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Cross-validation of inferred daytime airborne CO_2 urban-regional scale surface fluxes with eddy-covariance observations and emissions inventories in Greater London

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Abstract

Data obtained from eleven flight surveys on six days during October 2011 were used to characterize the urban CO_2 dome in Greater London (GL) and to calculate CO_2 fluxes at the city scale. Flights crossed GL along two transects (SW-NE and SSE-NNW) at an altitude of 360 m. Increments as high as 23 ppmv were measured. The maximum CO_2 mixing ratios were localized over GL under low wind speeds, whereas a displacement of the urban plume downwind from the centre of the urban area occurred during high wind speeds. The urban-regional surface CO_2 flux was calculated for four days by the Integrative Mass Boundary Layer (IMBL) method. The diurnal CO_2 flux in GL obtained from the aircraft observations ranged from 46 to 104 µmol CO_2 $m^{-2}\,s^{-1}$ during the day time. The mean CO_2 fluxes estimated from the IMBL method were statistically similar to those observed by eddy-covariance systems located in central London and a spatially integrated emissions inventory for GL. This study provides an important cross-validation of two independent measurement-based methods to infer the contribution of urban areas to climate change in terms of CO_2 surface fluxes, both of which complement bottom-up emissions inventories. The uncertainties of fluxes estimated by the IMBL method are considered and the limits of implementation of atmospheric methods to infer city-scale fluxes are discussed.

1 Introduction

Urban areas are responsible for 70 % of the emissions of greenhouse gases despite covering only 2 % of the planet's land surface (UN-Habitat, 2011). Measurements of atmospheric CO_2 mixing ratios in cities are becoming an increasingly common means to study local greenhouse gas emissions and urban carbon cycles (Grimmond et al., 2002; Pataki et al., 2006). CO_2 mixing ratios in urban areas can show a high degree of spatial and temporal variability due to different local sources and atmospheric stability (Pataki et al., 2006). Cross-transects of rural/suburban to urban in-situ continuous measurements of CO_2 have been derived in a number of cities: Nottingham in the UK (Berry and Colls, 1990); Vancouver in Canada (Reid and Steyn, 1997); Phoenix (Idso et al., 1998; Day et al., 2002), Baltimore (George et al., 2007) and Portland (Rice and Bostrom, 2011) in the United States; and Paris in France (Widory and Javoy, 2003), among others. The quantified enhancement of the CO_2 mixing ratio in the urban boundary layer has been termed the urban CO_2 dome (Idso et al., 1998).

Accurate estimates of CO_2 surface fluxes in cities are needed to understand how urban emissions and land modifications affect the regional carbon exchange (Velasco and Roth, 2010). There is also a need to link top-down estimates of fluxes (data derived from atmospheric observations) with bottom-up information (emission inventories) in order to validate emission estimates and reduce the uncertainty on the urban carbon cycle (Duren and Miller, 2012). CO_2 fluxes in urban environments have been studied by eddy covariance (EC) systems in different cities at the local scale (e.g. Grimmond et al., 2002; Kordowski and Kuttler, 2010). Urban areas are a net source of CO_2 resulting in positive fluxes with maximum emissions occurring during the daytime (Grimmond et al., 2002; Charron et al., 2003; Moriwaki and Kanda, 2004) and with peak values during rush hours (Velasco et al., 2005; Matese et al., 2009). Road traffic and local heating with natural gas, oil or coal govern the exchange of CO_2 over cities. However, CO_2 anthropogenic emissions are reduced by uptake from vegetation in parks and other green areas during the growing season (Kordowski and Kuttler, 2010).

EC towers are typically installed 2–3 times the mean building height to yield fluxes representative of the neighbourhood or local scale (Grimmond and Oke, 1999). Urban areas have a patchwork of neighbourhoods (residential areas, green areas, commercial, industrial, etc.) each with different CO_2 emission rates. However, the city as a whole can be considered different from its surroundings. Under this assumption urban-regional-scale fluxes can be estimated by the analysis of the mass balance in the Boundary Layer (BL) (McNaughton and Spriggs, 1986; Raupach et al., 1992; Denmead et al., 1996). Under unstable convective conditions, a BL develops over the land surface. The top of the BL separates the air that has been influenced by the surface

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processes from the free troposphere. The BL grows from the early morning, when it is of the order of a hundred of meters or so, to a maximum height of ∼ 1–3 km in the late afternoon, by entraining air from the free troposphere into the BL. Temporally and spatially integrated surface fluxes can be inferred from measured changes in CO_2 mixing ratios in the BL over the day and by quantifying the entrainment. This method is called Integrative Mass Boundary Layer (IMBL). Since the BL acts as a natural chamber that smoothes the CO_2 signal from surface processes (anthropogenic emissions and natural fluxes) over a heterogeneous land cover, regional surface fluxes (10^2–10^4 km^2) are estimated. This approach has been applied to calculate mean regional CO_2 surface flux over heterogeneous areas in the Amazonian basin (Lloyd et al., 2001, 2007) and the central part of the Ebre watershed in Spain (Font et al., 2010), among others.

In an urban environment, emissions from the lowest level in the surface layer mix through the urban boundary layer (UBL) or urban mixing layer (UML) as a consequence of atmospheric turbulence. Measurements taken in a well-mixed UBL are representative of the heterogeneity of processes taking place in the city in contrast with measurements at the surface which are influenced by emissions nearby and by microscale transport processes, for example within street canyons. The diurnal variation of concentrations within the UML responds to changes in surface emissions, boundary layer growth, entrainment processes and horizontal transport (advection). Observations from light aircraft within the UML can characterize different parts of the mass budget to permit calculation of integrated regional surface CO_2 fluxes at the city scale. A similar approach was used to calculate the turbulent sensible heat and latent heat fluxes in Sacramento, California (Cleugh and Grimmond, 2001).

