

# *Daytime CO<sub>2</sub> urban surface fluxes from airborne measurements, eddy-covariance observations and emissions inventory in Greater London*

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Accepted Version

Font, A., Grimmond, C. S. B., Kotthaus, S., Morgu, J. -A., Stockdale, C., O'Connor, E., Priestman, M. and Barratt, B. (2015) Daytime CO<sub>2</sub> urban surface fluxes from airborne measurements, eddy-covariance observations and emissions inventory in Greater London. *Environmental Pollution*, 196. pp. 98-106. ISSN 0269-7491 doi:  
<https://doi.org/10.1016/j.envpol.2014.10.001> Available at  
<https://centaur.reading.ac.uk/37905/>

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Published version at: <http://dx.doi.org/10.1016/j.envpol.2014.10.001>

To link to this article DOI: <http://dx.doi.org/10.1016/j.envpol.2014.10.001>

Publisher: Elsevier

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1 **Daytime CO<sub>2</sub> urban surface fluxes from airborne measurements, eddy-covariance observations and**  
2 **emissions inventory in Greater London**

3 A. Font<sup>1</sup>, C. S. B. Grimmond<sup>2</sup>, S. Kotthaus<sup>2,4</sup>, J.-A. Morgui<sup>3</sup>, C. Stockdale<sup>2</sup>, E. O'Connor<sup>2</sup>, M. Priestman<sup>1</sup> and B.  
4 Barratt<sup>1</sup>

5 1 MRC HPA Centre for Environment and Health, King's College London, 150 Stamford Street, SE1 9NH,  
6 London, UK

7 2 Department of Meteorology, University of Reading, Earley Gate, PO Box 243, Reading, RG6 6BB, UK

8 3 Institut Català de Ciències del Clima, Dr. Trueta 203, 08005, Barcelona, Spain

9 4 King's College London, Department of Geography, The Strand, WC2R 2LS, London, UK

10 Corresponding author: A. Font (anna.font\_font@kcl.ac.uk, telephone: +44 2078484018, fax: +44 2078484045)

11 **Abstract**

12 Airborne measurements within the urban mixing layer (360 m) over Greater London are used to quantify CO<sub>2</sub>  
13 emissions at the meso-scale. Daytime CO<sub>2</sub> fluxes, calculated by the Integrative Mass Boundary Layer (IMBL)  
14 method, ranged from 46 to 104 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> for four days in October 2011. The day-to-day variability of  
15 IMBL fluxes is at the same order of magnitude as for surface eddy-covariance fluxes observed in central  
16 London. Compared to fluxes derived from emissions inventory, the IMBL method gives both lower (by -37%)  
17 and higher (by 19%) estimates. The sources of uncertainty of applying the IMBL method in urban areas are  
18 discussed and guidance for future studies is given.

19 **Capsule:** CO<sub>2</sub> airborne-derived fluxes by Boundary Layer Mass balance are an independent measure of meso-  
20 scale urban fluxes complementing urban eddy-covariance fluxes and emissions inventory

21 **Key words:** carbon dioxide; urban fluxes; aircraft surveys; eddy covariance; megacity, emissions inventory

22 **1 Introduction**

23 Urban areas are responsible for 70% of greenhouse gas (GHG) emissions despite covering only 2% of the  
24 world's surface (IEA 2008). Knowledge of both concentrations and fluxes are needed to understand how urban  
25 emissions affect regional carbon exchanges (Duren and Miller 2012).

26 Measurements of urban atmospheric CO<sub>2</sub> concentrations are becoming a common means to study local GHG  
27 emissions and urban carbon cycles (Velasco and Roth 2010; Christen 2014). An enhancement of the CO<sub>2</sub>  
28 concentration of the urban canopy layer (UCL) is consistently observed in cities (e.g. Idso et al. 1998).  
29 However, urban CO<sub>2</sub> concentrations can show a high degree of spatial and temporal variability due to different  
30 local sources, atmospheric stability and observation locations (e.g. Pataki et al. 2006).

31 Observations of CO<sub>2</sub> fluxes by eddy covariance ( $F_{CO_2,EC}$ ) systems in urban areas have been proven to be a  
32 reliable tool to assess carbon exchanges at the neighbourhood or local-scale when conducted above the  
33 roughness sublayer (RSL) (e.g. Grimmond et al. 2002; Nemitz et al. 2002; Feigenwinter et al. 2012). Urban  
34 areas are a net source of CO<sub>2</sub> (positive fluxes) due to emissions from road traffic, electricity production and local  
35 heating with natural gas, oil or coal. Daytime fluxes can be reduced by uptake from vegetation during the  
36 growing season, but the nocturnal respiration source remains (Kordowski and Kuttler 2010; Crawford et al.  
37 2011; Ward et al. 2013). Where vegetation is scarce in cities, biogenic fluxes contribute little to the total net  
38 flux.

39 Diurnal concentrations of CO<sub>2</sub> vary within the boundary layer (BL) as a response to changes in surface  
40 emissions, boundary layer growth, entrainment processes and horizontal transport (advection). Taking into  
41 account the changing boundary layer (BL) volume and exchanges at its vertical and horizontal ‘boundaries’,  
42 meso-scale fluxes ( $10^2$ - $10^4$  km<sup>2</sup>) can be inferred from diurnal changes in CO<sub>2</sub> concentrations observed in the BL,  
43 using the Integrative Mass Boundary Layer (IMBL) method (McNaughton and Spriggs 1986; Raupach et al.  
44 1992; Denmead et al. 1996; Strong et al. 2011; Christen et al. 2014). The IMBL method has been applied over  
45 heterogeneous areas to calculate the mean regional CO<sub>2</sub> surface flux across, for example., the Amazonian basin  
46 (Lloyd et al. 2001, 2007) or an agricultural area in Spain (Font et al. 2010), while urban applications include  
47 nocturnal CO<sub>2</sub> and CH<sub>4</sub> emissions for Krakow (Poland) (Zimnoch et al. 2010) and turbulent sensible and latent  
48 heat fluxes in Sacramento (California, USA) (Cleugh and Grimmond 2001).

