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Controls of carbon dioxide concentrations and fluxes above central London

Carole Helfter¹, Daniela Famulari¹, Gavin J. Phillips¹, Janet F. Barlow², Curtis R. Wood², C. Susan B. Grimmond³, Eiko Nemitz¹

[1] Centre for Ecology and Hydrology (Edinburgh Research Station), Penicuik, EH26 0QB, United Kingdom

[2] Department of Meteorology, University of Reading, Reading, RG6 6BB, United Kingdom

[3] Department of Geography, King's College London, London, United Kingdom

Correspondence to: C. Helfter (caro2@ceh.ac.uk)

Abstract

Eddy-covariance measurements of carbon dioxide fluxes were taken semi-continuously between October 2006 and May 2008 at 190 m height in central London (UK) to quantify emissions and study their controls. Inner London, with a population of 8.2 million (~5000 inhabitants per km²) is heavily built up with 8% vegetation cover within the central boroughs. CO₂ emissions were found to be mainly controlled by fossil fuel combustion (e.g. traffic, commercial and domestic heating). The measurement period allowed investigation of both diurnal patterns and seasonal trends. Diurnal averages of CO₂ fluxes were found to be highly correlated to traffic. However changes in heating-related natural gas consumption and, to a lesser extent, photosynthetic activity that controlled the seasonal variability. Despite measurements being taken at ca. 22 times the mean building height, coupling with street level was adequate, especially during daytime. Night-time saw a higher occurrence of stable or neutral stratification, especially in autumn and winter, which resulted in data loss in post-processing. No significant difference was found between the annual estimate of net exchange of CO₂ for the expected measurement footprint and the values derived from the National Atmospheric Emissions Inventory (NAEI), with daytime fluxes differing by only 3%. This agreement with NAEI data also supported the use of the simple flux footprint model which was applied to the London site; this also suggests that individual roughness elements did not

significantly affect the measurements due to the large ratio of measurement height to mean building height.

1 Introduction

In recent years, monitoring of carbon dioxide (CO₂) exchange with natural and semi-natural environments has benefited from communication through international flux networks (FLUXNET and its regional components such as CarboEurope, AmeriFlux, AsiaFlux, etc.). Within some of these communities considerable effort has been made to standardise measurement techniques and data processing methods (Aubinet et al., 2000; Foken et al., 2004; Moncrieff et al., 2004). Databases with long-term micrometeorological data, heat and trace gas fluxes for sites on five continents have been set up. These span latitudes from 30 °S to 70 °N and encompass boreal, temperate and tropical forests, wetlands, crops and tundra vegetation types (Baldocchi et al., 2001). In contrast, relatively few measurements of CO₂ exchange have been performed in urban environments, where over 50% of the world's population are estimated to live (United Nations, 2007)¹, and the majority of studies were conducted in temperate areas of the Northern hemisphere, e.g. Basel, Switzerland (Vogt et al., 2006); Chicago, USA (Grimmond et al., 2002); Edinburgh, UK (Nemitz et al., 2002); Tokyo, Japan (Moriwaki and Kanda, 2004), as compiled in the database of the International Association for Urban Climate². As a consequence of this data shortage, while large anthropogenic point sources are relatively-well characterised, emissions from diffuse area sources and their variability in space and time are less-well represented in bottom-up emissions inventories. As many countries are pledging large percentage cuts in greenhouse gas emissions, the monitoring of trace gas emissions through flux measurements at the urban neighbourhood or local scale becomes an attractive and important approach to evaluating the success in reaching emission targets and to identify potential underestimated sources.

Published urban CO₂ exchange studies vary in length, from a few weeks (Velasco et al., 2005) to several months (Vesala et al., 2008) to a few years (Soegaard and Moller-Jensen, 2003; Coutts et al., 2007). Whilst a rather diverse range of urban environments (e.g. in terms of mean building height, vegetation cover) has been investigated, measurement heights were overall of the order of 2–3 times mean building height, i.e. near the minimum threshold above

¹ <http://unstats.un.org/unsd/demographic/products/dyb/dyb2.htm>

² <http://www.geog.ubc.ca/urbanflux/>

which eddy-covariance measurements can be considered to be representative of the local scale (Grimmond and Oke, 1999).

In this study, we examine the dynamics of CO₂ emissions above central London (UK) based on eddy-covariance measurements taken atop a 190 m telecommunication tower. The instruments were located at ca. 22 times the mean building height (z_H) (Wood et al., 2009; Wood et al., 2010a), i.e. ca. 4–5 times larger than the ratios reported for most urban sites in the literature, and took place between October 2006 and May 2008.

Of the different pollutants, emissions of CO₂ are probably best understood, because emissions are directly linked to fuel use, rather than combustion conditions and evaporation sources (as it is the case, e.g. for CH₄, N₂O, CO, VOCs and aerosols) (Allan et al., 2010; Langford et al., 2010). The aim of the present study was to determine the drivers of CO₂ emissions on both a diurnal and a seasonal basis and evaluate the suitability of the measurement site for the purpose of establishing robust urban budgets of CO₂ and, by extension, other pollutants. Fluxes of CO, O₃, VOCs, aerosol number and aerosol chemical species measured at the same site during two intensive observation periods (Oct 2006 and Oct/Nov 2007) are presented elsewhere (Martin et al., 2009; Langford et al., 2010; Nemitz et al., 2010; Phillips et al., 2010).

2 Methods

2.1 Measurement environment and instrumentation

Fluxes of CO₂ and H₂O were measured continuously in central London from October 2006 until May 2008 from a 190 m telecommunication tower (BT Tower; 51° 31' 17.4'' N 0° 8' 20.04'' W). Mean building height is 8.8 ± 3.0 m within 1 – 10 km of the tower and 5.6 ± 1.8 m for suburban London beyond this (Evans, 2009; Wood et al., 2010a). Three sites deviating substantially from the mean building height were identified within the 1–10 km region:

- The Regent's Park, a 197 ha green space located ca. 1 km north-west of the tower;
- Hyde Park, a 142 ha park whose north-east corner lies ca. 1.5 km south-west from the tower;
- Canary Wharf (8–10 km east-south-east of the tower), where a large number of London's tallest buildings are found (the tallest three buildings are 200, 200, 235 m). Building heights in this area range from 37 m to ca. 69 m (Evans, 2009).

The conurbation of Greater London, with 12.3 million inhabitants, extends at least 20 km into all directions.

The eddy-covariance system consisted of an ultrasonic anemometer (R3-50 Gill Instruments, Lymington, UK) operated at 20 Hz and a LI-COR 6262 infrared gas analyser (IRGA; LI-COR, Lincoln, NE, USA) fitted with an in-house auto-calibration system. Zero and CO₂ span calibration using a 404 ppm standard were scheduled to occur every 72.5 h, gradually spreading the associated loss in measurement over the full 24 h cycle. Calibration pressure, which was adjusted so as to match sampling pressure as closely as possible, was recorded along with all relevant calibration parameters (CO₂ and H₂O readings on zero, CO₂ span value) in order to correct the CO₂ and H₂O concentrations ([CO₂] and [H₂O]) during post-processing. A custom National Instruments LabView program was used to log wind and trace gas concentration data and to trigger auto-calibration events.

Air was sampled 0.3 m below the sensor head of the ultrasonic anemometer - which was itself mounted on a 3 m mast to the top of a 15 m lattice tower situated on the roof of the tower (instrument head at 190 m above street level) - and pulled down 45 m of 12.7 mm (1/2") OD Teflon tubing.

In addition, meteorological variables (temperature, relative humidity, pressure, precipitation, wind speed and direction) were also measured with a multi-sensor (Weather Transmitter WXT510, Vaisala).

The traffic-activity data used in this paper were measured at the Marylebone Road traffic census site, one of the busiest urban arteries in Europe, 1.5 km west of the BT tower; this data was compared to traffic counts from four Transport for London (TfL)³ sites located in central London (Fig. S1, Supplementary Material).

2.2 Flux calculations, quality assurance and filtering

Local fluxes (F_g) of trace gas g , calculated offline by a second custom LabView program use the core eddy-covariance equation:

$$F_g = \overline{w'\chi_g'} \quad (1)$$

³ <http://www.tfl.gov.uk/>

Equation (1) uses the covariance between the deviation from their respective means of the vertical wind velocity component (w) and of the trace gas concentration (χ_g). The 30-minute flux calculations used the time-lag corrected and despiked time series and two-dimensional co-ordinate rotation. In line with other urban flux measurement, no corrections were applied for storage and advection in relating this local flux to the surface flux.

Processed data were filtered using a three-step quality assurance algorithm whereby data were deemed of satisfactory quality if:

- a) The level of turbulence was sufficient, i.e. locally-derived friction velocity $u_* \geq 0.2 \text{ m s}^{-1}$.
- b) The stationarity test described by Foken et al. (Foken and Wichura, 1996; Foken et al., 2004), which requires the flux for the complete averaging interval (here 30 min) to be within 30 % of the fluxes calculated for the sub-intervals (6×5 minutes), was satisfied.
- c) The outcome of the integral turbulence characteristics test (ITC; Foken and Wichura, 1996; Foken et al., 2004) - which compares the turbulence statistics of wind components, temperature or trace gas concentration to that of modelled values for a given stability class - was a quality class of 3 at the very maximum (i.e. with a discrepancy of 50% or less between model and measurement).

The ITC similarity relationships were determined for w and $[\text{CO}_2]$ respectively under unstable atmospheric conditions ($-6.2 < \zeta < -0.05$) using:

$$\frac{\sigma_w}{u_*} = C_1 (1 + C_2 |\zeta|)^{C_3} \quad (2)$$

$$\frac{\sigma_{\text{CO}_2}}{\chi_*} = C_1 (1 + C_2 |\zeta|)^{C_3} \quad (3)$$

$$\chi_* = \frac{-\overline{w'[\text{CO}_2]}}{u_*} \quad (4)$$

where σ_i is the standard deviation of quantity i , u_* is the locally-derived friction velocity, C_j ($j= 1, 2, 3$) are parameters obtained by fitting to the entire dataset (cf. Section 3.2 below) and the atmospheric stability parameter (ζ) is:

$$\zeta = \frac{z_m - d}{L} \quad (5)$$

Here z_m is the measurement height (190 m), d is the zero-plane displacement length (4.3 ± 1.9 m within 10 km of the tower; (Wood et al., 2010a) and L is the locally-derived Obukhov length.

Data were rejected due to insufficient turbulence (13 %), non-stationarity (6 %) and non-fulfilment of the ITC criterion (2%). Combined with downtime of the measurement system, this left 54 % of data coverage, equating to ca. 9500 measurement points in 2007.