Estimates of the BL mass budget are often limited by the advection term (Shashkov et al., 2004). The significance of the advection flux depends on the degree of heterogeneity of the atmospheric CO_2 mixing ratio field due to a non-uniform distribution of the biospheric sources/sinks and their response to changing meteorological drivers. The error due to advection can be minimized by undertaking Lagrangian observations (Martins et al., 2009; Sarrat et al., 2009) that track changes in the CO_2 content of air

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masses while they travel in the main flow direction. Sampling upwind and downwind profiles accounts for the advection term and surface fluxes can be calculated.

Flights conducted between the 12 and the 25 October 2011 across Greater London (GL) which measured atmospheric carbon dioxide, ozone, particles and meteorological variables are used to quantify the CO_2 urban enhancement and to calculate the mean urban CO_2 surface flux in London.

2 Material and methods

2.1 Instrumentation and survey design

The flight campaigns undertaken between the 12 and 25 October 2011 in South East England (Fig. 1a) were conducted by the Natural and Environment Research Council-Airborne Research and Survey Facility (NERC-ARSF) airplane (http://arsf.nerc.ac.uk/). It was instrumented with an AIMMS-20 Air Data Probe supplied by Aventech Research Inc. that measured temperature, barometric pressure, the three components of the wind speed and horizontal wind direction. The accuracy for the weather variables are 0.05 °C (temperature), 0.1 kPa (pressure), 0.5 $m\,s^{-1}$ (horizontal wind) and 0.75 $m\,s^{-1}$ (vertical wind) (Beswick et al., 2008). Atmospheric CO_2 dry mole fractions were measured with the non-dispersive infrared portable instrument AOS Inc. CO_2 Airborne Analyzer System. CO_2 mixing ratio, position (longitude, latitude, altitude and universal time) and ambient pressure were recorded at a mean frequency of 0.5 Hz. Two standard gases were used to build the calibration curve in each flight. The traceable standards (International Standards WMO-X2007 scale) had a mixing ratio of 373.13 ppmv (Lowfield) and 394.34 ppmv (Highfield). The Lowfield Standard Gas was used as the Reference Gas to correct for thermal drift during each flight. In the AOS instrument, pressure fluctuations and changes during the flight are controlled by a pressure buffer at the end of the sampling system that controls the inlet and outlet flows through the analyzer. The mean precision of the CO_2 instrument under flight conditions is estimated to be

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±0.23 ppmv. Further details about this system are described in Font et al. (2008). An isokinetic aerosol intake fed the GRIMM 1.129 Sky-optical particle counter that measured particle mixing ratio in the size range 0.25–32 µm at a frequency of 0.17 Hz. O_3 mixing ratio was measured with a Thermo Analyzer 49i O_3 photometer with a sampling frequency of 1 measurement each minute.

The plane took off and landed at Gloucestershire airport (Fig. 1a). Flights passed over Greater London (GL) at a constant height of approximately 360 m via two paths that crossed central London: from SW to NE (e.g. 12 October) and from SSE to NNW (e.g. 25 October) (Fig. 1a). The directions were chosen based on the wind direction to allow upwind conditions first to be obtained. This allowed changes in the CO_2 mixing ratio to be tracked as the air crossed GL. Two vertical profiles (up to 2200 m) were undertaken just after take-off and before landing at Gloucester (Fig. 1b). Additional vertical profiles were done along the flight track.

Concurrently, surface CO_2 mixing ratios were observed in central London at two London Air Quality Network (LAQN) sites classified as "urban background": North Kensington (abridged "KC"; 51.52° N, 0.21° W, inlet at 2 m above ground level, m a.g.l.) and Tower Hamlets ("TH"; 51.51° N, 0.02° W, 9.2 m a.g.l.) (Fig. 1a). CO_2 mixing ratios for 15 min averages were obtained from samples from a non-dispersive infrared (NDIR) analyzer LiCOR-820. Two-point calibrations are carried out every 15 days with a zero-scrubber (soda lime) and a CO_2 span gas with a mixing ratio ∼ 500 ppmv referred to the International Scale (WMO-X2007).

Turbulent fluxes of carbon dioxide were measured at two long-term Eddy Covariance (EC) sites of King's College London (KCL), located on the Strand campus in central London (referred to as "KSS" and "KSK"; 51.51° N, 0.12° W). Measurement towers (KSS: Aluma T45-H triangular tower; KSK: single tube mast, Clark Masts CSQ T97/HP) are installed on top of buildings so that sensors operate at 49 m a.g.l. (KSS) and 39 m a.g.l. (KSK) (about 2.2 and 1.9× mean building height in the flux source area, respectively). At both KSS and KSK, the EC system consists of a CSAT3 sonic anemometer (Campbell Scientific) and a Li7500/Li7500A open path infrared gas anal-

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yser (LiCOR Biosciences). The data were sampled at 10 Hz and fluxes calculated for 30 min intervals. Data processing and quality control of these data are described in Kotthaus and Grimmond (2012).

2.2 Regional scale surface fluxes from aircraft observations

The Integrative Mass Boundary Layer (IMBL) has been used to calculate spatially and temporally integrated urban-scale CO_2 surface fluxes from aircraft observations. The method considers the boundary layer as a box where scalars are conserved (Denmead et al., 1996; Guenther et al., 1996). The variation of the mean mixed-layer CO_2 concentration (expressed in µmol CO_2 m^{-3}, $[CO_2]$) in time ($\partial[CO_2]/\partial t$) at the measurement height (h) within the BL can be split into three components: a surface flux term (F_{CO_2}), an entrainment flux (F_e) and an advection term (F_{adv}):

$$h\frac{\partial[CO_2]}{\partial t} = F_{CO_2} + F_e + F_{adv} \quad (1)$$

The entrainment term expresses the entrainment of air masses from above the BL with a concentration $[CO_2]_+$ down to the BL, with concentration $[CO_2]$ due to the increase of the mixing layer in time ($\partial h/\partial t$) and due to the vertical velocity (subsidence) (w_+) on top of h:

$$F_e = \left(\frac{\partial h}{\partial t} - w_+\right)([CO_2]_+ - [CO_2]) \quad (2)$$

