but an interlaboratory round robin comparison exercise for the Eurohydros project showed that the RGD is not linear at low values of CO. This is particularly noticeable for CO levels below 150 ppb.

The long-term record of CO at Royal Holloway shows a significant decline since the start of the record: the annual mean CO mixing ratio in 2008 was three times lower than in 1997. Flux calculations, by ratio against $^{222}$Rn, $CH_4$ and $CO_2$, suggest CO emissions declined rapidly in the period 1996-2003, but with less change since.

Peaks in $H_2$ and CO mixing ratio occur around the times of the morning and early evening rush hours and are thought to be predominantly from boiler emissions and vehicles. The winter $H_2$:CO ratio during the morning rush hour period was 0.27 (DJF 2007-2008). In summer this ratio was lower: 0.19 (JJA 2007).

Both $H_2$ and CO mixing ratios usually decrease overnight. The dry deposition rate of $H_2$ calculated by considering the overnight decline in $H_2$ as $^{222}$Rn built up during anticyclonic conditions was $6.7 \pm 3.6 \times 10^{-4}$ m.s$^{-1}$.

Diurnal experiments allow characterisation of local sources in the West London region. dD of the $H_2$ source has been investigated.