2.3 Comparison of emissions estimates with NAEI

The official UK National Atmospheric Emissions Inventory (NAEI)⁴ provided annual CO₂ emissions estimates for 2006 at a 1 km × 1 km spatial resolution in central London (Bush et al., 2008). The spatial inventory consisted of eleven CO₂ emission categories, including emissions from industrial / commercial electricity and gas consumption, domestic electricity and gas consumption, diesel railways, agriculture, domestic oil and fuel usage and road traffic. Emission sources and intensities for 2006 were assumed to also be valid for 2007, for which spatially disaggregated emissions were not yet available at the time this paper was written, and were consequently compared with emissions estimates obtained by eddy-covariance measurements of CO₂ fluxes taken at the BT tower. Statistics of gas provision are available at London borough level, which vary in area. To compare activity figures with the measured fluxes, the NAEI emission information was used to estimate the flux that the NAEI implies should have been measured on the tower. For this it is necessary to estimate the contribution of the various boroughs to each 30-minute flux measurements.

There are no operational footprint models for urban environments that fully account for topography and spatial variations in building height and surface heat flux. Here, as an approximation, the analytical footprint model proposed by Kormann and Meixner (2001) was applied, which accounts for non-neutral stratification but assumes homogeneous surfaces. The aerodynamic roughness length for momentum (z_0) was estimated to be 0.87 ± 0.48 m in central London (Padhra, 2009), with 1 m used in the present study. The Kormann-Meixner (KM) model - which requires z_0 , u^* , L and z_m - was used to estimate the flux footprint on a

⁴ <http://www.naei.org.uk>

half-hourly basis. A software tool coded in Microsoft Excel - described by Neftel et al. (2008) - which allows footprint contributions to user-defined spatial elements to be mapped was used to determine the individual contributions of all 32 London boroughs to the total flux measured at the BT tower. Formally, the flux $F(0, 0, z_m)$ at measurement height z_m can be expressed as (Kormann and Meixner, 2001):

$$F(0,0, z_m) = \int_{-\infty}^{\infty} \int_0^{\infty} F(x, y, 0) \phi(x, y, z_m) dx dy \quad (6)$$

Here, the x -axis is aligned with the average horizontal wind direction, y is the crosswind coordinate and $\phi(x, y, z_m)$ is the flux footprint (i.e. the flux portion originating from a point source of strength F located at $(x, y, 0)$ and observed at (x, y, z_m)). In practice, the integrals in Eq. (6) were replaced by a discrete sum due to the finite number of sources (boroughs):

$$F(0,0, z_m) = \sum_{i=1}^N F_i \phi_i \quad (7)$$

with F_i and ϕ_i the emissions and flux footprint of borough i , and N the total number of boroughs within the footprint area.

CO₂ emissions per borough (F_i) were obtained from the NAEI data (contributions from commercial and domestic electricity consumption were subtracted since the associated CO₂ emissions occur at the power plant) whilst borough contributions to the flux footprint (ϕ_i) were calculated on a half-hourly basis by the KM Excel tool. For the purpose of comparing eddy-covariance measurements with NAEI data, only half-hourly averaging intervals for which at least 99% of the flux footprint lay within the boroughs were considered here. Diurnal trends were super-imposed onto CO₂ emissions from natural gas usage and traffic, whilst other sources of CO₂ considered by the NAEI were assumed to have constant emission rates. Further details about the methodology are provided in Section 2.2 of the Supplementary Material.

2.4 Estimation of CO₂ uptake by photosynthetic activity

Net ecosystem exchange (NEE) was estimated from tree productivity and grassland light-response data with a view to evaluate the fluxes obtained by eddy-covariance. According to a report released by the Mayor of London in March 2005 (Mayor of London, 2005), 95% of trees in central London are broadleaved species ranging from 25 to 300 years in age. Within the tower footprint, average tree densities are of the order of 30 to 40 trees ha⁻¹, with most

trees considered to be isolated rather than part of stands. For the estimation of the magnitude of atmospheric CO₂ uptake by trees (all boroughs), net assimilation was assumed to be independent of age and species; as an approximation, a benchmark value of 6 kg C tree⁻¹ y⁻¹ (growing season), reported for a dominant beech specimen, was used (Lebaube et al., 2000). Net assimilation due to grassy areas (borough of Westminster only as grass coverage for the entire footprint area was approximated to the surface areas of Hyde Park and the Regent's Park, both located in Westminster) was estimated from light and temperature response curves parameterised on the productivity of a managed grassland, dominated by *Lolium perenne* (ryegrass), near Edinburgh (UK, 55° 51.323' N, 3° 11.705' W; data obtained from the Centre for Ecology and Hydrology, Edinburgh station).

3 Results and discussion

3.1 Local atmospheric stability and footprint analysis

For the year (01/01/2007 to 31/12/2007), 54 % of half-hourly averages of all observed and calculated quantities were available. This period was divided into four seasons (Table 1). In spring and autumn, the < 50 % data availability was largely due to prolonged technical difficulties rather than a surge in filtering.

Dominant south-westerly winds accounted for 46 % of the annual and over 60 % in both winter and summer time periods. The North-West quadrant had the second largest frequency in spring and autumn. The footprint is sensitive to atmospheric stability. As expected, unstable periods were longer and more frequent in spring and summer due to thermal mixing (Fig. 1). Unstable conditions occurred frequently during night-time and in winter when the average sensible heat flux was positive. Stable conditions were most common in autumn, presumably when the net radiative and anthropogenic heat fluxes were at their minimum. On individual days in autumn and winter the sensible heat fluxes remained negative. However simultaneous sensible heat flux measurements at a rooftop site at the Westminster Council building, 2.1 km west of the BT tower, observed $\zeta > 0.1$ for only 3% of the half-hour periods and the sensible heat fluxes were found to be almost always positive (Wood, et al. 2010b).

The footprint of the two sites is obviously different and the BT tower measurement will be more affected by the urban parks, but the observation of stable stratification at the tower height also points to the presence of an inversion layer, during which the tower height is

above the layer connected to the urban surface below, consistent with investigation of the vertical boundary layer structure during the REPARTEE-II campaign (Barlow et al., 2010). In these conditions, the use of the measured stability may still underestimate the footprint. Nevertheless, using the local stability on the BT tower, the KM footprint model predicts that the distance from the BT tower contributing the maximum to the measured trace gas flux (x_{\max}) peaked at 1600 m and 3000 m under unstable and stable atmospheric stratification, respectively (Fig. 2). Under unstable atmospheric stratification ($-6 < \zeta < -0.05$), sources contributing to CO₂ fluxes measured atop the BT tower were contained within ca. 2 to 22 km radius circles (based on 90% of the total flux), centred on the BT tower.

The boroughs contributing the most to the flux measured at the BT tower were located in the south-west quadrant (Fig. 3). The central borough of Westminster, which stretches ca. 3 - 4 km from the tower mainly in the south-west quadrant, contributed 65.1% averaged over the whole year with a maximum of 82.8% reached in summer (daytime values – 09:00 – 18:00). This is consistent with increased occurrences of unstable atmospheric conditions during the warmer summer months and the associated contraction of the flux footprint.

3.2 Surface and turbulence characteristics

Building heights, and consequently roughness length, exhibit a heterogeneous distribution in the circular central area stretching approximately 5 km from the tower (Evans, 2009). Beyond this circle, building heights become more homogeneous towards residential areas. Stability and hence flux footprint exhibited seasonal variations in 2007 (Table 1); turbulence characteristics based on relationships between normalised wind and [CO₂] standard deviations and stability parameter (ζ) – Eqs. (2) and (3) – were evaluated. They presented some seasonal variability (Figs. 4a and b) which was not deemed to be statistically significant due to the relatively large spread across all datasets.

Coefficients of $\frac{\sigma_w}{u_*}$ for 2007 were comparable with those derived by Wood et al. (2010a) for the 2007/08 data measured at the tower and C_1 values were also in agreement with those reported by Vesala for a Helsinki site (Vesala et al., 2008). Values for parameter C_1 have been reported to decrease with increasing surface roughness (Roth and Oke, 1995; Vesala et al., 2008). In 2007, the C_1 coefficient was largest in winter, followed by autumn, spring and summer; this is consistent with seasonal changes in mean atmospheric stability (Table 1) as larger flux footprints in autumn and winter probably entrain residential and peripheral areas

with more homogeneous roughness values than in central London. Values of C_2 in London were found to be significantly lower than in Helsinki for both σ_w/u_* and σ_{CO_2}/χ_* (Table 3).

Furthermore, the best-fit lines for both σ_w/u_* and σ_{CO_2}/χ_* lie below the parameterisations for the urban and vegetation land-use types at the Helsinki site and exhibit a weaker dependence on stability. Wood et al. (2010a) also noted that the parameterisations of the normalised standard deviations of the wind velocity components resembled more those found in the rural surface layer than above cities, which could be an effect of the high measurement height.

3.3 Concentrations

Carbon dioxide concentrations measured at the BT tower were in the range 370 ppm to 397 ppm for the period October 2006 to December 2007, with peak values in February and minimum values in July and August (Fig. 5). This is consistent with the effect of the annual photosynthetic uptake of vegetation, which provides a net sink for CO_2 in summer and a net source in winter (Hall et al., 1975; Keeling et al., 1996; Buermann et al., 2007).

The BT tower data were compared to a second tall tower site (87 m) at the Imperial College of London (Rigby et al., 2008), located ca. 3.5 km south-west of the BT tower along the dominant wind direction (Fig. S1, Supplementary Material). The CO_2 concentrations exhibited a similar trend, with a near-constant offset of 11.5 ppm, except for the peak in November 2006, which was observed solely at the Imperial College tower. For this month the difference in the mean monthly values is 23.5 ppm. Although a common calibration was not conducted, the increased concentration at the lower level is consistent with the expected concentration gradient above a city. Furthermore, the Imperial College tower measurements could have been more influenced by nearby micro/local-scale sources. Since vertical mixing is likely to be more efficient during summer, the gradient would be expected to show an annual cycle, being largest in winter. However, this was not reflected in the measurements. Possibly, the rooftop measurement at the Imperial College site was already made above the stable boundary layer during winter inversion conditions.

The common peak concentration in February 2007 coincided with the coldest month of the 2006/07 winter, which is consistent with inverse correlation to mean air temperatures. This suggests that commercial, industrial and residential fossil fuel consumption for heating purposes contribute to the seasonal trend of CO_2 emissions. The magnitude of this

contribution could not be separated from the natural photosynthetic/respiration cycle. Road transport emissions, which amounted to 12 % of the annual emissions estimates for the borough of Westminster in 2006 and 23 % for all boroughs (NAEI, 2009), were fairly constant from February to July 2007 (Fig. 5). Traffic volume measured on Marylebone Road decreased by ca. 6 % in December 2006, August - September 2007 and December 2007, compared with all other months, but this was not unequivocally linked to changes in CO₂ concentrations measured at the BT tower. Marked drops in traffic loads (Table 2) were recorded between June and October at three out of four Transport for London (TfL) monitoring sites (Fig. S1, Supplementary Material). Whilst these sites are located in the boroughs contributing the most to the flux footprint measured at the tower (Westminster, Camden and Kensington & Chelsea), [CO₂] did not reflect these changes in traffic loads. This could suggest that traffic contributed to the baseline or background CO₂ concentration rather than dominating its seasonal fluctuations. Furthermore, traffic loads at the four TfL sites used in this study were strongly correlated with traffic counts observed at Marylebone Road. ($R^2 \sim 0.8 - 0.9$; data not shown) which supports the use of the latter site as a proxy representative of central London.