The advection flux is quantified as the product of the horizontal wind speed U to the CO_2 spatial gradient ($\partial[CO_2]/\partial x$):

$$F_{adv} = -h\left(U\frac{\partial[CO_2]}{\partial x}\right) \quad (3)$$

Reorganizing and integrating Eq. (1) in time, the surface flux can be calculated:

$$F_{CO_2} = \langle h\rangle\frac{[CO_2]_2 - [CO_2]_1}{t_2 - t_1} - \left(\frac{h_2 - h_1}{t_2 - t_1} - w_+\right)([CO_2]_+ - \langle[CO_2]\rangle) + \langle h\rangle\langle U\rangle\left\langle\frac{\Delta[CO_2]}{\Delta x}\right\rangle \quad (4)$$

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where $\langle\rangle$ denotes temporal and spatial mean values; $[CO_2]_2$ and $[CO_2]_1$ are the concentrations measured at times t_1 and t_2, respectively; h_1 and h_2 denote the mixing layer heights; w_+ is the vertical velocity above h_1; $[CO_2]_+$ is the concentration in a layer of 100 m depth just above the mixing-layer height at time t_1 (Martins et al., 2009); and $\langle[CO_2]\rangle$ is the mean concentration in the boundary layer as measured in GL boundaries. The first term on the RHS of Eq. (4) is the storage flux (F_{stg}); the second is the entrainment term (F_e); and the last is the advection flux (F_{adv}). This is the basis of the Integration Mass Boundary Layer (IMBL) budget method. This method assumes that turbulent horizontal fluxes and the vertical advection are negligible at the sampling height, and that the vertical flux profile in the mixed-layer is linear. These assumptions are commonly satisfied in the well-mixed boundary layer (Guenther et al., 1996).

Equation (4) has been applied in two ways. First, by calculating changes in the $[CO_2]$ measured in the horizontal transects over GL at different times of the day. Changes in the $[CO_2]$ in the urban mixing layer are expected to respond to urban emissions, entrainment and advection. Vertical profiles of CO_2 and O_3 mixing ratios and particulates, temperature, wind speed and direction near Gloucester at takeoff and landing were used to examine the depth of the mixing layer and its changes in time. The CO_2 spatial gradient, $\langle\frac{\Delta[CO_2]}{\Delta x}\rangle$, was calculated by fitting a linear least square regression through the $[CO_2]$ measured in the transects over GL against distance when the plane track was perpendicular to the main wind direction. Second, by quantifying changes of $[CO_2]$ above upwind conditions by sampling a vertical profile downwind of the city. The downwind profile is expected to sample air that has been transported by the wind across the urban area.

In both cases, $[CO_2]$ were calculated from CO_2 dry mole mixing ratios (expressed in ppmv), temperature and barometric pressure measurements through the law of ideal gases.

In order to calculate the uncertainty on F_{CO_2}, a propagation of error analysis is applied. The standard deviation for each of the components in Eq. (4) is calculated from

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the ambient measurements used to estimate the mean value and propagated. The final uncertainty is reported as $\pm 1\sigma$.

2.3 Spatial representativeness of flight based fluxes

To determine the likely source area for the flight based fluxes, the Lagrangian Particle Dispersion Model FLEXPART (Stohl et al., 2005) is used in backward mode. FLEXPART is driven by the European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological model with resolution $0.2^\circ \times 0.2^\circ$, 91 vertical levels and 3 h resolution. Ten thousand particles were released from a box defined by the aircraft track (longitude, latitude and altitude). The simulation run is set to end at midnight for each day. The model output, interpolated at a spatial resolution of $0.05^\circ \times 0.05^\circ$ and 5 min, provides the mean residence time of the air in the layer between 0 and 300 m a.g.l. This indicates the areas that might potentially influence the CO_2 mixing ratios measured onboard the aircraft at a given point and time.

2.4 Emissions inventory for Greater London

Annual emissions of CO_2 for each borough in Greater London are reported by the Department of Energy and Climate Change (DECC). At the time when this study was carried out only emissions from 2010 were available (DECC, 2012a). The uncertainty of the emissions inventory is estimated to be 2 % (DECC, 2012b). In order to compare IMBL with bottom-up fluxes, a spatially integrated surface flux from the emissions inventory was calculated for each survey. Annual emissions are scaled by the residence time that air masses spent in each borough as given by the FLEXPART model, and divided by the total surface and by the total residence time that air masses spent in the GL surface layer.

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3 Results

3.1 CO_2 mixing ratio observations

Aircraft measurements provide a snapshot of the spatial variability of CO_2 in and outside the urban boundary layer (Fig. 2). When lower wind speed conditions occurred ($< 8\,m\,s^{-1}$), higher CO_2 mixing ratios were measured over central London, with peaks at 400 (12 October 2011), 420 (13 October) and 399 ppmv (25 October), compared to $\sim$ 394–398 ppmv above outer GL. With higher wind speed conditions ($> 8\,m\,s^{-1}$), the differences in average mixing ratio inside and outside GL were smaller, ranging from −0.7 ppmv (17 October 2011) to 0.8 ppmv (19 October). For these days, the maximum CO_2 mixing ratio measured from aircraft was registered downwind GL. On the 17 and 24 downwind measurements were available and the maximum CO_2 mixing ratio were observed 29 and 48 km downwind from central GL with enhancements of 14.0 and 5.9 ppmv above the upwind mixing ratio, respectively.

3.2 Temporal and spatial integrated CO_2 fluxes in Greater London

Time and space integrated urban-scale CO_2 surface fluxes were calculated for the 13, 17, 24 and 25 October 2011, when all terms of the IMBL budget analysis could be identified and quantified. Changes in time of the [CO_2] as measured in the transects over GL were used to calculate surface fluxes on the 13 and 17 October. Enhancements in the [CO_2] in the downwind profile sampled parallel to the main wind direction above an upwind profile were used for the 24 and 25 October surveys. The data obtained from other flights were incomplete to use for IMBL calculations as only one transect was measured over GL (12 October) and the advection term could not be quantified (19 October).