49 The aim of this study is to estimate top-down CO<sub>2</sub> emissions at the urban boundary layer (UBL) scale  
50 by the IMBL method using airborne observations taken in the UBL of Greater London (GL). This approach  
51 assumes that a representative urban CO<sub>2</sub> concentration can be calculated from a transect across a large area of  
52 the city or downwind of it. Results of the IMBL method are presented for four case study days, with a sensitivity  
53 analysis of the influence of different assumptions being made, and then compared to neighbourhood-scale eddy-  
54 covariance measurements and bottom-up emission inventory estimates. Conclusions from this study highlight

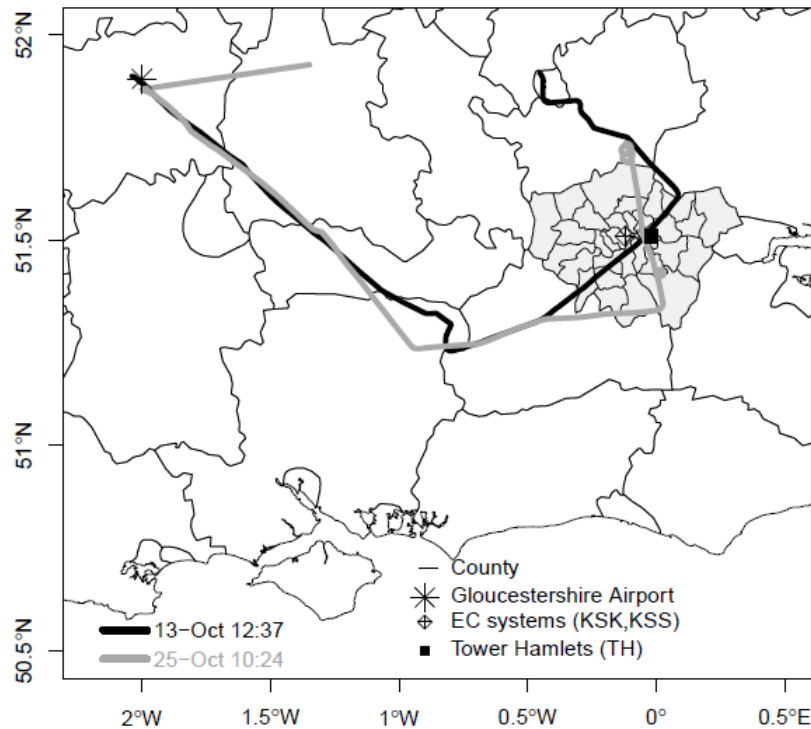
55 the applicability of such airborne observations to quantify CO<sub>2</sub> exchanges of a large city and also highlight the  
56 methodological challenges encountered.

## 57 **2 Methods**

### 58 **2.1 Instrumentation and survey design**

59 The NERC-ARSF aircraft provided the BL observations between the 12 and 25 October 2011 over  
60 South-East England (Table 1). The plane instrumented with an AIMMS-20 Air Data Probe (Aventech Research  
61 Inc.) measured temperature, barometric pressure, three components of wind speed and horizontal wind direction,  
62 with an instrument accuracy of 0.05°C (temperature), 0.1 kPa (pressure), 0.5 m·s<sup>-1</sup> (horizontal wind) and 0.75  
63 m·s<sup>-1</sup> (vertical wind) (Beswick et al. 2008). Atmospheric CO<sub>2</sub> dry mole fractions were measured with a non-  
64 dispersive infrared (NDIR) portable instrument, the CO<sub>2</sub> Airborne Analyzer System AOS Inc., at a frequency of  
65 0.5 Hz with a mean precision and accuracy of ±0.23 ppm and ±0.28 ppm, respectively (Font et al. 2008 provide  
66 further details). CO<sub>2</sub> concentrations were traceable to the International Standards (WMO-X2007 scale). An  
67 isokinetic aerosol intake fed the GRIMM 1.129 Sky-optical particle counter that measured particle mixing ratio  
68 in the size range 0.25-32 µm at a frequency of 0.17 Hz.

69 Flights passed over GL at a height of ~360 m above ground level. The air security authority permitted  
70 two paths: SW to NE and SSE to NNW (Fig. 1). Flight path directions were chosen from these options to be  
71 best aligned with the prevailing wind direction on the respective day. Vertical profiles (up to 2200 m) were  
72 undertaken: just after take-off, before landing and on the perimeter of GL (Fig. 1).



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Figure 1. Flight tracks for 13 and 25 October 2011. GL is shaded and symbols indicate site locations of relevant surface stations.

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UCL CO<sub>2</sub> mixing ratios were observed at Tower Hamlets ('TH'; 51.51°N, 0.02°W, 9.2 m agl) (Fig. 1) every 15 minutes from the LiCOR-820 NDIR analyzer. Two-point calibrations are carried out every 15 days with a zero-scrubber (soda lime) and a CO<sub>2</sub> span gas referenced to the International Scale (WMO-X2007).

79

80

Neighbourhood-scale turbulent surface fluxes ( $F_{CO_2,EC}$ ) were measured at two long-term eddy covariance (EC) sites in central London ('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) had sensors at 49 m (KSS) and 39 m agl (KSK), about 2.2 x and 1.9 x mean building height in the flux source area, respectively. At both KSS and KSK, the EC system consisted of a CSAT3 sonic anemometer (Campbell Scientific) and a Li7500/Li7500A open path infrared gas analyser (LiCOR Biosciences). The data were sampled at 10 Hz and fluxes calculated for 30 minute intervals. Data processing and quality control are described in Kotthaus and Grimmond (2012, 2013a).