The range of CO₂ concentrations observed is comparable with data in the literature for other urban areas, although no other measurements have been taken at similarly large a z_m/z_H ratio ($z_m/z_H \approx 22$, compared to buildings within 1 – 10 km from the BT tower site; Wood et al., 2010a).

Diurnal courses of [CO₂] are affected by temporal changes in boundary layer height, anthropogenic emissions, biosphere exchange and vertical mixing. The measurements have distinct hourly and diurnal spatial patterns (Fig. 6a-b). Increased concentrations were observed in the north-east and south-east quadrants in the latter part of the evening (20:00 – 00:00) (Fig. 6a) as well as during the night (00:00 – 08:00) in the north-east and north-west quadrants. These concentration build-ups are consistent with a reduction in mixing due to night-time boundary layer shrinkage. The build-up in the north-west quadrant was accompanied by a marked daytime reduction in concentrations (~ 10:00 – 16:00). Because this wind sector has a large fractional vegetation cover, especially in the daytime footprint due to The Regent's Park, the diurnal pattern for north-westerly wind was very likely more affected by diurnal plant assimilation/ respiration cycles. Overall, daytime concentrations were less than at night-time, consistent with fluctuations in boundary layer height. Analysis of mean concentrations as a bi-variate function of wind speed and direction (Fig. 6c) shows

that the largest concentrations were observed north and north-east of the tower especially at high wind speed ($\geq \sim 10 \text{ m s}^{-1}$).

CO₂ fluxes (which are not influenced by background concentrations and less affected by boundary layer dynamics) exhibit a spatial variation by direction: in 2007, they were largest in the south-east quadrant where they ranged from $\sim 20 - 60 \mu\text{mol m}^{-2} \text{ s}^{-1}$ whilst fluxes in the three other quadrants were in the $0 - 40 \mu\text{mol m}^{-2} \text{ s}^{-1}$ range. This suggests that rises in CO₂ concentrations in the north-east quadrant could have been caused by horizontal transport (north-east winds in London are often associated with cyclonic transport of polluted European continental air masses) and reduced vertical mixing. Averages for north and north-east conditions may further be affected by the relative small number of observations under these conditions (Fig. 6g). This is also true for the south-east quadrant which had the lowest wind occurrence but the highest CO₂ fluxes.

In winter and autumn a gradual decrease in concentrations occurs from ca. 10:00 until a minimum at mid-afternoon (ca. 14:00 - 15:00) (not shown). Concentrations increase from this point until ca. 17:00 - 18:00 after which they remain relatively constant throughout the night. These diurnal patterns are consistent with those observed in Edinburgh (Nemitz et al., 2002), Tokyo (Moriwaki and Kanda, 2004) and Basel (Vogt et al., 2006). In contrast, spring and summer concentrations have local minima at around 12 noon and 16:00, and local maxima around 14:00. Summer time concentrations were generally lower than any other season, whilst spring time values were the highest, especially at night time.

On a diurnal basis, CO₂ concentrations appear not to be correlated with traffic density with the minimum [CO₂] associated with afternoon peak traffic counts and whilst [CO₂] increased during the night when traffic counts were at their minimum. This is consistent with the observations made by Rigby et al. (2008) and can be explained by the overriding effect of the growth of the mixed layer and entrainment of air less concentrated in CO₂ from above during the day (Reid and Steyn, 1997). Fluctuations in CO₂ concentrations on the BT tower were thus driven by dilution rather than changes in local sources strength. The local turbulent sensible heat fluxes and stability (Fig. 1) indicate that throughout the year the noon to 17:00 period was dominated by unstable stratification.

3.4 Fluxes

3.4.1 Flux losses due to high-pass filtering

Comparison of 30-minute fluxes with calculations based on 2-hour averaging showed that losses due to high-pass filtering were < 5% irrespective of time of day and season (Fig. S4, Supplementary Material).

In contrast, for 25-minute averaging times, Langford et al. (2010) derived flux losses of 5.8% and 8% for H_{3-30} (1.5 h block-averaged sensible heat fluxes compared to averaging over 25-minute averages within three consecutive half-hourly periods) and H_{4-30} , respectively, for measurements taken during October 2006 at the BT tower site (day and night regimes were not segregated from one another). Those results suggested a moderate flux loss using the shorter averaging periods due to failure to capture low-frequency components.

Given that the flux loss of 30-min periods was < 5% and that shorter averaging times (a) are less likely to be affected by non-stationarities and (b) provide more information on variability and processes, an averaging time of 30 min was selected.

3.4.2 Traffic and seasonal controls

Unlike CO₂ concentrations, the fluxes of CO₂ (F_c) are correlated with Marylebone Road traffic counts throughout the year (Fig. 7). The data in Fig. 7 are the observed fluxes so include the net exchange from all the sources and sinks, and the diurnal variability. On average, F_c ranged between ca. 7 and 47 $\mu\text{mol m}^{-2} \text{s}^{-1}$ although excursions towards much larger values (maximum 167 $\mu\text{mol m}^{-2} \text{s}^{-1}$) were sometimes observed (Fig. 8a). From fitting a first order exponential function, background emissions (i.e. intercepts for zero traffic counts) were estimated. They ranged from 4 to 7 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and correspond to an emission of 33400 t CO₂ km⁻² y⁻¹ from non-traffic-based activities. This is 11% higher than the 2006 NAEI value of 29919 t CO₂ km⁻² y⁻¹ for non-traffic emissions, but unlike the NAEI also includes the biospheric signal, which at night-time (when traffic volume is lowest) reflects emission from net respiration.

Possible reasons for the non-linearity in the traffic dependence of the flux include: (a) other activities scale non-linearly with traffic, (b) fuel consumption increases at high traffic volumes, (c) the Marylebone Road traffic counts underestimate the full dynamic range of the

average traffic activity in the flux footprint due to saturation at high traffic volumes, and (d) changing meteorology (e.g. boundary layer height) with season at rush hours. Similar explanations are needed to explain the difference between weekday and weekend, in averaged diurnal cycles in Marylebone Road traffic volume and measured CO₂ flux (Fig. 9). Although measured traffic counts are virtually identical at midday (difference of 1.7%), measured fluxes were $\sim 29.2 \pm 6.7 \mu\text{mol m}^{-2} \text{s}^{-1}$ at weekends compared with $38.0 \pm 8.0 \mu\text{mol m}^{-2} \text{s}^{-1}$ on weekdays (23% discrepancy). The weekday / weekend comparison also suggests that traffic volumes may not dominate the flux at night time. Measured fluxes were very similar despite considerable difference in the traffic patterns: traffic was $\sim 35\%$ heavier between midnight and 04:00 at the weekends and reached a minimum at around 05:00 (possibly coinciding with night-club closing time and the resuming of public transport services). Traffic increased steadily - and almost linearly - thereafter before reaching an almost constant value from $\sim 13:00$ until 19:00. Weekday traffic volumes were on average 15% higher between 05:00 and 13:00 and grew more rapidly from 05:00 until 08:00. However, weekday and weekend CO₂ fluxes were almost identical in magnitude and trend between midnight and 08:00 which suggests that the net CO₂ flux is dominated by other (non-traffic) sources or that night time weekend Marylebone Road traffic loads are not representative of other areas within the flux footprint. Traffic and CO₂ flux trends were however well correlated from midday onwards.

Although fluxes remained positive, daytime values did decrease in the summer (8 to 35 $\mu\text{mol m}^{-2} \text{s}^{-1}$); this was accompanied by an increase in latent heat fluxes (LE) (Fig. 8c). The mean decrease in F_c observed during the summer months is equivalent to 567 t CO₂ km⁻² month⁻¹ compared with winter (winter and summer data were used so as to compare periods of vegetative dormancy with the fully-developed growing season) which is 13% larger than the summer to winter deficit obtained from the cumulative contributions of $F_{c\text{-gas}}$, human CO₂ emissions and biosphere exchange in Sections 2.5 and 2.6. In contrast, seasonal fluctuations in traffic observed at Marylebone Road and TfL sites 20, 35 and 48 were negligible (e.g. 0.02% smaller in winter than in summer at Marylebone Road), whilst traffic counts were on average 10% fewer in summer than in winter at TfL 21, which is located within the dominant wind sector. Furthermore, the marked drops in traffic counts observed at TfL 20, 21 and 35 (traffic counts at TfL 48 and Marylebone Road remained approximately constant) between June and October (Table 2) were not accompanied by a decrease in flux values. On the contrary, these were found to increase to levels comparable to winter and spring time. This

illustrates the spatial heterogeneity of traffic volumes within the flux footprint (and the difficulty to identify a robust proxy site) and suggests that seasonal emissions trends are largely driven by the demand for natural gas and, to a lesser extent, by changes in biospheric exchange. CO₂ fluxes exhibited clear diurnal trends (Fig. 6d) with maximum values observed in all quadrants between ca. 08:00 and 20:00. Unlike concentrations which peaked in the north-east quadrant, which covers a busy commercial area, the largest fluxes (~ 20 – 60 μmol m⁻² s⁻¹) were found in the south-east quadrant independent of day of the week and wind speed (Fig. 6e-f). The south-east quadrant had the lowest wind occurrence in 2007 (ca. 5%; Fig. 6f) and made consequently a small contribution to the total flux measured at the tower (Fig. 3) despite the seemingly strong sources located in that quadrant.

The north-west quadrant exhibited the lowest fluxes ranging between ~ -10 and + 20 μmol m⁻² s⁻¹ and their diurnal cycles were in phase with those of the concentrations. Fluxes were positive and reached their maxima between ~ 08:00 and 16:00 (coinciding with peak concentrations), which could be explained by photosynthetic activity in The Regent's Park area (1 - 2 km NW of the BT Tower). Wind occurrence from the north-west quadrant was however relatively low and observations extreme could have affected flux and concentration averages.

Peak fluxes (~ 50 – 70 μmol m⁻² s⁻¹) in the dominant south-west wind sector occurred at relatively low wind speed (< 7-8 m s⁻¹; Fig. 6f) and can probably be attributed to emissions from highly-populated inner boroughs with high traffic loads such as Westminster which, according to the KM footprint, contributed 65.1 ± 11.9% to the flux measured atop the tower over the whole year (Westminster ~ 8000 inhabitants km⁻² (Office for National Statistics)⁵, 433150 tons CO₂ from traffic emissions in 2006 (NAEI)).