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3.2.1 CO_2 fluxes calculated from horizontal transects

The mean wind speed at 360 m over GL on the 13 October 2011 was 4.4 m s^{-1} and 6.0 m s^{-1} with an E-SE component in the morning and afternoon transects, respectively. Visual inspection of vertical profiles of CO_2, particulates, O_3, temperature and wind data near Gloucester showed a well-formed mixing layer at 757 m (in the morning profile) and at 1180 m (afternoon profile). Mixing ratios measured at the surface sites were broadly in agreement with those measured at 360 m (within 2σ): 406.7 ppmv (KC), 405.6 ppmv (TH) and 404.4 ppmv (aircraft) at 13:15 UTC; 418.7 ppmv (KC), 407.7 ppmv (TH) and 405.1 ppmv (aircraft) at 15:30 UTC (Table 2). This was in accordance with the well-mixed boundary layer as seen in the vertical profiles near Gloucester. The mean urban-regional CO_2 surface flux was 50.7 ± 18.8 µmol CO_2 m^{-2} s^{-1} between 13:15 and 15:30 UTC. The surface flux was representative for the eastern and central boroughs in GL (Fig. 3a, b).

The advection term was not included in the budget as transects parallel to the main wind direction were not available that day. Taking into account the CO_2 spatial gradient calculated in other surveys (Table 2) and the mean wind speed measured on the transect, the advection term would represent a flux of 1.6 µmol CO_2 m^{-2} s^{-1}. Not including the advection term in the budget represents an error of 4 % in the calculated surface flux, smaller than the overall flux error (37 %).

On 17 October, the strong winds over GL (8–9 m s^{-1} at 360 m of altitude) were from the SW. Vertical profiles of temperature and wind speed near Gloucester in the morning showed the presence of inversion layers at 390–436 m and at 460–500 m. The presence of these inversion layers translated into a decrease in the CO_2 mixing ratios with altitude: ~ 401.5 ppmv at the ground-level and 395.1 ppmv at the cruise altitude. Later that day, the CO_2 mixing ratio was homogenous below the cruise altitude (384 m) and the mixing layer was located at 1130 m at 11:56 UTC, as observed in the afternoon profile near Gloucester. Given the strong wind conditions on the 17, the advection term is considered in the IMBL budget analysis. As the flight track was parallel to the main

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wind flow, $\left\langle \frac{\Delta[CO_2]}{\Delta x} \right\rangle$ from Eq. (4) was calculated and F_{adv} quantified (Table 2). The resulting flux for the 17 October 2011 was 46.0 ± 27.2 μmol CO_2 m^{-2} s^{-1}. The flux was representative for the central and south-west areas of GL (Fig. 3c, d).

3.2.2 CO_2 fluxes calculated from upwind and downwind vertical profiles

On the 24 and 25 October, strong wind conditions and the prevalent wind direction allowed Lagrangian observations of two vertical profiles, one upwind and the other downwind of GL. As can be seen in Figs. 4 and 5, an increase of the CO_2 mixing ratio was observed in the downwind profiles compared to those upwind. Similarly, a depletion of O_3 is found in the downwind profiles. During daytime under moderate sunlight, nitrogen oxide (NO) emissions from vehicles and industries react with O_3 forming nitrogen dioxide (NO_2). This is translated into a depletion of the O_3 mixing ratio (Mazzeo et al., 2005).

Strong winds from the SE with an average speed of 12 m s^{-1} were measured over GL on 24 October 2011 at 360 m. Vertical profiles of temperature and gas tracers revealed strong inversion conditions in the lower troposphere (Fig. 4). Large CO_2 mixing ratios were measured at low altitudes (< 500 m; > 400 ppmv), and they decreased in altitude (391 ppmv) as shown by the two spiral vertical profiles upwind (51.31° N, 0.58° E) and downwind (51.88° N, 0.98° W) of GL. The height of the lowest inversion layer increased from 410 m to 460 m. The flux calculated, 37.2 ± 3.2 μmol CO_2 m^{-2} s^{-1} between 10:10 and 10:57 UTC, was representative for the western part of GL (Fig. 3e).

On 25 October 2011, the main wind direction was southerly with an average speed of 7 m s^{-1}. There was an increase of about 5 ppmv in the downwind profile compared to the upwind one (Fig. 5). The vertical profile of temperature showed an inversion layer at 450 m, so [CO_2] below this inversion height was used to calculate surface fluxes. The integrated CO_2urban-regional flux was calculated as 104.3 ± 8.0 μmol CO_2 m^{-2} s^{-1} between 11:05 and 11:15 UTC. The boroughs in north, central and south London contributed to the estimated surface flux (Fig. 3f).

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3.2.3 Comparison of CO_2 surface fluxes in Greater London

The CO_2 fluxes obtained from the EC systems in central London during the time period of this study are shown in Fig. 6a. CO_2 surface fluxes estimated by the IMBL equation from aircraft observations are indicated as well. Differences between EC fluxes observed at KSK and KSS reflect the variability of turbulent carbon dioxide fluxes in the complex dense urban environment, where CO_2 sources show large changes at small temporal and spatial scales. Sensors at the two EC sites operate at different heights, so that differences can be partly explained by differences in source area locations (Kotthaus and Grimmond, 2012). EC and IMBL fluxes cannot be directly compared because of the spatial (neighbourhood vs. city-scale) and temporal mismatch between the estimates, but Fig. 6a offers an insight of how both methods compare. A *t* test showed that the CO_2 mean flux by the two methods (47.7 µmol CO_2 $m^{-2}\,s^{-1}$ given by the EC observations and 59.6 µmol CO_2 $m^{-2}\,s^{-1}$ for the IMBL method) are statistically similar at the 0.05 significance level.

