

First continuous measurements of CO₂ mixing ratio in central London using a compact diffusion probe

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ABSTRACT

We present one year of data from the first continuous measurements of carbon dioxide mixing ratio in central London. Measurements were made at an 87 m tower site using the new Vaisala CARBOCAP GMP343 instrument, which was found to provide a compact and inexpensive method for mixing ratio monitoring, in an environment where conventional CO₂ sensors could not be accommodated. Measurements were compared with a monitoring site outside London, showing that the city's CO₂ "dome" was an order of magnitude smaller than measured at lower levels in other cities. During the night time in the summer, the mixing ratio in central London was found to be significantly lower than at the rural site. This was thought to be explained by the proximity of biogenic sources to the rural sensor, differences between urban and rural mixing heights and/or the interception of a vertical mixing ratio gradient at two different measurement heights. Estimation of the CO₂ loading of the air entering the city therefore proved problematic during the summer. As a result, we propose that monitoring of CO₂ emission rate using this type of measurement may only be possible in the winter when the influence of these factors is minimal.

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1. Introduction

Approximately 9% of the UK's carbon dioxide emissions are thought to originate from within the Greater London area (AEA, 2006). However, to date no measurements have been made of the magnitude or variability of CO₂ mixing ratio in London, or any other UK city. In this paper we present one year of data from London's first CO₂ monitoring experiment.

CO₂ mixing ratio has been measured in several other cities around the world using conventional detectors, highlighting some important implications for air quality monitoring and vegetation in urban environments. For example, Idso et al. (1998, 2001) used transects of Phoenix,

Arizona, at 2 m to infer the presence of an urban CO₂ "dome". They find a persistent increase in concentration in the city centre, where the average mixing ratio was 43% (~100 ppmv) higher than the rural background, primarily as a result of fossil fuel combustion. A similar CO₂ dome is proposed in Rome, again based on low level (2 m) measurements (Gratani and Varone, 2005).

Seasonal concentrations have been examined in several cities, including 40 m tower measurements in suburban Melbourne, Australia (Coutts et al., 2007). The monthly mean mixing ratio was found to vary by approximately 16 ppmv throughout the year, with a peak in the winter and minimum in the summer. This was thought to be largely due to the cycle of gas space heating and photosynthetic uptake.

Diurnal mixing ratio cycles have also been investigated by several authors. For example, the diurnal cycle in CO₂ surface flux and mixing ratio found in Vancouver, averaged over 11 days in June 1993 (Reid and Steyn, 1997), was explained through the interaction of a number of processes.

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At night a stable boundary layer forms trapping carbon dioxide close to the surface. During this period, photosynthetic activity stops and vegetated surfaces show a net positive flux leading to a build-up of CO_2 until the morning. Growth of the mixed layer after sunrise results in a rapid decrease in mixing ratio early in the morning which then falls below “background” levels, due to CO_2 uptake by vegetation. After reaching a minimum in the late afternoon, the boundary layer begins to collapse and anthropogenic emission strength increases leading to a rise in concentration.

Significant variations in the magnitude of the diurnal cycle have been found in previous studies. The 11-day study in Vancouver observed a 29 ppmv cycle whilst [Grimmond et al. \(2002\)](#) measured 35 ppmv over 35 days in Chicago. A larger magnitude still was found in Basel where a mean cycle of 61 ppmv was measured above and within a street canyon during a 28 day campaign ([Vogt et al., 2006](#)).

As well as observations of CO_2 mixing ratio, flux measurements have been carried out using the eddy covariance method in a number of cities, including year-long studies in Copenhagen ([Soegaard and Moller-Jensen, 2003](#)) and Melbourne ([Coutts et al., 2007](#)) and shorter campaigns in Marseille ([Grimmond et al., 2004](#)) and Edinburgh ([Nemitz et al., 2002](#)). In each case, cities were found to be net producers of CO_2 . The seasonal cycle observed in Copenhagen showed a minimum net flux in July and a maximum, with a flux four times larger, between December and March. The flux diurnal cycle measured in Edinburgh (throughout November 2000) was approximately symmetrical with an increase throughout the morning and a gradual decline after mid-day. The average flux diurnal cycle in suburban Melbourne, however, was dominated by traffic with peaks around the morning and evening rush-hours.