Annual average daytime (09:00 – 18:00) CO₂ emissions rates from London boroughs measured by eddy-covariance at the telecom tower (4242 ± 609 tons CO₂ km⁻² month⁻¹) were 3% smaller than the bottom-up BT Tower Flux estimated from the 2006 NAEI (4377 ± 345 tons CO₂ km⁻² month⁻¹). The NAEI derived flux includes neither biosphere exchange nor human exhalation, which would have contributed to the flux measurement. It is estimated, however, that these two fluxes are small, similar in magnitude and approximately cancel each other out. In contrast, annual averages obtained from all available data (no restriction to the daytime period 09:00 – 18:00) yield emissions rates of 4194 ± 612 tons CO₂ km⁻² month⁻¹ and

⁵ <http://www.statistics.gov.uk>

4650 ± 254 tons CO₂ km⁻² month⁻¹ for eddy-covariance and NAEI, respectively (NAEI exceeds the eddy-covariance by ca. 11%). This might indicate an underestimation of the eddy-covariance approach over stable night time periods when the tower becomes either decoupled from the surface or entrainment from peripheral/ rural areas occurs. However, bottom-up inventory and top-down eddy-covariance figures for CO₂ emissions are statistically similar (based on standard deviations of the means) and it can therefore be concluded that the BT tower was an adequate location for monitoring trace gas fluxes in central London and that the KM footprint model provided a reasonable approximation for that site, especially during daytime. This is in line with the observations made by Wood et al. (2010a) that locally-normalised turbulence at high levels above central London is similar to that above rural terrain. This suggests that the measurements are representative of the urban morphology surrounding the site and that advection errors were limited.

Measured winter time emissions of CO₂ in central London were estimated to have been dominated by natural gas emissions (71.1%) whilst traffic and other fossil fuel burning contributed 22.9% (Table 5). Emissions from natural gas combustion reached their lowest point in autumn (47.8%), with traffic emissions amounting to ca. 48.9%. These figures reflect not only the seasonal variations of source strengths but crucially also of the position of the footprint. The latter was dominated throughout 2007 by emissions from the City of Westminster (up to 82% of daytime summer fluxes measured at the tower were attributed to that borough) which is a densely populated but also greener than average borough. The net impact of vegetation during the 2007 growing season was ca. 174 t CO₂ km⁻² month⁻¹ for the borough of Westminster (Table S1, Supplementary Material) where green space accounts for ca. 15% of the plan area (compared to 8% for London taken as a whole). Data records of first and last annual lawn cuts in central England from 2000 to 2004 were used to define the growing season (mid-March and late October) (Sparks et al., 2005). Assuming leaf-on was complete from early May to mid-September for the species within the tower footprint, the vegetative growth in the borough of Westminster assimilates ~ 4330 t CO₂ or 0.4% of the annual emissions of carbon dioxide (based on the 2006 NAEI CO₂ emissions figure).

For comparison, Nemitz et al. (2002) estimated that gas combustion accounted for 52% and other fossil fuel combustion sources (dominated by traffic) accounted for 41% of autumn conditions in central Edinburgh, while the London autumn values of 47.8% and 48.9%, respectively, reveal a smaller contribution from gas combustion. Annual emissions in central London were comparable to the 10 kt C km⁻² y⁻¹ reported for Edinburgh, but were nearly

three times larger than for measurement sites in Tokyo, Mexico City and Copenhagen, and roughly four times higher than in Melbourne (Table 6). This reflects the fact that measurements in London and Edinburgh were conducted above the city centre, rather than residential areas. Annual emissions in London, Mexico City, Tokyo and Melbourne exhibit a correlation with vegetation cover (Fig. 10) but not with population density. Whilst industrial, commercial and domestic fossil fuel usage (e.g. traffic, heating) are the main sources of urban CO₂ and are likely to vary between sites due to, e.g., climate, vehicle fleet or land use, Fig. 10 illustrates the combined impact of plant assimilation on urban CO₂ emissions.

4 Conclusions

The close agreement between measured fluxes and bottom-up emission inventory estimates (within 3% during daytime) suggests that the 190 m tall BT Tower in central London was a suitable measurement site for characterising average emissions during daytime, while some care needs to be taken to interpret night-time fluxes. This would imply that long-term flux measurements can be used to track changes in emissions, and to quantify emissions of pollutants for which urban area sources are more poorly understood and more variable than those of CO₂. Measurements for a year reveal that the seasonal dynamics of atmospheric carbon dioxide concentrations are strongly linked to the natural background vegetation cycle. Seasonal variations in natural gas consumption (e.g. commercial and domestic heating, referred to as background emissions) and their diurnal trends were regulated by dilution, consistent with cycles of growth and shrinkage of the boundary layer. In contrast, diurnal fluxes of CO₂ are strongly correlated with traffic counts but also reflect seasonal variations in heating-related emissions and vegetative assimilation through photosynthesis during the growing season. Whilst the urban environment of central London was a net source of CO₂ in 2007, summer net emissions were 20% lower than their wintertime counterparts due to the combined effects of a reduction in heating emissions and uptake by photosynthesising plants. Natural gas demand was found to dominate emissions (ca. 71%) in winter, whilst a more balanced partitioning, comparable to values reported for Edinburgh by Nemitz et al. (2002), was observed in autumn: 47.8% of autumn CO₂ emissions were attributed to natural gas burning, compared to 48.9% for traffic. Gross plant assimilation in the central London borough of Westminster - where green spaces account for ca. 15% of borough surface area compared to ca. 8% elsewhere - was estimated at 4330 t CO₂ y⁻¹, which represents only 0.4% of the total annual emissions. Grass was estimated to make the largest contribution to net

assimilation, with trees being responsible for a mere 5%. These results suggest that the total surface area allocated to green spaces would have to be increased by a factor of 250 in order to neutralise anthropogenic emissions of carbon dioxide in central London. Considering how heavily-urbanised the studied area was in 2007, it seems likely that central London will remain a strong source of CO₂ in the foreseeable future. It is recommended that future flux measurements at such high measurement heights should be accompanied with concentration gradient measurements to reduce remaining uncertainties due to storage effects.

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References

- Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, *Atmos. Chem. Phys.*, 10, 647-668, 2010.
- Aubinet, M., Grelle, A., Ibrom, A., Rannik, U., Moncrieff, J., Foken, T., Kowalski, A. S., Martin, P. H., Berbigier, P., Bernhofer, C., Clement, R., Elbers, J., Granier, A., Grunwald, T., Morgenstern, K., Pilegaard, K., Rebmann, C., Snijders, W., Valentini, R., and Vesala, T.: Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology, *Adv. Ecol. Res.*, Vol 30, 30, 113-175, 2000.
- Baldocchi, D., Falge, E., Gu, L. H., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., Evans, R., Fuentes, J., Goldstein, A., Katul, G., Law, B., Lee, X. H., Malhi, Y., Meyers, T., Munger, W., Oechel, W., U, K. T. P., Pilegaard, K., Schmid, H. P., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S.: FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities, *B. Am. Meteorol. Soc.*, 82, 2415-2434, 2001.
- Barlow J.F., Dunbar T.M., Nemitz E.G., Wood C.R., Gallagher I.M., Davies F., O' Connor E., and Harrison R.M.: Boundary layer dynamics over London, UK as observed using Doppler lidar. Submitted to *Atmos. Chem. Phys.*, 2010.
- Buermann, W., Lintner, B. R., Koven, C. D., Angert, A., Pinzon, J. E., Tucker, C. J., and Fung, I. Y.: The changing carbon cycle at Mauna Loa Observatory, *P. Natl. Acad. Sci. USA*, 104, 4249-4254, 2007.
- Bush, T., Tsagatakis, I., King, K., and Passant, N.: NAEI UK Emission Mapping Methodology 2006, AEAT/ENV/R/2696, 2008.
- Carslaw, D., and Ropkins, K.: openair: Open-source tools for the analysis of air pollution data. R package version 0.2-5/r68. <http://R-Forge.R-project.org/projects/openair/>, 2010.
- Coutts, A. M., Beringer, J., and Tapper, N. J.: Characteristics influencing the variability of urban CO₂ fluxes in Melbourne, Australia, *Atmos. Environ.*, 41, 51-62, 2007.
- Evans, S.: 3D cities and numerical weather prediction models: An overview of the methods used in the LUCID project (<http://eprints.ucl.ac.uk/17404/1/17404.pdf>), UCL, London, 2009.

Foken, T., and Wichura, B.: Tools for quality assessment of surface-based flux measurements, *Agr. Forest Meteorol.*, 78, 83-105, 1996.

Foken, T., Gödecke, M., Mauder, M., Mahrt, L., Amiro, B., and Munger, W.: Post-field data quality control, in: *Handbook of micrometeorology*, edited by: Lee, X., Kluwer Academic Publishers, 2004.

Grimmond, C. S. B., and Oke, T. R.: Aerodynamic properties of urban areas derived, from analysis of surface form, *J. Appl. Meteorol.*, 38, 1262-1292, 1999.

Grimmond, C. S. B., King, T. S., Cropley, F. D., Nowak, D. J., and Souch, C.: Local-scale fluxes of carbon dioxide in urban environments: methodological challenges and results from Chicago, *Environ. Pollut.*, 116, S243 - S254, 2002.

Grimmond, C. S. B., Salmond, J. A., Oke, T. R., Offerle, B., and Lemonsu, A.: Flux and turbulence measurements at a densely built-up site in Marseille: Heat, mass (water and carbon dioxide), and momentum, *J. Geophys. Res.-Atmos.*, 109, D24101, 2004.

Hall, C. A. S., Ekdahl, C. A., and Wartenberg, D. E.: 15-year record of biotic metabolism in northern-hemisphere, *Nature*, 255, 136-138, 1975.

Keeling, C. D., Chin, J. F. S., and Whorf, T. P.: Increased activity of northern vegetation inferred from atmospheric CO₂ measurements, *Nature*, 382, 146-149, 1996.

Kormann, R., and Meixner, F. X.: An analytical footprint model for non-neutral stratification, *Bound.-Lay. Meteorol.*, 99, 207-224, 2001.

Langford, B., Davison, B., Nemitz, E., and Hewitt, C. N.: Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK), *Atmos. Chem. Phys.*, 9, 1971-1987, 2009.

Langford, B., Nemitz, E., House, E., Phillips, G. J., Famulari, D., Davison, B., Hopkins, J. R., Lewis, A. C., and Hewitt, C. N.: Fluxes and concentrations of volatile organic compounds above central London, UK, *Atmos. Chem. Phys.*, 10, 627-645, 2010.

Lebaube, S., Le Goff, N., Ottorini, J. M., and Granier, A.: Carbon balance and tree growth in a *Fagus sylvatica* stand, *Ann. For. Sci.*, 57, 49-61, 2000.

Martin, C. L., Longley, I. D., Dorsey, J. R., Thomas, R. M., Gallagher, M. W., and Nemitz, E.: Ultrafine particle fluxes above four major European cities, *Atmos. Environ.*, 43, 4714 - 4721, 2009.