IMBL fluxes were also compared with the spatially and temporally integrated fluxes as calculated from the DECC emissions inventory (Fig. 6b). A *t* test indicates that both means were not statistically different. Comparing individual surveys (Table 2), the flux calculated from the emissions inventory was within the uncertainty range of the IMBL method for the 13 and 17 October, 10 % higher for 25 October and 28 % for 24 October.

4 Discussion

Monitoring trends in urban CO_2 concentrations or "domes" has been suggested as a means of directly assessing the efficacy of stabilization policies aiming to reduce greenhouse gases emissions from urban areas (Hoornweg et al., 2010). Previous studies have quantified urban concentrations by transects in the canopy layer (e.g. Berry and Colls, 1990; Idso et al., 1998, 2001), above the roughness sub-layer (RSL) (e.g. Reid and Steyn, 1997) or by column averages as documented by satellites (Kort et al.,

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2012). McKain et al. (2011) suggests that increasing the number of canopy layer measurement sites across a city would be ineffective in detecting changes in emissions at the city scale as they are sensitive to local sources. To measure over a larger area tall towers, aircraft or column data are needed. These are sensitive to regional-scale meteorology and regional emissions but are useful in quantifying trends in emissions for an urban region. Kort et al. (2012) estimate that changes in the column average of 0.7 ppmv in Los Angeles, corresponding to a 22 % change in emissions, could be detected by the GOSAT satellite at the 95 % confidence level. Similarly, aircraft surveys, as in the current study, provide an integrated view of the regional CO_2 concentrations ("dome") over urban areas. Aircraft measurements also allow observation of the displacement of urban domes that should be taken into account when monitoring from fixed measurement sites.

Aircraft surveys permit temporally and spatially integrated fluxes at the city scale to be calculated and offer a top-down approach to validate bottom-up emissions inventories. However, IMBL fluxes are subject to uncertainties. Using instrument noise figures as listed in Sect. 2.1 in the uncertainty analysis (except for the vertical wind component, as the accuracy of the vertical wind is difficult to determine as found by Beswick et al., 2008) the uncertainty is 12 % (13 October) and 43 % (17 October). Including the atmospheric variability in CO_2 concentration in the propagation of error analysis increases the uncertainties for the IMBL fluxes to 37 % and 59 % for the 13 and 17 October, respectively (Table 2).

The spatial distribution of the $[CO_2]$ is heterogeneous in an urban environment, given the presence of point source emissions. The choice of the representative $[CO_2]$ for the urban atmosphere has an impact on the calculated fluxes. In order to evaluate the impact of the mean $[CO_2]$ on the calculated fluxes, changes in time of the 5 % and 95 % percentile $[CO_2]$ values have been used instead. The resulting flux for the 13 October varied between 44.8 and 67.7 µmol CO_2 $m^{-2}\,s^{-1}$; and between 40.5 and 59.6 µmol CO_2 $m^{-2}\,s^{-1}$ for the 17 October. The use of extreme values might represent an increase or decrease of about 30 % from the flux calculated from the mean $[CO_2]$ in the city. Since

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the reported fluxes are within the uncertainty of the IMBL method (2σ), the impact of the spatial variability in the [CO_2] over a city on the calculated fluxes is reflected in the uncertainty of the IMBL.

Clearly, aircraft measurements along a single transect (e.g. Fig. 3) do not cover the entire area of the city. Ideally future surveys will permit multiple transects across GL to derive a mean [CO_2] representative of the urban mixing layer. Lagrangian observations are expected to overcome this by sampling the increment in [CO_2] downwind urban areas above upwind conditions. The uncertainty reported for the IMBL fluxes calculated from downwind profiles (8–9 %) are lower than the ones from transects over the city. Lower variability in [CO_2] was reported to the propagation of errors analysis (Table 2). However, the uncertainty relies on how representative the [CO_2] is of the urban atmosphere. When sampling a single downwind vertical profile, it is assumed that the downwind enhancement of CO_2 is homogenous in the horizontal extent of the urban plume. However, Gaussian plumes have their maximum concentration at the centre and decrease exponentially at the edges. Lower fluxes would be calculated if the downwind profile was not sampled at the plume's centreline. IMBL fluxes from Lagrangian downwind profiles appeared to be underestimated compared to the emissions given by the DECC inventory by 30 % (24 October) and 10 % (25 October). Despite this, the minimum flux estimated by the IMBL method is 5–7 % higher than the mean EC fluxes. The footprint of the vertical profiles includes not only the GL urban area but also rural regions (see Fig. 3e), this might explain the discrepancies on the flux values given by different methods. Multiple cross-sectional transects sampled downwind perpendicular to the main wind direction at different heights and at different distances from the city would help determine the amplitude, vertical and horizontal extent of the urban plume so that advective fluxes representative of the city-scale could be better quantified.

Surface fluxes in this study include anthropogenic and biogenic components. To distinguish the anthropogenic signal, fast-response measurements of urban pollutants (e.g. nitrogen oxides, carbon monoxide), which are tracers of traffic-related emissions, and methane as a tracer of gas system emissions, would aid interpretation. Similarly,

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isotopic analysis of carbon and the $^{13}C/^{12}C$ ratio of CO_2 or the $\Delta^{14}CO_2$ could help identification of the anthropogenic signal. An emissions ratio approach (e.g. Turnbull et al., 2011) would allow apportionment and identification of the sectors emitting more CO_2 into the atmosphere and thus facilitate evaluation of policy effectiveness to reduce the contribution of greenhouse gases emissions from urban areas.

5 Conclusions

Atmospheric observations of CO_2 mixing ratios onboard aircraft in the urban mixing layer have been shown to be a valuable approach to quantify the CO_2 urban enhancement under different meteorological conditions. The CO_2 enhancement in the urban boundary layer of Greater London was observed from a light aircraft at 360 m altitude on six days during two weeks of October 2011 (eleven flights). Under low wind speeds, the CO_2 mixing ratio peaked in central GL and decreased towards the city boundaries (e.g. 12 and 13 October). Under windy conditions, the peak concentration was displaced downwind from the urban centre along the main wind direction (e.g. 17 and 24 October).