87

## 88 2.2 Surface fluxes from aircraft observations

89

The Integrative Mass Boundary Layer (IMBL) method, used to calculate spatially and temporally

90

integrated urban CO<sub>2</sub> surface fluxes from the aircraft observations, treats the BL as a box with conserved scalars

91 (Denmead et al. 1996; Guenther et al. 1996). The variation of the mean mixed-layer CO<sub>2</sub> concentration  
 92 (expressed in μmolCO<sub>2</sub> m<sup>-3</sup>, [CO<sub>2</sub>]) in time ( $\partial[CO_2]/\partial t$ ) at the measurement height ( $h$ ) within the BL, also  
 93 known as storage flux ( $F_{sig}$ ), is the result of the surface flux ( $F_{CO_2,IMBL}$ ), entrainment ( $F_e$ ) and advection ( $F_{adv}$ ):

$$94 \quad h \frac{\partial[CO_2]}{\partial t} = F_{CO_2,IMBL} + F_e + F_{adv} \quad (1)$$

95  $F_e$  is a function of the difference in concentration in the air entrained from above ( $[CO_2]_+$ ), as the BL height ( $h_L$ )  
 96 changes in time ( $\partial h_L/\partial t$ ), under a vertical velocity ( $w_+$ ), and within the BL ( $[CO_2]$ ):

$$97 \quad F_e = \left( \frac{\partial h_L}{\partial t} - w_+ \right) ([CO_2]_+ - [CO_2]) \quad (2)$$

98  $F_{adv}$  is the product of the horizontal wind speed  $U$  and the spatial CO<sub>2</sub> gradient ( $\partial[CO_2]/\partial x$ ) at height  $h$ :

$$99 \quad F_{adv} = -h \left( U \frac{\partial[CO_2]}{\partial x} \right) \quad (3)$$

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

$$101 \quad F_{CO_2,IMBL} = \langle h \rangle \frac{[CO_2]_2 - [CO_2]_1}{t_2 - t_1} - \left( \frac{h_{L2} - h_{L1}}{t_2 - t_1} - w_+ \right) ([CO_2]_+ - \langle [CO_2] \rangle) + \langle h \rangle \langle U \rangle \left\langle \frac{\Delta[CO_2]}{\Delta x} \right\rangle \quad (4)$$

102 where  $\langle \rangle$  denotes temporal and spatial mean values, i.e.  $\langle [CO_2] \rangle$  is the mean concentration over the whole spatial  
 103 and temporal domain,  $[CO_2]_2$  and  $[CO_2]_1$  are the concentrations measured at times  $t_1$  and  $t_2$ , respectively, with  
 104 the respective mixing heights  $h_{L1}$  and  $h_{L2}$ , and  $w_+$  and  $[CO_2]_+$  refer to  $h_{L1}$  and  $t_1$ .  $\left\langle \frac{\Delta[CO_2]}{\Delta x} \right\rangle$  is calculated via linear  
 105 regression fit to  $[CO_2]$  measured at time  $t_1$  with distance when the plane track was perpendicular to the main  
 106 wind direction.

107  $[CO_2]$  is calculated from CO<sub>2</sub> mixing ratios, temperature and barometric pressure measurements by the  
 108 ideal gas law. Equation 4 is applied in two ways. The first approach assumes that the same temporal changes in  
 109 emission rates occur at different locations so that the relative spatial distribution of CO<sub>2</sub> is constant in time. In  
 110 this case temporal profiles of  $[CO_2]$  measured during the horizontal transects are used. Vertical profiles of CO<sub>2</sub>,  
 111 particulates, temperature, wind speed and direction at take-off and landing were used to examine the depth of  
 112 the BL and its changes in time. The second approach, the ‘‘column model’’ (Jacob, 1999), quantifies differences  
 113 in  $[CO_2]$  within vertical columns upwind and downwind of the city, both observed along vertical profiles. The  
 114 composition of the well-mixed column varies while travelling across the surface due to emissions within the  
 115 observational footprint.

116

### 117 **2.3. Spatial representativeness of the measurements**

118 To determine the likely source area of the BL observations used to calculate  $F_{CO_2,IMBL}$ , the Lagrangian  
119 Particle Dispersion Model FLEXPART (Stohl et al. 2005) was used in backward mode. Using urban roughness  
120 values, FLEXPART is driven by the ECMWF meteorological model with  $0.2^\circ \times 0.2^\circ$ , 91 vertical levels and 3 h  
121 resolution. Ten thousand particles were released from a box defined by the aircraft track (longitude, latitude and  
122 altitude) for each transect or profile. Each simulation runs back to midnight at the start of the flight day.  
123 Analysis at 5 min intervals ( $0.05^\circ \times 0.05^\circ$  spatial resolution) allows estimation of the mean residence time of the  
124 air in the layer 0 to 300 m agl that potentially influences the  $CO_2$  concentrations.

125 The source area for the local-scale  $F_{CO_2,EC}$  is calculated for both flux towers for every 30 min period  
126 using the Kormann and Meixner (2001) footprint model. Sources located within a radius of about 1000 m  
127 around the KSS site contribute to the turbulent fluxes, with the closest 300 m responsible for 50% of the impact  
128 (Kotthaus and Grimmond, 2013b). The source area at KSK is a bit smaller, and individual roughness elements  
129 can impact the observations at times when the EC system is within the RSL. The source areas of both sites are  
130 dominated by road surfaces and buildings, with only very little contribution from vegetation. Kotthaus and  
131 Grimmond (2012) provide further details on micro-scale emissions within the EC source areas.

132 The source area for the concentration observations within the RSL are not formally calculated, but it is  
133 known that the integration area is larger for concentrations than flux measurements (Schmid, 1994) and within  
134 the RSL individual roughness elements and sources/sinks are more influential than at larger scales. It can be  
135 assumed that the local-scale  $F_{CO_2,EC}$  footprints are larger than the concentration source areas in the RSL and that  
136 flow channelling may elongate the latter along the streets.

#### 137 **2.4 Emissions inventory for Greater London**

138 The Department of Energy and Climate Change reported annual  $CO_2$  emissions by Local Authority  
139 (LA) for 2011 (DECC, 2014), segregated into four main categories: industrial and commercial; domestic;  
140 transport; and land use change and forestry. The uncertainty of the inventory for the LAs in GL ranges from 1.6  
141 to 2.6% (MacCarthy, 2014).