- Mayor of London: Connecting Londoners with trees and woodlands, http://www.london.gov.uk/mayor/environment/forest/docs/ltwf_full.pdf, 2005.
- Moncrieff, J., Clement, R., Finnigan, J., and Meyers, T.: Averaging, detrending and filtering of eddy covariance time series, in: Handbook of Micrometeorology, edited by: Lee, X., Kluwer Academic Publishers, 2004.
- Moriwaki, R., and Kanda, M.: Seasonal and diurnal fluxes of radiation, heat, water vapor, and carbon dioxide over a suburban area, *J. Appl. Meteorol.*, 43, 1700-1710, 2004.
- Neftel, A., Spirig, C., and Ammann, C.: Application and test of a simple tool for operational footprint evaluations, *Environ. Pollut.*, 152, 644-652, 2008.
- Nemitz, E., Hargreaves, K. J., McDonald, A. G., Dorsey, J. R., and Fowler, D.: Meteorological measurements of the urban heat budget and CO₂ emissions on a city scale, *Environ. Sci. Technol.*, 36, 3139-3146, 2002.
- Nemitz, E., Phillips, G. J., Di Marco, C. F., Allan, J. D., Barlow, J. F., Coe, H., Thorpe, A., Dall'Osto, M., Harrison, R. M., and Williams, P. I.: Concentrations, gradients and fluxes of inorganic reactive gases and aerosol components above London Atmospheric Chemistry and Physics Discussion, In preparation, 2010.
- Padhra, A.: Estimating the sensitivity of urban surface drag to building morphology. PhD, University of Reading, Reading, 2009.
- Phillips, G. J., Thomas, R., Famulari, D., Williams, P. I., Crosier, J., Allan, J. D., Coe, H., Gallagher, M., Flynn, M., and Nemitz, E.: Fluxes of submicron aerosol components above three UK cities, Atmospheric Chemistry and Physics Discussion, In preparation, 2010.
- R Development Core Team: R: A language and environment for statistical computing. <http://www.R-project.org>, 2009.
- Reid, K. H., and Steyn, D. G.: Diurnal variations of boundary-layer carbon dioxide in a coastal city - Observations and comparison with model results, *Atmos. Environ.*, 31, 3101-3114, 1997.
- Rigby, M., Toumi, R., Fisher, R., Lowry, D., and Nisbet, E. G.: First continuous measurements of CO₂ mixing ratio in central London using a compact diffusion probe, *Atmos. Environ.*, 42, 8943-8953, 2008.

- Roth, M., and Oke, T. R.: Relative efficiencies of turbulent transfer of heat, mass, and momentum over a patchy urban surface, *J. Atmos. Sci.*, 52, 1863-1874, 1995.
- Soegaard, H., and Moller-Jensen, L.: Towards a spatial CO₂ budget of a metropolitan region based on textural image classification and flux measurements, *Remote Sens. Environ.*, 87, 283-294, 2003.
- Sparks, T. H., Croxton, P. J., Collinson, N., and Grisenthwaite, D. A.: The grass is greener (for longer), *Weather*, 60, 121-125, 2005.
- Tans, P., NOAA/ ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/), 2009.
- Velasco, E., Pressley, S., Allwine, E., Westberg, H., and Lamb, B.: Measurements of CO₂ fluxes from the Mexico City urban landscape, *Atmos. Environ.*, 39, 7433-7446, 2005.
- Vesala, T., Jarvi, L., Launiainen, S., Sogachev, A., Rannik, U., Mammarella, I., Siivola, E., Keronen, P., Rinne, J., Riikonen, A., and Nikinmaa, E.: Surface-atmosphere interactions over complex urban terrain in Helsinki, Finland, *Tellus B*, 60, 188-199, 2008.
- Vogt, R., Christen, A., Rotach, M. W., Roth, M., and Satyanarayana, A. N. V.: Temporal dynamics of CO₂ fluxes and profiles over a central European city, *Theor. Appl. Climatol.*, 84, 117-126, 2006.
- Wood, C.R., Arnold, S.J., Balogun, A.A., Barlow, J.F., Belcher, S.E., Britter, R.E., Cheng, H., Dobre, A., Lingard, J.J.N., Martin, D., Neophytou, M., Petersson, F.K., Robins, A.G., Shallcross, D.E., Smalley, R.J., Tate, J.E., Tomlin, A.S., and White, I.R.: Dispersion experiments in central London: the 2007 DAPPLE project. *Bull. Am. Meteorol. Soc.* 90:955–969, 2009.
- Wood, C.R., Lacser, A., Barlow, J., Padhra, A., Belcher, S., Nemitz, E., Helfter, C., Famulari, D., and Grimmond, C.S.B.: Turbulent flow at 190 metres above London during 2006-2008: a climatology and the applicability of similarity theory. *Bound.-Lay. Meteorol.*, 2010a. Doi: 10.1007/s10546-010-9516-x
- Wood, C.R., Barlow, J.F., Belcher, S.E., and Bohnenstengel, S.I.L.D.: Decoupled stable air above London, UK. American Meteorological Society, Ninth Symposium on the Urban Environment, Keystone, CO, USA. August 2010b.

Table 1: Median seasonal daytime (9:00 – 18:00) stability and fetch parameters x_{\max} (distance from the measurement point contributing the most to the observed flux) and x_{90} (distance from the measurement point where 90% of the cumulative flux is realised). x_{\max} and x_{90} were obtained from the Kormann-Meixner model for each 30 min stability value.

	Definition	Data coverage [%]	Daytime stability	x_{\max} [km]	x_{90} [km]
Winter	December - February	63	-0.2	1.7	13.9
Spring	March - May	42	-0.4	1.3	10
Summer	June - August	72	-0.8	1	6.9
Autumn	September - November	41	-0.2	1.7	13.9

Table 2: Average daily traffic counts at Marylebone road and four Transport for London (TfL, with permission) sites in March, June and October 2007.

Unit: number of vehicles	March	June	October
Marylebone Road	76955	76201	76465
TfL 20 (Camden)	49384	50141	18357
TfL 21 (Kensington & Chelsea)	57815	52564	29497
TfL 35 (Westminster)	29809	30721	15367
TfL 48 (Camden)	14438	14422	14248

Table 3: Coefficients for normalised standard deviation of vertical wind velocity and CO₂ concentration (Eq. 2 and 3) by seasons (2007, this study), 2007/08 (Wood et al., 2010a) and for two land-use classes (urban and vegetation) observed in a study in Helsinki, Finland (Vesala et al., 2008).

	σ	C_1	C_2	C_3
Winter 2007	w	1.36	0.28	1/3
	CO ₂	2.02	0.30	-1/3
Spring 2007	w	1.31	0.44	1/3
	CO ₂	2.12	0.54	-1/3
Summer 2007	w	1.24	0.66	1/3
	CO ₂	2.00	0.66	-1/3
Autumn 2007	w	1.33	0.38	1/3
	CO ₂	2.00	0.22	-1/3
London (2007/08)	w	1.31	0.65	1/3
Urban (Helsinki)	w	1.11	6.18	1/3
	CO ₂	5.36	0.06	-1/3
Vegetation (Helsinki)	w	1.42	1.68	1/3
	CO ₂	4.65	1.01	-1/3

Table 4: Recent measurements of CO₂ concentrations ([CO₂]) and fluxes (F_C) in different urban sites (CC- city centre, SR –suburban/residential, IN - institutional). To aid inter-annual comparison, [CO₂] were normalised by their concurrent background levels measured at the Mauna Loa observatory (Tans, 2009).

City	Year	Season	Site type	Height [m]	Normalised [CO ₂] range	F _C range [μmol m ⁻² s ⁻¹]
Basel (Vogt et al., 2006)	2002	Summer	CC	29	0.97-1.13	3 to 15
Chicago (Grimmond et al., 2000)	1992	Summer	SR	27	1.04-1.15	-2 to 10
Copenhagen (Soegaard and Moller-Jensen, 2003)	2001	Four seasons	CC	40		6 to 32
Edinburgh (Nemitz et al., 2002)	2000	Autumn	CC	65	0.96-1.13	-12 to 135
Helsinki (Vesala et al., 2008)	2007	Winter-Summer	IN	31		-10 to 17
London – this study	2007	Four seasons	CC	190	0.96-1.03	7 to 47
London (Rigby et al., 2008)	2006-2007	Four seasons	CC	87	1.01-1.11	
Marseille (Grimmond et al., 2004)	2001	Summer	CC	44		5 to 30
Melbourne (Coutts et al., 2007)	2004-2005	Four seasons	SR	40	0.94-1	2 to 11.5
Mexico City (Velasco et al., 2005)	2003	Spring	CC	37	1.06-1.18	-5 to 36.4
Tokyo (Moriwaki and Kanda, 2004)	2001-2002	Four seasons	SR	29	0.91-1.21	4.5 to 25

Table 5: Comparison of observed fluxes with daytime (09:00 – 18:00) carbon dioxide fluxes (F_c), emissions from natural gas usage, biosphere exchange and human respiration (by season in 2007). The relative contribution from traffic emissions is the difference of F_c and ground sources.

	<i>Winter</i>	<i>Spring</i>	<i>Summer</i>	<i>Autumn</i>
Observed F_c [t CO ₂ km ⁻² month ⁻¹]	+ 4041	+ 4802	+ 3474	+ 4651
Natural gas contribution [%]	+ 71.1	+ 59.0	+ 59.0	+ 47.8
Total biosphere exchange [%]	+ 1.2	- 2.5	- 4.3	- 1.6
Total human exhalation [%]	+ 4.8	+ 4.4	+ 5.9	+ 4.9
Traffic (+ oil and coal combustion) [%]	+ 22.9	+ 39.1	+ 39.5	+ 48.9

Table 6: Annual emissions estimates for six cities, plan area of vegetation and population density around the study areas (see Table 5 for references).

	London (this study)	Copenhagen	Edinburgh	Melbourne	Mexico City	Tokyo
Emissions [t CO ₂ km ⁻² y ⁻¹]	35500	12800	36000	8490	12800	12290
Vegetation cover [%]	8	-	20	38	16	21
Population density [persons km ⁻²]	10000	-	7500	2940	12000	11800