This study has shown that temporally and spatially integrated fluxes obtained by means of the Integrative Mass Boundary Layer from CO_2 observations obtained onboard aircraft can provide a relevant observational methodology for validating both tower-flux observations and emissions inventory estimates of CO_2 fluxes. While such surveys are likely to always be occasional, they have the advantage of being able to provide estimates during a mix of meteorological conditions and over a wide geographical area. The agreement shown by the EC fluxes and those derived from aircraft observations with the emissions inventory endorse the use of these direct methods to verify CO_2 emissions at the urban scale.

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Table 1. Mean wind speed (U), mean ($\pm 1\sigma$) and maximum CO_2 mixing ratio measured onboard of the NERC-ARSF aircraft for the transects across Greater London (GL) on October 2011 and outside GL (outGL) below 400 m.

Date and time of the flight (UT)	U in GL ($m\,s^{-1}$)	CO_2 $\pm 1\sigma$ in GL (ppmv)	Max CO_2 in GL (ppmv)	CO_2 $\pm 1\sigma$ outGL (ppmv)
12 Oct 10:13	7.7	396.1 ± 1.6	400.5	392.8 ± 1.1
13 Oct 12:37	4.4	404.4 ± 3.3	411.4	397.5 ± 3.4
13 Oct 15:05	6.0	405.1 ± 7.5	421.8	398.2 ± 3.3
17 Oct 08:47	9.9	395.1 ± 2.8	399.2	394.9 ± 3.5
17 Oct 10:00	8.5	392.8 ± 1.4	396.1	393.5 ± 3.4
19 Oct 12:29	8.8	392.8 ± 0.9	395.9	392.3 ± 1.6
19 Oct 15:11	9.1	392.1 ± 0.9	396.6	391.3 ± 0.7
24 Oct 09:07	12.0	404.2 ± 1.5	407.9	404.4 ± 1.9
25 Oct 10:24	6.9	395.4 ± 1.7	399.1	394.3 ± 0.9
25 Oct 13:46	7.0	394.9 ± 1.0	397.0	393.7 ± 0.8

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Table 2. Values used to calculate the spatial and time integrated CO_2 urban-regional scale flux (F_{CO_2}) in Greater London (GL) using the IMBL budget method, F_{stg} is the storage flux, F_e the entrainment flux and F_{adv} the advection term. F_{DECC} refers to the spatial integrated emissions for each survey calculated from the DECC emissions inventory (DECC, 2012a) calculated as explained in Sect. 2.4.

	13 Oct	17 Oct	24 Oct	25 Oct
t_1(UTC)	13:15	9:40	10:15	11:05
t_2(UTC)	15:30	10:15	10:55	11:15
CO_2 (t_1) ± 1σ (ppmv)	404.4 ± 3.5	394.8 ± 2.8	401.4 ± 0.3	394.6 ± 0.2
CO_2 (t_2) ± 1σ (ppmv)	405.1 ± 8.0	392.8 ± 1.4	406.7 ± 0.4	398.7 ± 0.3
CO_{2+} ± 1σ (ppmv)	391.3 ± 0.5	390.0 ± 0.4	401.0 ± 1.2	394.1 ± 0.2
$\langle CO_2 \rangle$ ± 1σ (ppmv)	404.7 ± 5.8	393.7 ± 2.3	401.4 ± 0.3	394.6 ± 0.2
h_1 (m)	815	400	410	450
h_2 (m)	1180	1130	480	450
w_+ (mm s^{-1})	−2.5 ± 0.76	−0.18 ± 3.6	−2.2 ± 3.1	−5.6 ± 3.6
$\langle U \rangle$ (m s^{-1})	4.5 ± 0.5	9.9 ± 1.5	–	–
$\left\langle \frac{\Delta[CO_2]}{\Delta x} \right\rangle$ (µmol CO_2 m^{-2})	–	(1.1 ± 0.1) × 10^{-2}	–	–
F_{stg} (µmol CO_2 m^{-2} s^{-1})	0.3 ± 16.0	−21.5 ± 19.0	25.7 ± 2.7	103.3 ± 8.0
F_e (µmol CO_2 m^{-2} s^{-1})	−50.4 ± 9.8	−29.5 ± 18.6	−11.6 ± 1.6	−1.1 ± 0.8
F_{adv} (µmol CO_2 m^{-2} s^{-1})	–	−37.9 ± 6.1	–	–
F_{CO_2} (µmol CO_2 m^{-2} s^{-1})	50.7 ± 18.8	46.0 ± 27.2	37.2 ± 3.2	104.3 ± 8.0
F_{DECC} (µmol CO_2 m^{-2} s^{-1})	38.0 ± 0.8	45.0 ± 0.9	57.2 ± 1.1	133.5 ± 2.7

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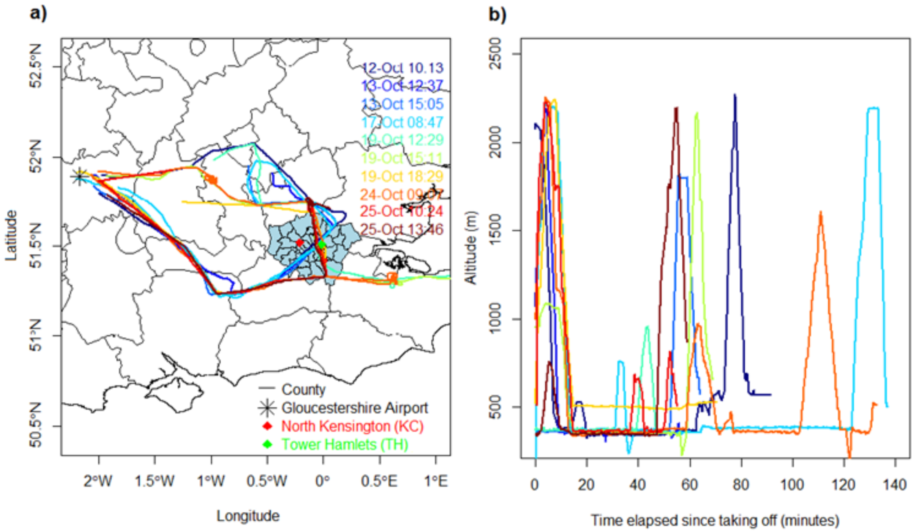

Fig. 1. (a) Flight tracks for 12 to 25 October 2011. Greater London (GL) is shaded in blue. **(b)** Altitude profiles for the flights tracks for the surveys. See **(a)** for key.