142 To compare  $F_{CO_2,IMBL}$  with bottom-up fluxes ( $F_{CO_2,inv}$ ), the annual flux for GL in 2011 was scaled for  
143 the footprint area that influenced the airborne measurements as:

$$144 \quad F_{CO_2,inv} = \frac{E_{LA} * R_{t,LA}}{A_{GL} * \sum R_{t,LA}} \quad (5)$$



145 where  $E_{LA}$  are annual emissions for each LA ( $\text{ktCO}_2 \text{y}^{-1}$ ),  $R_{i,LA}$  is the residence time of air masses in  
 146 each LA based on the FLEXPART analysis, and  $A_{GL}$  is the area of influence over London. Temporal profiles  
 147 accounting for diurnal, day-of-week, and monthly variations of industrial and domestic emissions were  
 148 calculated from energy demand statistics. Variations of transport emissions were calculated from temporal  
 149 variations of roadside  $\text{NO}_x$  increments in London. Further details on how temporal profiles were calculated are  
 150 given in Appendix A.

### 151 3 Results

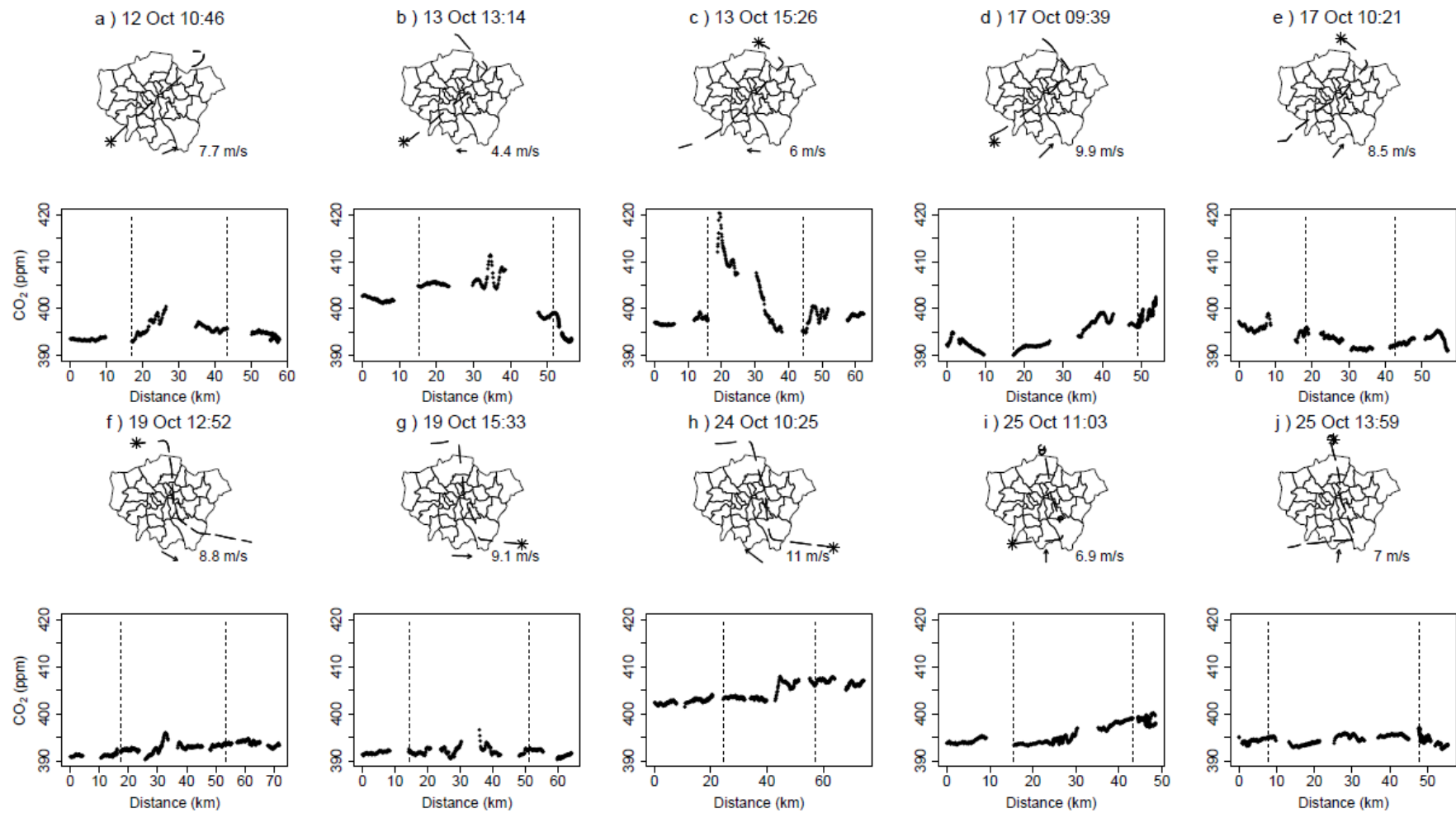
#### 152 3.1 $\text{CO}_2$ mixing ratio observations

153 The spatial variability of  $\text{CO}_2$  within and beyond the GL UBL during each flight is shown in Fig. 2. For lower  
 154 wind speed conditions ( $<8 \text{ m s}^{-1}$  at 360 m), higher  $\text{CO}_2$  mixing ratios were measured over central London, with  
 155 peaks at 400.5 ppm (12 October 2011), 421.5 ppm (13 October) and 399.1 ppm (25 October), compared to  $\sim 394$ -  
 156 398 ppm outside the GL area (Figure 2). With higher wind speed conditions ( $>8 \text{ m s}^{-1}$ ), the differences in  
 157 average mixing ratio within and surrounding GL were within the instrument noise (e.g. 17, 24 October) (Table  
 158 1). However, for these conditions the maximum measured  $\text{CO}_2$  mixing ratio in the mixing layer (407.2 and  
 159 409.5 ppm for 17 and 24 October, respectively) was registered downwind of GL at a distance of 29 km (17  
 160 October) and 48 km (24 October) from central GL (Fig. SB1).

