# UK Report: Greenhouse gases in the London urban hotspot 1996-2009 D. Lowry, S. Sriskantharajah, R. E. Fisher, M. Lanoisellé, M. Bouvier and E.G. Nisbet, Dept. Earth Sciences, Royal Holloway University of London, Egham, TW20 0EX, UK

#### 1. Introduction

The Egham station (EGH) at Royal Holloway University of London (RHUL) is on the first significant hill WSW of the London conurbation (Fig 1a). The station is ideally located to receive air masses from Europe, the Arctic and the Atlantic, as well as being able to discern London's greenhouse gas emissions.

Greenhouse gas monitoring commenced at the station in 1995 with the installation of a HP5890 GC – FID system for recording CH<sub>4</sub> in air arriving at the station's rooftop inlet (Fig 1b). To add to this, a Reduction Gas Detector to measure CO mixing ratios and a Licor CO<sub>2</sub> analyzer were installed in 1996 and 1999 respectively. In 2007, a Peak Performer 1 (PP1) was installed to record H<sub>2</sub> and CO mixing ratios. The station also has an IUP-Heidelberg Radon monitor, which has been in operation since 2003.

NOAA primary standards have been used to calibrate all the instruments at the station for  $CH_4$ , CO and  $CO_2$  analysis since 1996.



Figure 1. a) Map showing location of RHUL relative to London, b) The air inlet at the Egham station c) Air arriving at the station from London is unobstructed



### 2. Egham Station Records

Figure 2 shows the average monthly trends of  $CO_2$ ,  $CH_4$  and CO over a 10-13 year timescale. For CO<sub>2</sub>, an annual average growth of approximately 2.5 ppm/ year has been seen at the station in Egham over the last ten years. CO<sub>2</sub> levels do not look likely to drop in the near future, although there was a downturn in 2004.

Average monthly CH<sub>4</sub> mixing ratios dropped between the late 1990's and the early part of this decade and it looked very much like levels of CH4 were levelling off. However, at the Egham station, like at other stations around the world, CH4 levels rose at the end of 2007 and beginning of 2008. There is some debate about the actual cause of this rise, but CH<sub>4</sub> levels have now returned to pre-2007 levels, and in the summer of 2009 the station saw record low methane levels.

CO levels dropped dramatically at the end of the 1990's and early part of this decade due to the introduction of catalytic converters in vehicles. Since 2003, CO levels have levelled off. The red diamonds overlain on the green data points show the CO mixing ratio of air arriving at the station as measured by the PP1. There is a good correlation between the two instruments.

Figure 2. Egham station record of CO2, CH4 and CO showing longterm trends in the mixing ratios of these gases in air arriving at the station.

ratios, with higher mixing ratios being recorded when the air masses cross London and nearby motorways (sector shaded in light blue), as opposed to coming over the less populated south/

For all other gases, the highest mixing ratios are seen when the wind is coming from the NNE to NNW sector (shaded in light green), which implies that national sources have influenced these gases. The Rn<sup>222</sup> concentration from this sector, in particular, is double that from background levels (coming from SW). An important (and known) Rn<sup>222</sup> source rock is located upwind in this sector, but more than 100 km from Egham. However, the Rn<sup>222</sup> concentration from the easterly sector is a mix of low-radon Arctic air masses and high-radon continental air masses.



CO/CH<sub>4</sub> averaged over 1 week (Excess over background)

# Excess over background - CO<sub>2</sub> vs CH<sub>4</sub> (ppb)







10

Methane

3800

### 4. Analysis of Egham Data

Comparison of the excess over background mixing ratios between the carbon gases during periods of week-long easterlies in October 1999, 2003 and 2007 highlights dramatic shifts in emission patterns over the last decade (Figure 4). For example, there has been an increase in the excess CO<sub>2</sub> over excess CO ratio from 42 to 149.There has also been an increase in the excess CO<sub>2</sub> over excess CH<sub>4</sub> ratio from 85 to 125.

The UK and London inventories imply that CO<sub>2</sub> emissions have remained constant over the last decade  $(\pm 5\%)$ . If this is correct, then the ratios above indicate that CO and CH<sub>4</sub> emissions have declined by 72 and 31 % respectively. This would be consistent with national inventories that quote a 72.4 % reduction in transport derived CO and 34 % reduction in CH<sub>4</sub>.

In terms of London emissions, the latest inventories from the Mayor of London's office (2004) state that London emits 3.2 and 1.2 % of the country's CO and CH<sub>4</sub> respectively. Our calculations suggest that these proportions are actually higher: 11.2 % for CO and 12.6 % for CH<sub>4</sub>.

The 2004 London inventory has a zero entry for landfill emissions,

Figure 4. Changes in excess over background of carbon gases for 7 consecutive days of Easterly (London) air in October1999, 2003 and 2007. The trajectories beside the graphs show the origins of the air masses during these periods.

because there are no open landfills in the area. However, landfills are known to continue emitting methane for many years after closure. The London inventory does not take into consideration the newer landfills just outside the London orbital motorway (often considered the outer boundary of the conurbation) which will ultimately contribute to the methane emissions of the greater London region. Our calculations for methane have incorporated these sources and suggest annual regional emissions of 282 ktonnes ± 26 %.

Graphs of the variation of excess ratios by time of day (Figure 5) clearly show that the two daily rush hour peaks of CO relative to CO<sub>2</sub> and CH<sub>4</sub> had mostly disappeared from the cycle by 2007, with evidence of a small but delayed morning peak and slightly more pronounced evening peak. This can be linked to local evidence of better morning traffic movement on the M25 London orbital and the positive effects of congestion charging on inner London boroughs. The dominant influence by 2007 on the diurnal ratio trends was the local biological CO<sub>2</sub> cycle, with low CO/CO<sub>2</sub>, producing a sinusoidal trend of excess during overnight respiration and higher ratios during daytime photosynthesis.

### 5. The Radon Tracer Method

The radon tracer method (Levin et al., 1999) was used to verify the figures calculated above. The method was applied to an overnight period between 00:00 and 06:00 over five consecutive days in October 2007 when the wind was coming from the East (Figure 6). The correlation between radon and  $CH_4$  was at least 0.5 and there were overnight increases in concentrations for both gases. Using the ratio of the  $CH_4$  and radon during this time (Figure 7) the  $CH_4$  flux was calculated to be 2.46 gkm<sup>-2</sup>s<sup>-1</sup>, which would give estimated an annual London  $CH_4$  emission of 191.3 ± 34.5 ktonnes, 32 % lower than the ratio method. The 11.7 % population proportion for Greater London suggests, using national methane emissions figures for 2007, a greater London proportion of 272 kt.



## Conclusions

 CO<sub>2</sub> mixing ratios have continued to increase over the last decade. However CH<sub>4</sub> and CO mixing ratios first decline significantly and have now stabilised.

4000



Figure 6. A five-day period in October 2007 when there was a good correlation between CH<sub>4</sub> and radon and the wind was predominantly coming from London. This period was chosen to calculate London CH<sub>4</sub> emissions using the Radon Tracer method.

References: Levin et al., (1999) JGR, 104, 3447 - 3456

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y = 319x + 1648

Our results suggest that the London inventory published by the Mayor's office has underestimated methane emissions. It states that 30 ktonnes of methane are released annually, whilst our calculations have shown them to be 6 -10 times higher than this.