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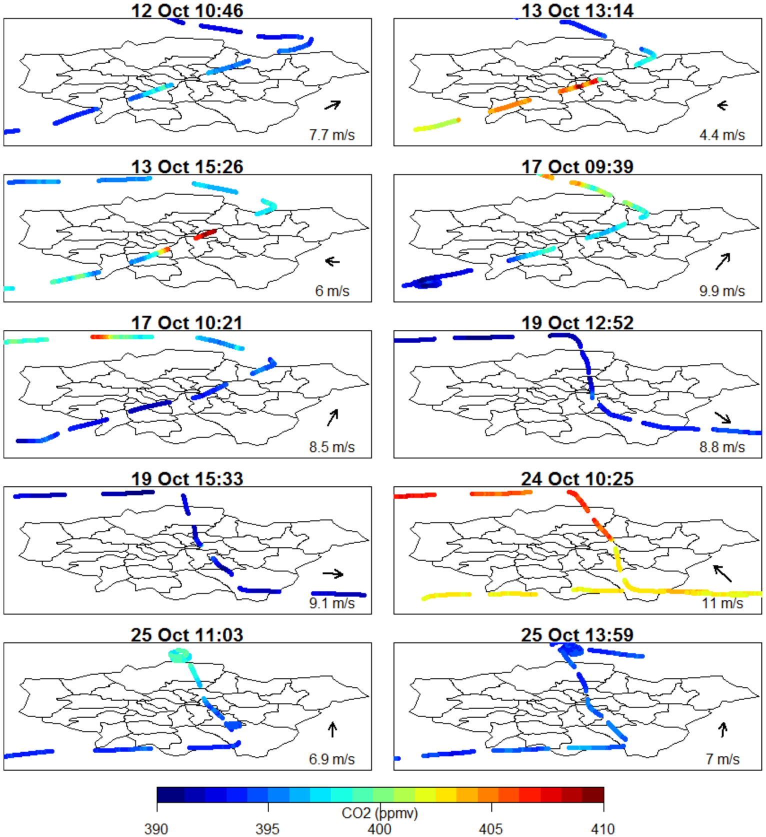

Fig. 2. CO_2 measured on each flight with mean speed and direction (arrow) measured onboard of the NERC-ARSF aircraft over GL. Time indicates the starting for the transect over GL.

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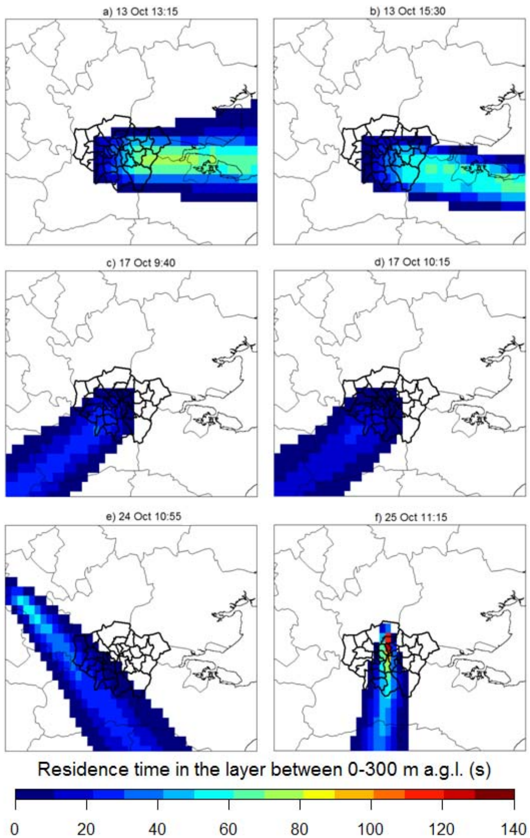

Fig. 3. Residence time in the layer 0–300 m a.g.l. for the air masses sampled over GL for the research surveys carried out in October 2011 as estimated by the Lagrangian Particle Dispersion Model FLEXPART.

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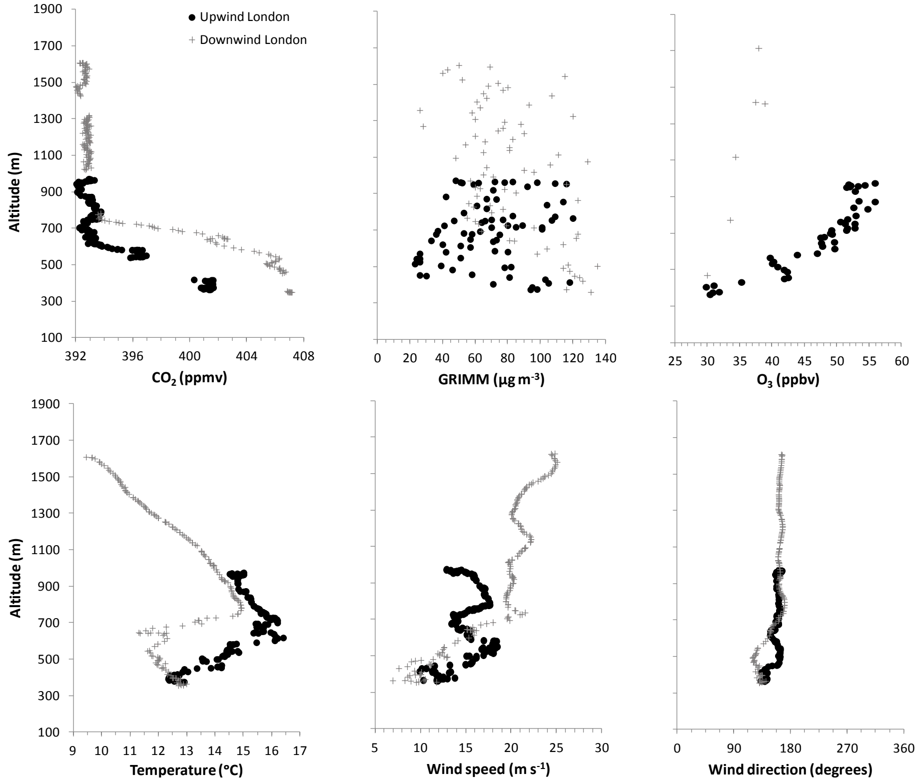