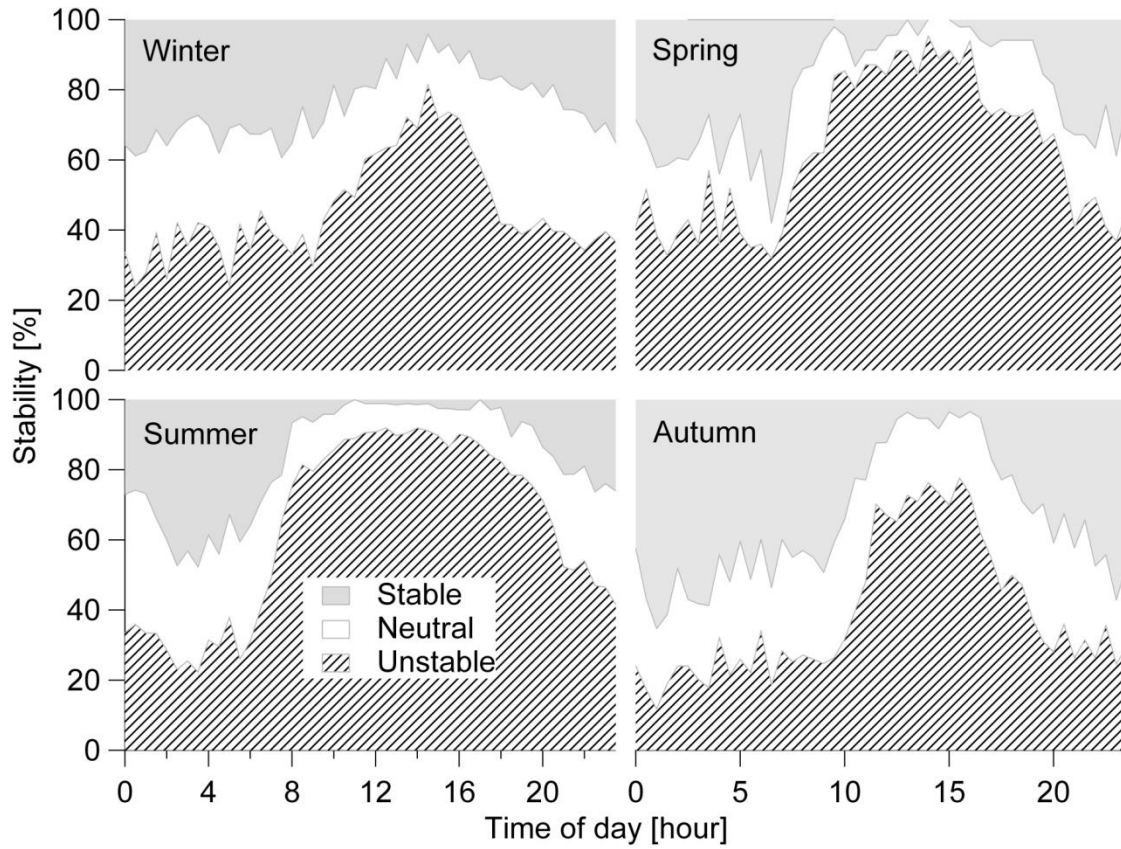


Figure 1: Frequency distributions of unstable ($\zeta < -0.05$), near-neutral ($-0.05 \leq \zeta \leq 0.32$) and stable ($\zeta > 0.32$) stability conditions at the measurement height by time of day and season (a) winter (b) spring (c) summer (d) autumn (see Table 1 for definitions).

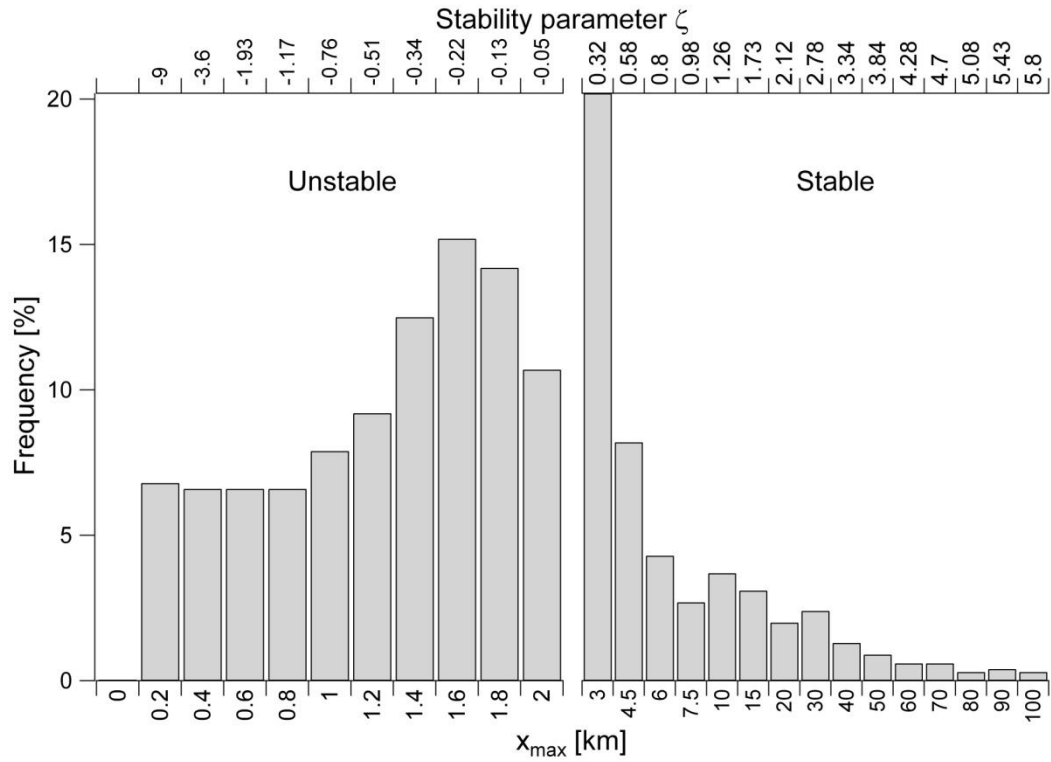


Figure 2: Frequency distribution of the KM footprint calculated maximum contribution (x_{\max}) to the measured CO_2 flux – in 2007, as a function of atmospheric stability for 30 min periods (x_{\max} and ζ values denote the beginning of each interval).

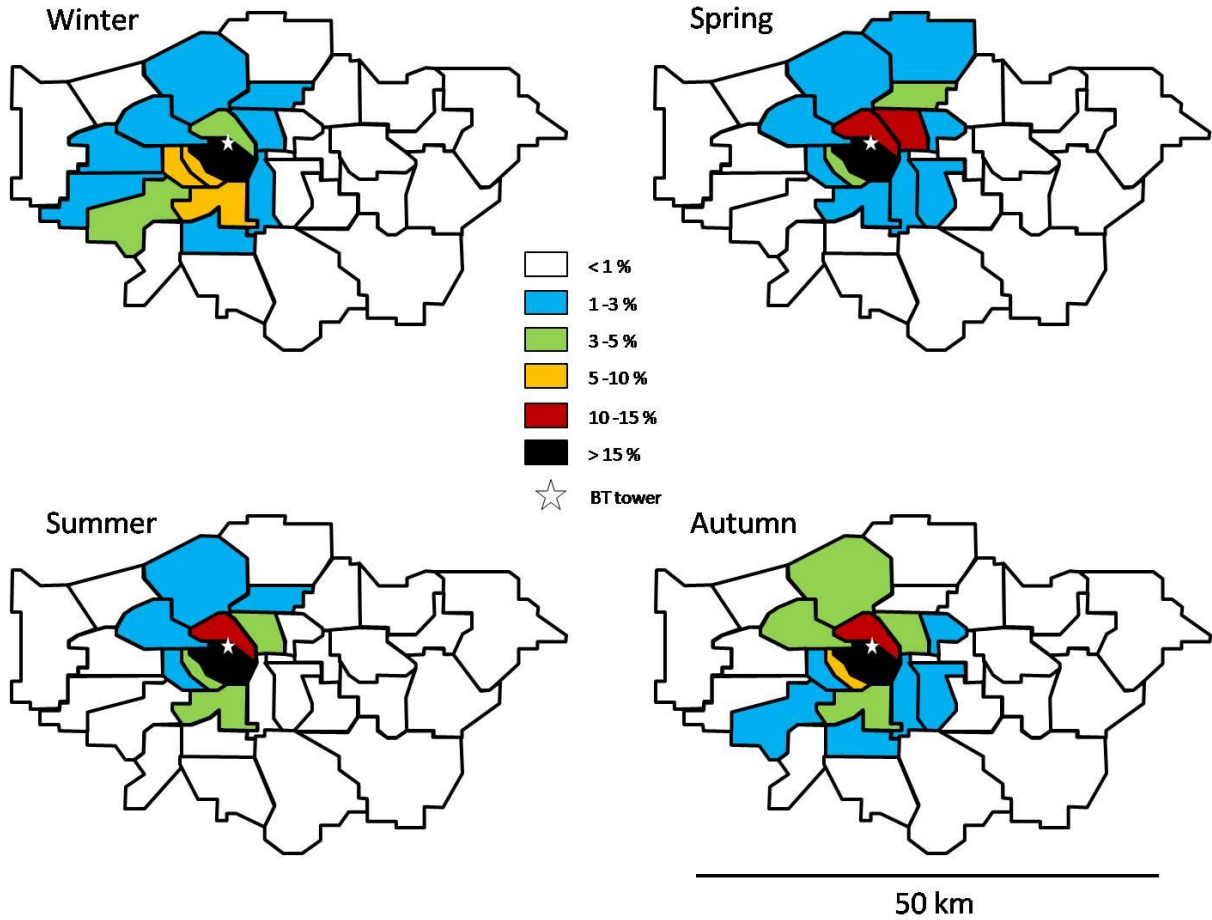


Figure 3: Seasonal distributions during 2007 of the flux footprint of the BT Tower over Greater London. The tower footprint was calculated on a half-hourly basis using the Kormann-Meixner model and daytime (09:00 – 18:00) values were used to derive seasonal averages. The colour scale reflects the contribution of individual boroughs to the total flux footprint. Map generated from 1 km² grid data (as used by the NAEI).

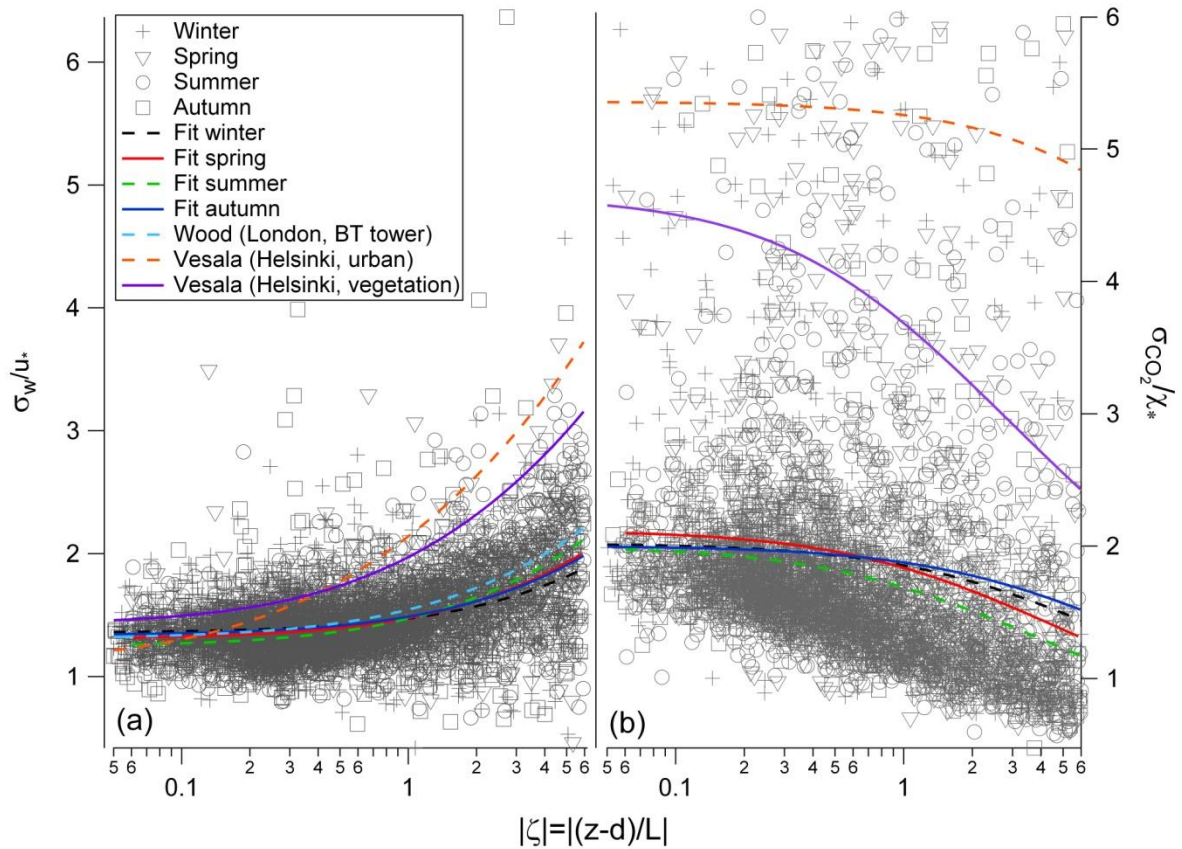


Figure 4: Normalised standard deviation of (a) w and (b) $[CO_2]$, as a function of seasonal stability ($\zeta < 0$, unstable; NB: the absolute value of ζ is used in the graph). The fit obtained by Wood (Wood et al., 2010a) using 2007/08 tower data (figure (a) only) and regression results for two land-use classes (urban and vegetation) in Helsinki (Vesala et al., 2008) are also plotted.