161

162 Table 1. Mean wind speed (U), mean ( $\pm 1$  standard deviation  $\sigma$ ), maximum and inter-quartile range (IQR) of  $\text{CO}_2$  mixing  
 163 ratios measured onboard the NERC-ARSF aircraft during the transects across GL (inGL) in October 2011 and  
 164 surrounding GL (outGL) below 400 m.

| Date, time of flight (UT) | U inGL ( $\text{m s}^{-1}$ ) | $\text{CO}_2 \pm 1\sigma$ inGL (ppm) | Max $\text{CO}_2$ inGL (ppm) | IQR $\text{CO}_2$ inGL (ppm) | $\text{CO}_2 \pm 1\sigma$ outGL (ppm) |
|---------------------------|------------------------------|--------------------------------------|------------------------------|------------------------------|---------------------------------------|
| 12 Oct 10:46              | 7.7                          | $396.1 \pm 1.6$                      | 400.5                        | 1.9                          | $392.8 \pm 1.1$                       |
| 13 Oct 13:14              | 4.4                          | $404.4 \pm 3.3$                      | 411.4                        | 1.2                          | $397.5 \pm 3.4$                       |
| 13 Oct 15:26              | 6.0                          | $405.1 \pm 7.5$                      | 421.8                        | 12.6                         | $398.2 \pm 3.3$                       |
| 17 Oct 09:39              | 9.9                          | $395.1 \pm 2.8$                      | 399.2                        | 5.1                          | $394.9 \pm 3.5$                       |
| 17 Oct 10:21              | 8.5                          | $392.8 \pm 1.4$                      | 396.1                        | 2.3                          | $393.5 \pm 3.4$                       |
| 19 Oct 12:52              | 8.8                          | $392.8 \pm 0.9$                      | 395.9                        | 0.9                          | $392.3 \pm 1.6$                       |
| 19 Oct 15:33              | 9.1                          | $392.1 \pm 0.9$                      | 396.6                        | 1.1                          | $391.3 \pm 0.7$                       |
| 24 Oct 10:25              | 11.0                         | $404.4 \pm 1.6$                      | 407.9                        | 2.7                          | $404.4 \pm 1.9$                       |
| 25 Oct 11:03              | 6.9                          | $395.3 \pm 1.7$                      | 399.1                        | 2.6                          | $394.3 \pm 0.9$                       |
| 25 Oct 13:59              | 7.0                          | $394.9 \pm 1.0$                      | 397.0                        | 1.3                          | $393.7 \pm 0.8$                       |



165

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Figure 2. (Upper) Aircraft flight path over GL starting at location marked by \*, with mean wind speed and direction (arrow) measured over GL. Time indicates the start of the transect over GL.

167

(Lower) Measured CO<sub>2</sub> mixing ratios with distance from the indicated start point; vertical dashed lines indicate locations of GL boundary.

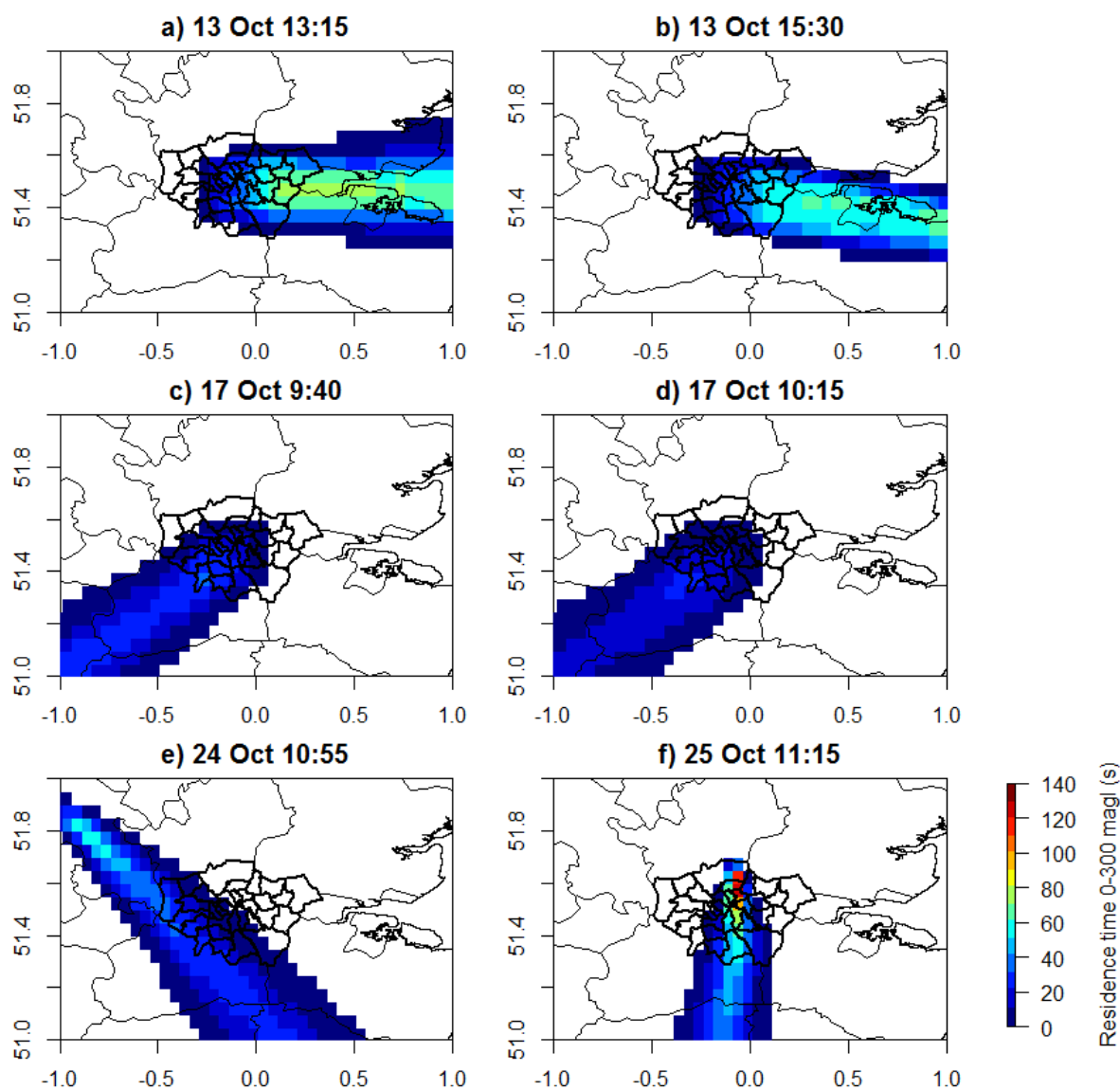
## 168 3.2 IMBL CO<sub>2</sub> fluxes in Greater London