Fig. 4. Vertical profiles of atmospheric CO_2 mixing ratio (ppmv), particulate matter measured by the GRIMM sensor (µg m^{-3}), O_3 mixing ratios (ppbv), temperature (°C), wind speed (m s^{-1}) and wind direction (degrees) measured onboard of the NERC-ARSF aircraft for the 24 October 2011. Upwind London denotes the vertical profile measured upwind of Greater London (GL) at 10:15 UTC, and downwind London the vertical profile measured downwind of GL at 10:55 UTC.

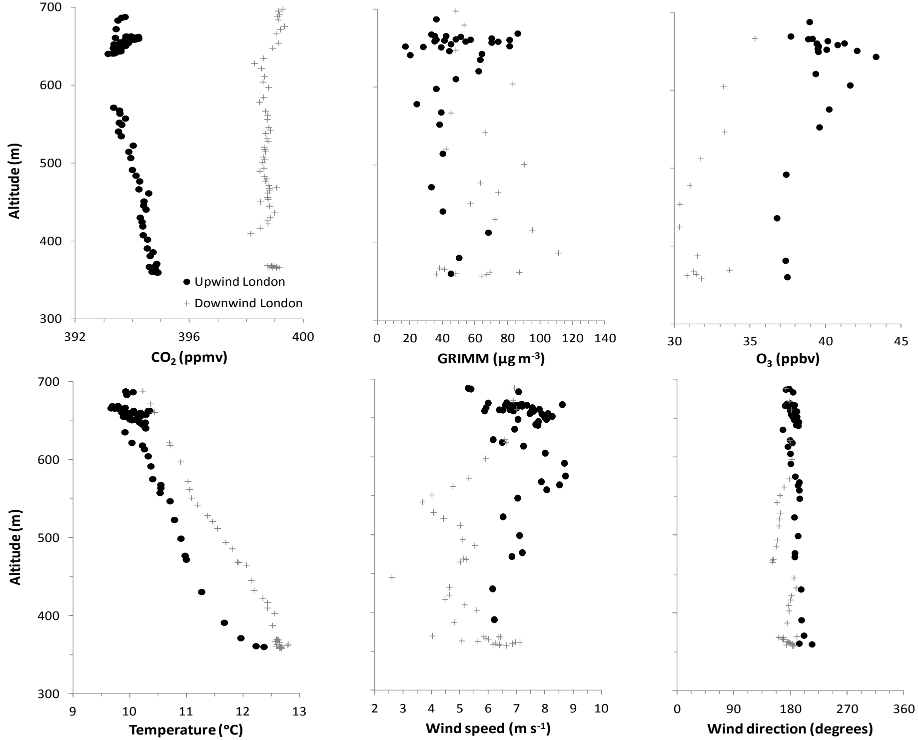

Fig. 5. Same as Fig. 4 but for the 25 October 2011. Upwind London denotes the vertical profile in south Greater London (GL) at 11:05 UTC, and downwind London the vertical profile at 11:15 UTC in north GL.

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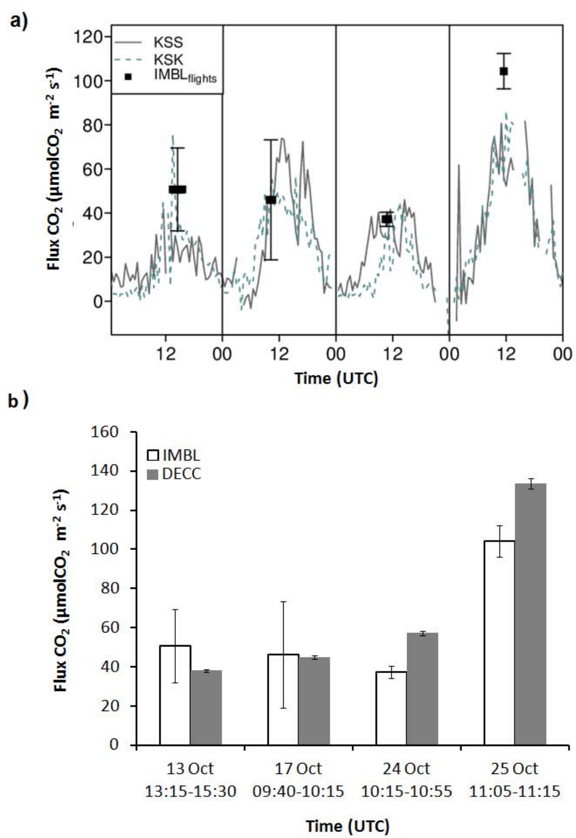

Fig. 6. (a) Time series of turbulent fluxes of CO_2 as observed at eddy covariance sites KSS and KSK in central London (lines) and estimates from the aircraft observations (rectangles). **(b)** Comparison of the surface fluxes calculated from aircraft observations (IMBL) against spatial integrated emissions as calculated from the DECC emissions inventory. Errors bars denote 1σ.