Whilst these eddy covariance techniques are becoming the established method for validating CO_2 emissions inventories, there is interest in emission rate estimation using mixing ratio measurements, because instrument siting conditions are generally not as stringent. The mixing ratio footprint is also an order of magnitude larger than the flux footprint ([Schmid, 1994](#)), so smaller tower heights can be used to achieve similar surface area coverage.

In this paper, the first measurements of London's CO_2 mixing ratio diurnal and seasonal cycles are presented, analysed with the available meteorology, and compared to other studies. To address siting constraints at our 87 m tower site, a new compact diffusion probe was deployed. We present a comparison of these measurements with those made outside the city and discuss the nature of London's CO_2 “dome”. Observations of the strength of this dome are used, with a simple dispersion model, to examine the feasibility of monitoring urban CO_2 emission rate with mixing ratio measurements.

2. Measurements

Two measurement sites were used; the 87 m Queen's Tower on the Imperial College campus in South Kensington ($51^\circ 30'N$, $0^\circ 11'W$), and Royal Holloway University of London in Egham, Surrey ($51^\circ 26'N$, $0^\circ 34'W$). The Queen's

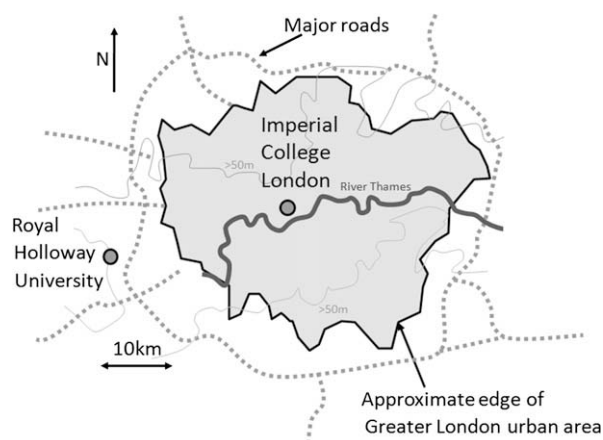


Fig. 1. Imperial College and Royal Holloway measurement sites in relation to the Greater London urban area (shaded) and major motorways (dashed lines).

Tower is located approximately 5 km to the West of the geometrical centre of London and is surrounded by buildings less than 20 m high (although the Imperial College campus contains some larger buildings, 40–50 m high). Royal Holloway is situated near the top of a small hill approximately 28 km West–South–West of Imperial College just outside the Greater London area ([Fig. 1](#)). The site is surrounded by vegetation. Measurements were made through a rooftop inlet approximately 15 m above ground, just above the building and tree canopy height, and 30–40 m above the main London basin. The site is ideally located to provide a “background” CO_2 mixing ratio for London, since the prevailing wind direction is South–Westerly.

The Queen's Tower suffers from some problems typical of a tower site in an urban area; primarily that instruments are required to fit into a relatively cramped and inaccessible environment. We therefore required a compact CO_2 sensor that could operate without large gas cylinders and needed calibrating relatively infrequently (e.g. once a month). Using the studies cited above we estimated a required accuracy of 1 ppmv (on ~hourly averages) to capture typical CO_2 variability in an urban area and a response time of around one minute or better. The Vaisala CARBOCAP GMP343 instrument was thought to provide an acceptable compromise between size, response time, accuracy and stability ([Table 1](#) outlines some key specifications). The probe was placed at a height of around 85 m on the tower, approximately 60 m higher than the average building height in the surrounding area. Measurements at Royal Holloway were made using a Li-Cor 6252 (Li-Cor Biosciences, Lincoln, Nebraska) non-dispersive infrared analyser (accurate to 0.1 ppm and daily corrected for drift).

Table 1

Vaisala CARBOCAP GMP343 key performance statistics ([Vaisala, 2005](#)).

Noise at 350 ppm	± 3 ppm
Short-term stability (up to 6 h) at 350 ppm	± 1 ppm
Long-term stability	$< \pm 2\%$ of reading year ⁻¹
Response time	75 s

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