169 Time and space integrated  $F_{CO_2,IMBL}$  for GL were calculated for 13, 17, 24 and 25 October when all  
170 terms of the IMBL budget could be identified and quantified. The two IMBL approaches outlined (Section 2.2)  
171 were each applied for two of the case study days. First, temporal variations of the mean [CO<sub>2</sub>] measured along  
172 the transects over GL were used to calculate surface fluxes on 13 and 17 October. Second, downwind profiles  
173 were compared to upwind references on 24 and 25 October. Given sufficient data were not available, the IMBL  
174 method could not be applied to 12 October (only one transect measured), and 19 October (advection could not be  
175 quantified as the flight track was perpendicular to the main wind direction under high wind speeds, see Fig. 2).

### 176 3.2.1 CO<sub>2</sub> fluxes calculated from horizontal transects

177 The mean wind speed at 360 m over GL on 13 October was  $4.4 \pm 1.1$  m s<sup>-1</sup> (morning) and  $6.0 \pm 1.2$  m s<sup>-1</sup>  
178 (afternoon). Visual inspection of vertical profiles showed a well-mixed BL reaching up to a height of 735 m  
179 (morning) and at 1180 m (afternoon; Fig. SC1). The flight track flew over the TH site. Mixing ratios measured  
180 within the UCL were similar to those measured at 360 m: 405.6 ppm (TH) and 404.4 ppm (aircraft) at 13:15  
181 UTC; 407.7 ppm (TH) and 405.1 ppm (aircraft) at 15:30 UTC, suggesting efficient mixing between the ground  
182 and flight altitude. The  $F_{CO_2,IMBL}$  estimate for this period (13:15 UTC to 15:30 UTC) was  $50.7 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ .  
183 According to the FLEXPART model, the probable source area of the airborne observations covered 71% of GL

184 and included the east (residence time of air 60-80 s) and central boroughs (~20 s) (Fig. 3a,b).



185

186 Figure 3. Air residence time in the layer 0-300 m above ground level (agl) estimated by FLEXPART for flights used in

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IMBL calculations (Table 2).

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193 Table 2. Values used to calculate the space and time integrated CO<sub>2</sub> urban-regional scale flux ( $F_{CO_2,IMBL}$ ) in GL using the  
 194 IMBL budget method.  $F_{stg}$  is the storage flux,  $F_e$  the entrainment flux and  $F_{adv}$  the advection term.  $F_{CO_2 inv}$  is the  
 195 emissions estimated by DECC (2014).

|   | 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 <sub>2</sub> ( $t_1$ ) (ppm)   | 404.4  | 394.8               | 401.4  | 394.6  |
| CO <sub>2</sub> ( $t_2$ ) (ppm)   | 405.1  | 392.8               | 406.7  | 398.7  |
| CO <sub>2+</sub> (ppm)  | 391.3  | 390.0               | 401.0  | 394.1  |
| <CO <sub>2</sub> > (ppm)  | 404.7  | 393.7               | 401.4  | 394.6  |
| $h_1$ (m)   | 735    | 400                 | 410    | 450    |
| $h_2$ (m)   | 1180   | 1130                | 480    | 450    |
| $w_+$ (mm s <sup>-1</sup> )   | -2.5   | -0.18               | -2.2   | -5.6   |
| <U> (m s <sup>-1</sup> )  | 4.5    | 9.9                 | ---    | ---    |
| $\langle \frac{\Delta[CO_2]}{\Delta x} \rangle$ ( $\mu\text{mol CO}_2 \text{ m}^{-2}$ ) | ---    | $1.1 \cdot 10^{-2}$ | ---    | ---    |
| $F_{stg}$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )                        | 0.3    | -21.5               | 25.7   | 103.3  |
| $F_e$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )                            | -50.4  | -29.5               | -11.6  | -1.1   |
| $F_{adv}$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )                        | ---    | -37.9               | ---    | ---    |
| $F_{CO_2,IMBL}$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )                  | 50.7   | 46.0                | 37.2   | 104.3  |
| $F_{CO_2 inv}$ ( $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ )                   | 42.7   | 54.5                | 60.4   | 145.1  |
| Area GL covered (%)   | 71     | 56                  | 50     | 30     |

196  
 197 Vertical profiles of temperature in the morning of 17 October indicated inversion layers at 390-436 m  
 198 and at 460-500 m (Fig. SC2). This translated into a decrease in the CO<sub>2</sub> mixing ratios with altitude: ~401.5 (TH)  
 199 and 395.1 ppm (aircraft). Later that day (11:56 UTC) the UBL attained 1130 m so that CO<sub>2</sub> mixing ratios were  
 200 observed to be vertically homogenous below the cruise altitude (392.3 ppm at TH, 392.8 ppm at 360 m). Given  
 201 the strong wind speed conditions and the flight track parallel to the main wind flow (Fig. 2), the 17 October was  
 202 the only case study day when it was possible to calculate  $\langle \frac{\Delta[CO_2]}{\Delta x} \rangle$  from Eq. 3 and  $F_{adv}$  (Table 2).  $F_e$  was negative  
 203 as air masses with less concentration than below were entrained and CO<sub>2</sub> was lost by advection.  $F_{stg}$  was  
 204 negative due to the expansion of the UBL in time. At  $46.0 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$   $F_{CO_2,IMBL}$  was in the same order of  
 205 magnitude as on 13 October. The source area coincides with large parts of GL (65%), encompassing areas in  
 206 central and south-west GL (Fig. 3c,d).