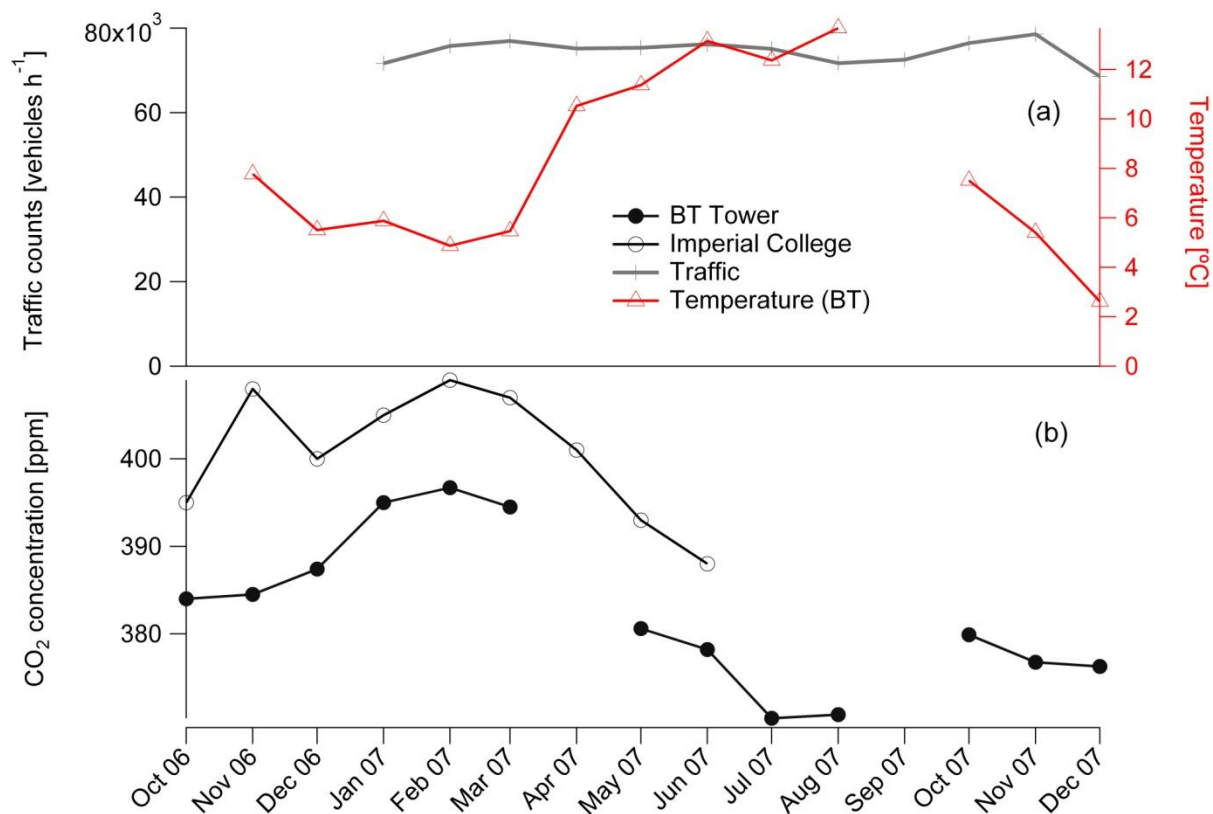


Figure 5: (a) Traffic counts at Marylebone Road and temperature measured at the BT Tower in 2007; (b) comparison of mean monthly CO₂ concentrations measured at the BT Tower and a tower site at Imperial College London (at 87 m) (Fig. S1, Supplementary Material) (Rigby et al., 2008). BT Tower data for April and September 2007 were excluded since the temporal data coverage was less than 10%.

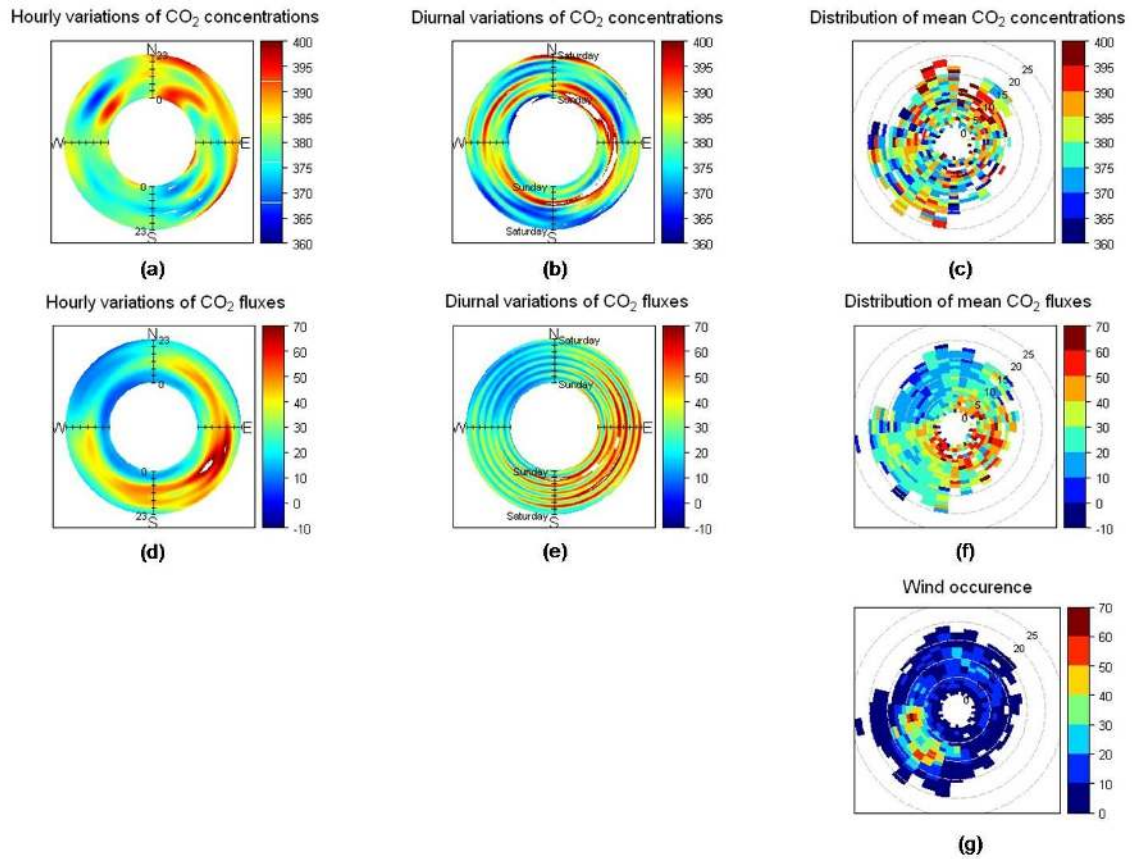


Figure 6: CO_2 concentrations (in ppm) as a function of wind direction average (a) hourly and (b) diurnal variations; variations of CO_2 fluxes (in $\mu\text{mol m}^{-2} \text{s}^{-1}$) as a function of wind direction average (d) hourly and (e) diurnal; (c), (f) distribution of CO_2 concentrations (ppm) and CO_2 fluxes ($\mu\text{mol m}^{-2} \text{s}^{-1}$) as a function of wind direction and wind speed; (g) wind occurrence (in hours) as a function of wind speed and direction. Plots were generated using the openair (Carslaw and Ropkins, 2010) package for R (R Development Core Team, 2009).

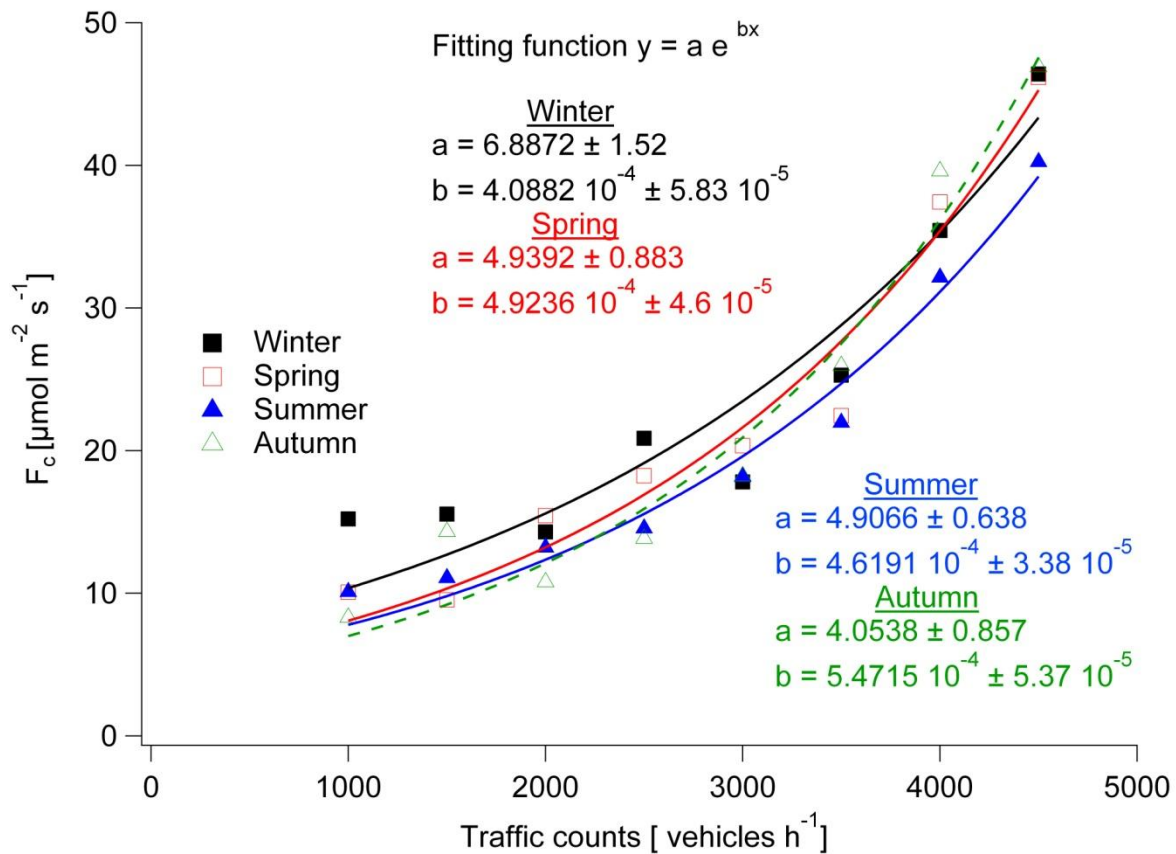


Figure 7: Observed 30 min carbon dioxide fluxes (F_c) binned for traffic counts measured at Marylebone Road during 2007 (by season).