### 207 3.2.2 CO<sub>2</sub> fluxes calculated from upwind and downwind vertical profiles

208 On 24 and 25 October, strong wind speed conditions and the prevalent wind direction allowed  
 209 Lagrangian observations of two vertical profiles, one upwind and the other downwind of GL. An increase of the  
 210 CO<sub>2</sub> mixing ratio was observed in the downwind profiles compared to those upwind by 4-5 ppm (Fig. SC3,  
 211 SC4).

212 Strong winds from the SE ( $12 \text{ m s}^{-1}$ ) were measured over GL at 360 m altitude on 24 October. Both the  
213 vertical profiles upwind and downwind of GL revealed large  $\text{CO}_2$  mixing ratios of  $>400$  ppm at low altitudes  
214 ( $<500$  m), with a sharp decrease to lower values (391 ppm) above a capping inversion. The strong inversion  
215 conditions on that day might have resulted in a residual layer with large  $\text{CO}_2$  mixing ratios. The height of the  
216 lowest inversion layer increased from 410 m (upwind) to 460 m (downwind). The derived flux  $F_{\text{CO}_2, \text{IMBL}}$  was  
217 similar in range to 13 and 17 October ( $37.2 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  between 10:10 and 10:57). The probable source  
218 area covered is 60% of GL with an emphasis of western parts (Fig. 3e).

219 On 25 October wind speeds were  $7 \text{ m s}^{-1}$  with a prevailing flow from the south. Given no strong  
220 inversion was present, absolute mixing ratios were lower than on the preceding day and remained below  
221 400 ppm. There was an increase of  $\sim 4$  ppm from the upwind to the downwind locations but the very low  
222 entrainment flux as no changes in the UBL height were considered (Fig. SC4), translated to a very high  $F_{\text{CO}_2, \text{IMBL}}$   
223 estimate of  $104.3 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  between 11:05 and 11:15. The source area was estimated to be smaller than  
224 on the other case study days, covering only 30% of the GL including areas in north, central and south London  
225 (Fig. 3f).

### 226 3.2.3 Sensitivity analysis of $F_{\text{CO}_2, \text{IMBL}}$

227 Sensitivity analyses allow quantification of the impact of values used within  $F_{\text{CO}_2, \text{IMBL}}$  calculations.  
228 Assuming uniform temporal changes, the spatial variability of  $[\text{CO}_2]$  at 360 m across GL relates to the  
229 differences in emissions at different locations (Table 1, Fig. 2). On one case study day (13 October), the  
230 standard deviation of  $[\text{CO}_2]$  measured along the transects were as high as 7.5 ppm and the inter-quartile range  
231 (IQR) reached up to 12.6 ppm. This spatial variation in mixing ratio suggests that there may have been a series  
232 of internal BL across GL and horizontal mixing did not have enough time to create a representative spatial  
233 pattern at the flight height (360 m). Standard deviation and IQR were generally lower for the other case studies  
234 (Table 1). As the  $[\text{CO}_2]$  values used to calculate  $F_{\text{CO}_2, \text{IMBL}}$  are critical, the variation of  $\text{CO}_2$  along the transect was  
235 used to assess the accuracy of the flux calculated. Other variables that are used for the  $F_{\text{CO}_2, \text{IMBL}}$  calculations are:  
236 mixing layer height, vertical velocity at the top of the UBL and temporal and spatial homogeneity of the  
237 background concentration. The impact of potential uncertainties in these components on the total uncertainty of  
238 the integrated boundary layer  $\text{CO}_2$  flux are assessed from the horizontal transects over the urban area and both  
239 upwind and downwind vertical profiles (Table 3).

240

241 Table 3. Sensitivity of  $F_{CO_2,IMBL}$  to data used in the analysis.  $mean [CO_2]_a$ : average mixing ratio from aircraft observations;  
 242  $mean [CO_2]_{a+s}$  average mixing ratio from aircraft and urban canopy layer;  $5^{th} p [CO_2]_a$ : 5<sup>th</sup> percentile mixing ratio  
 243 from aircraft observations;  $95^{th} p [CO_2]_a$  95<sup>th</sup> 95<sup>th</sup> percentile mixing ratio from aircraft observations;  $h+50m$  and  
 244  $h+100m$  refer to mixing layer height determined from visual inspection from profiles carried outside GL plus 50 and  
 245 100 m, respectively;  $no w_+$  and  $2 \cdot w_+$  refer to zero and double vertical wind speed above the mixing layer,  
 246 respectively;  $F_{adv,t_2}$  refers to advection term calculated using the spatial gradient at  $t_2$ . The median value and range  
 247 (maximum-minimum) for the fluxes for each day are also given.

| Method                          | $F_{CO_2,IMBL}(\mu molCO_2 m^{-2} s^{-1})$ |        |        |        |
|---------------------------------|--|--------|--------|--------|
|                                 | 13 Oct                                     | 17 Oct | 24 Oct | 25 Oct |
| $mean [CO_2]_a$                 | 50.7                                       | 46.0   | 37.2   | 104.3  |
| $mean \{[CO_2]_{a+} [CO_2]_s\}$ | 49.2                                       | 34.9   | ---    | ---    |
| $5^{th} p [CO_2]_a$             | 30.7                                       | 41.6   | 34.5   | 133.8  |
| $95^{th} p [CO_2]_a$            | 82.3                                       | 70.7   | 33.6   | 89.0   |
| $h + 50 m$                      | 56.1                                       | 48.0   | 42.8   | 136.8  |
| $h + 100 m$                     | 61.4                                       | 50.0   | 51.4   | 171.7  |
| $no w_+$                        | 47.5                                       | 46.0   | 33.6   | 100.8  |
| $2 \cdot w_+$                   | 54.0                                       | 46.0   | 45.2   | 146.3  |
| $F_{adv,t_2}$                   | ---  | 24.7   | ---    | ---    |
| Median $F_{CO_2}$               | 52.4                                       | 46.0   | 37.2   | 133.8  |
| Range $F_{CO_2}$                | 51.6                                       | 46.0   | 17.8   | 82.7   |

248  
 249 To evaluate the impact of horizontal spatial variability of  $[CO_2]$  on  $F_{CO_2,IMBL}$ , the mean values are  
 250 replaced with the 5<sup>th</sup> and 95<sup>th</sup> percentile of  $[CO_2]$ , respectively (Table 3). The resulting  $F_{CO_2,IMBL}$  varied from  
 251 30.7 to 82.3  $\mu molCO_2 m^{-2} s^{-1}$  (13 October) and from 41.6 to 73.0  $\mu molCO_2 m^{-2} s^{-1}$  (17 October). Use of these  
 252 extreme  $[CO_2]$  values generates a difference of up to 60% in the flux relative to that calculated from the mean  
 253  $[CO_2]$ .