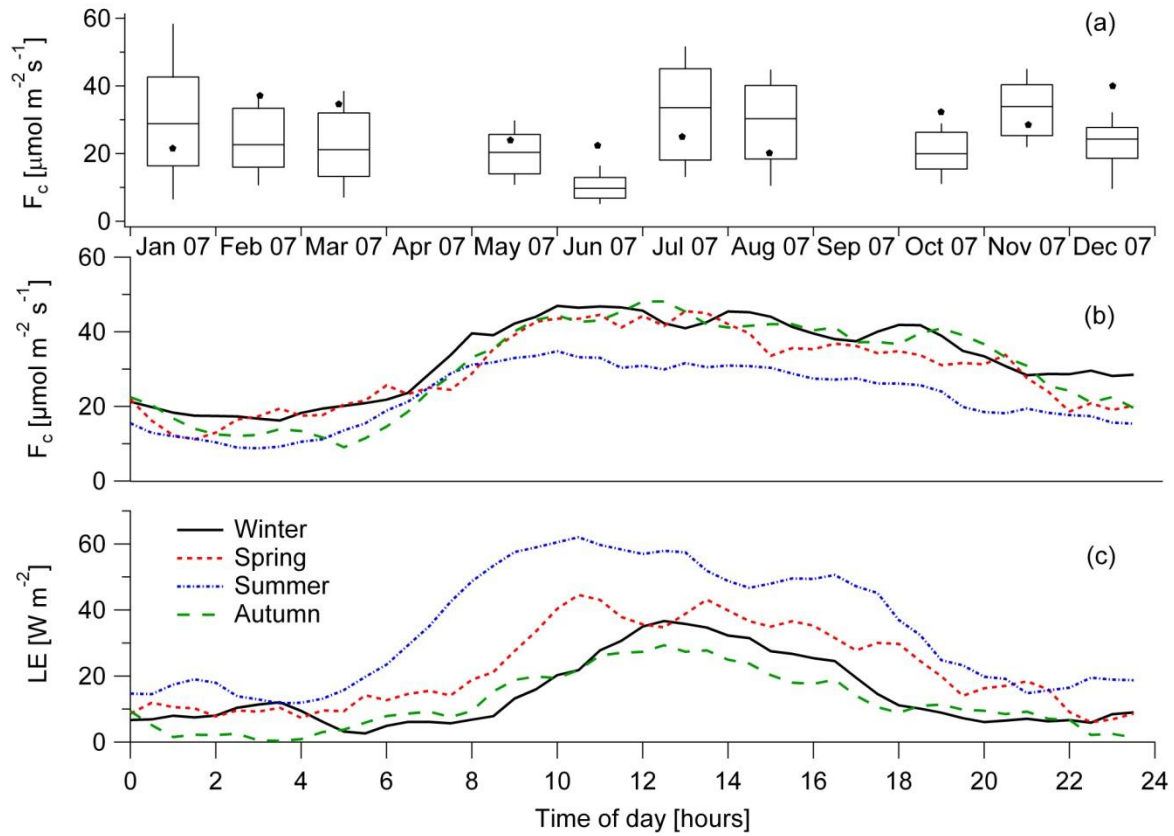


Figure 8: (a) Monthly breakdown of CO₂ flux statistics for 2007 (bottom and top of boxes correspond to 25th and 75th percentiles, respectively; bottom and top whiskers correspond to 10th and 90th percentiles, respectively; monthly means and medians are indicated by solid markers and horizontal lines, respectively), and seasonal trends in (b) CO₂ and (c) latent heat fluxes.

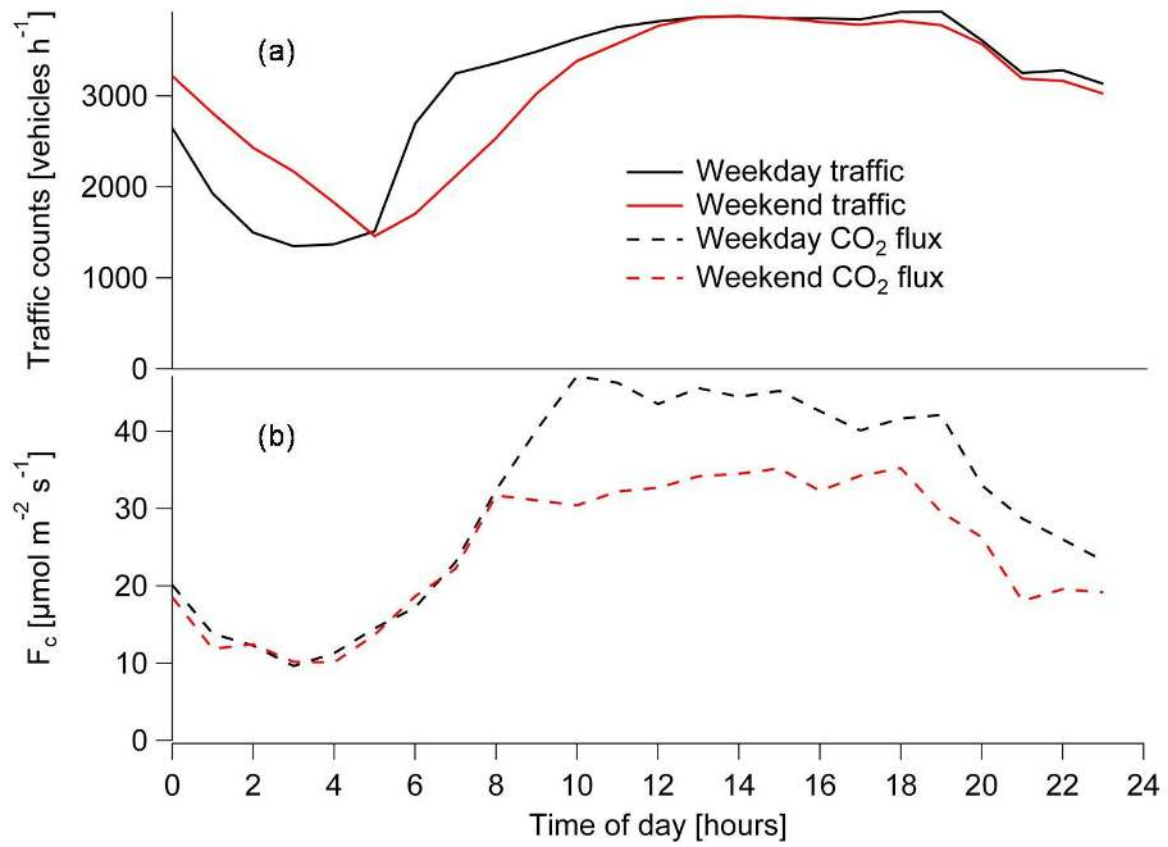


Figure 9: Weekday-weekend segregation of carbon dioxide fluxes measured at the BT Tower and traffic counts (figures for Marylebone Road used as a proxy for central London).

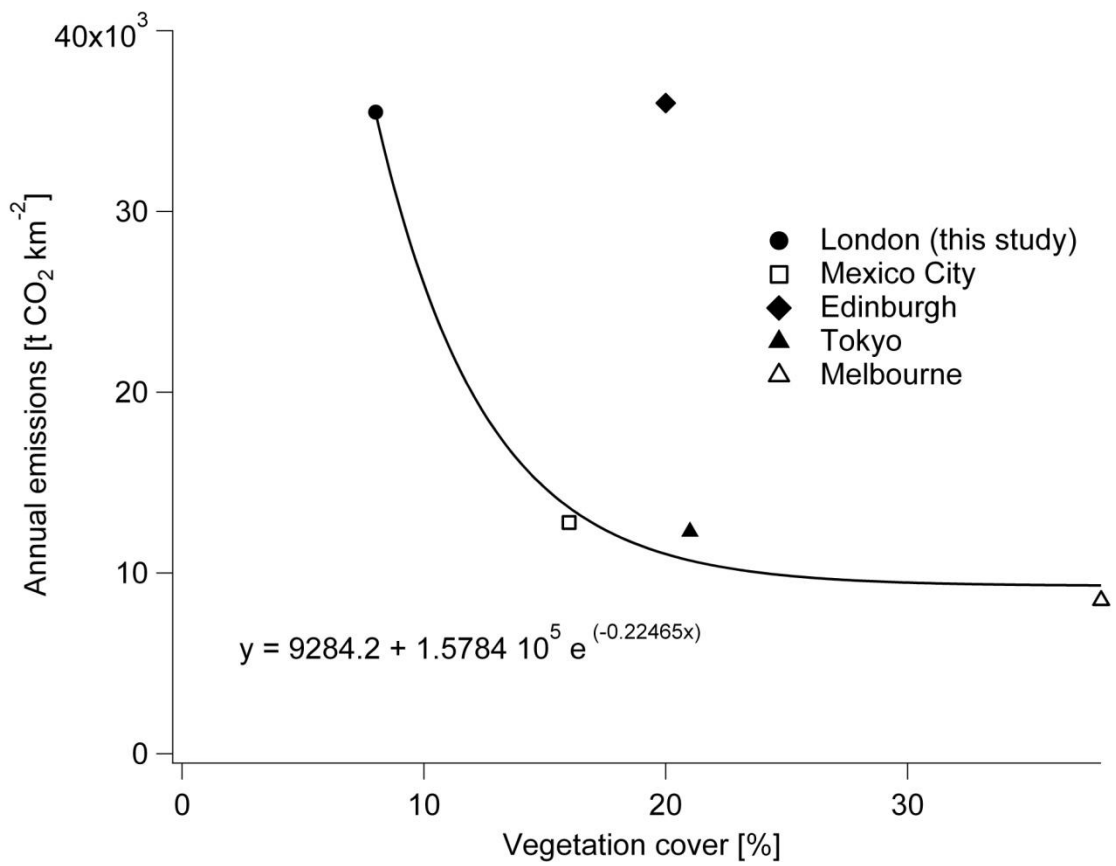


Figure 10: Annual CO₂ emissions in five cities compared with vegetation cover.