254 Aircraft measurements at 360 m might not capture the vertical gradient within the whole UBL.  $CO_2$   
 255 mixing ratios measured at TH were used to calculate  $F_{CO_2,IMBL}$ .  $F_{CO_2,IMBL}$  decreased from 50.7 (aircraft) to 49.2  
 256  $\mu mol CO_2 m^{-2} s^{-1}$  (aircraft+TH) (13 October), and from 46.0 (aircraft) to 34.9  $\mu mol CO_2 m^{-2} s^{-1}$  (aircraft+TH)  
 257 (17 October). Heterogeneity in the vertical domain in the UBL represent a change of 3% (13 October) and 25%  
 258 (17 October) from  $F_{CO_2,IMBL}$  calculated from the mean  $[CO_2]$  in the transects.

259 Similarly, to evaluate the impact of the variability of the  $[CO_2]$  in the air column for fluxes calculated  
 260 from upwind-downwind profiles, the 5<sup>th</sup> and 95<sup>th</sup> percentile values of  $[CO_2]$  were used. This resulted in an  
 261 increase of  $F_{CO_2,IMBL}$  to 33.6  $\mu mol CO_2 m^{-2} s^{-1}$  (using the 5<sup>th</sup> percentile) and to 34.5  $\mu mol CO_2 m^{-2} s^{-1}$  (95<sup>th</sup>

262 percentile) on 24 October (increase of ~56%). Whereas on 25 October, using the 5<sup>th</sup> percentile values of [CO<sub>2</sub>]  
263 fluxes were 89.0 (decrease of 15%) but the 95<sup>th</sup> percentile resulted in a higher flux of 133.8 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>  
264 (increment of 28%). Unfortunately, UCL measurements of CO<sub>2</sub> directly below the vertical profiles were not  
265 available. However, the comparison of observations within the UCL with aircraft measurements near TH reveals  
266 that CO<sub>2</sub> mixing ratios hardly differed: 400 ppm (TH) and 400-402 (aircraft) on 24 October; 396 ppm (TH) and  
267 395 ppm (aircraft) on 25 October. This indicates the CO<sub>2</sub> field below the aircraft was well-mixed, so little  
268 variation in  $F_{CO_2,IMBL}$  would be expected.

269 The advection term can be an important part of the CO<sub>2</sub> budget. Without transects parallel to the main  
270 wind direction (13 October) the spatial variability of CO<sub>2</sub> and therefore advection could not be quantified.  
271 Assuming that the spatial gradient measured on 17 October was the same as on 13 October, the estimated  
272 advection flux is 1.6 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> or a probable error in  $F_{CO_2,IMBL}$  of 4% from omitting advection for that  
273 day. However, for days with higher wind speeds (e.g. 17 October), omission of the advection term could  
274 represent an error of ~80%.

275 The uniformity in time of the spatial gradient might also be a source of uncertainty for the advection  
276 term. If the spatial gradient on 17 October was calculated at time  $t_2$ , the  $F_{CO_2,IMBL}$  would decrease by ~50%  
277 calculated to 24.7 μmolCO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>.

278 BL heights were estimated from profiles outside of London. Spanton and Williams (1988) found that  
279 the BL height in London could be 50-100 m higher than at a rural site. This in accordance with the difference  
280 found between the BL heights from the ceilometer at central London and from vertical profiles for the 24  
281 October (day when backscattered data from ceilometer were clearly detected, Appendix C).  $F_{CO_2,IMBL}$  calculated  
282 with a BL 100 m higher resulted in larger fluxes by 21% (13 October), 5% (17 October), 38% (24 October) and  
283 68% (25 October) compared to previous calculations. This test underlines the critical impact of the mixing  
284 height on CO<sub>2</sub> exchanges within the UBL.

285 As the small vertical velocity at the BL height is difficult to measure reliably from aircraft (Stull, 1988;  
286 Beswick et al. 2008), the sensitivity of  $F_{CO_2,IMBL}$  to errors in  $w_+$  were examined assuming  $w_+=0$  and doubling the  
287 observed  $w_+$ . Using the former ( $w_+=0$ )  $F_{CO_2,IMBL}$  decreases by 6.4% (13 October), 0.1% (17 October), 10% (24  
288 October), 3.3% (25 October). Whereas the latter (doubling) increases  $F_{CO_2,IMBL}$  by 6.4% (13 October), 21% (24  
289 October) and 40% (25 October).



290 The entrainment flux is also be affected by the determination of  $[CO_2]_+$ . In this study we have used the  
291 concentration just above the mixing layer in vertical profiles undertaken outside GL, assuming that this  
292 concentration is spatially homogenous for the area between the city and the location of the vertical profile, and  
293 also for the integration time used in the IMBL calculations. Ideally, measurements of the entrainment  
294 concentration above the UBL would be used.

295 The range of  $F_{CO_2,IMBL}$  was lower (50-80% the median value) for fluxes calculated from upwind-  
296 downwind profiles compared to the range of fluxes from horizontal transects over the city (100%). However,  
297 this is as expected as single pairs of vertical profiles sample a limited area of the urban region (30-50%)  
298 compared to the area covered by horizontal transects (60-70%).

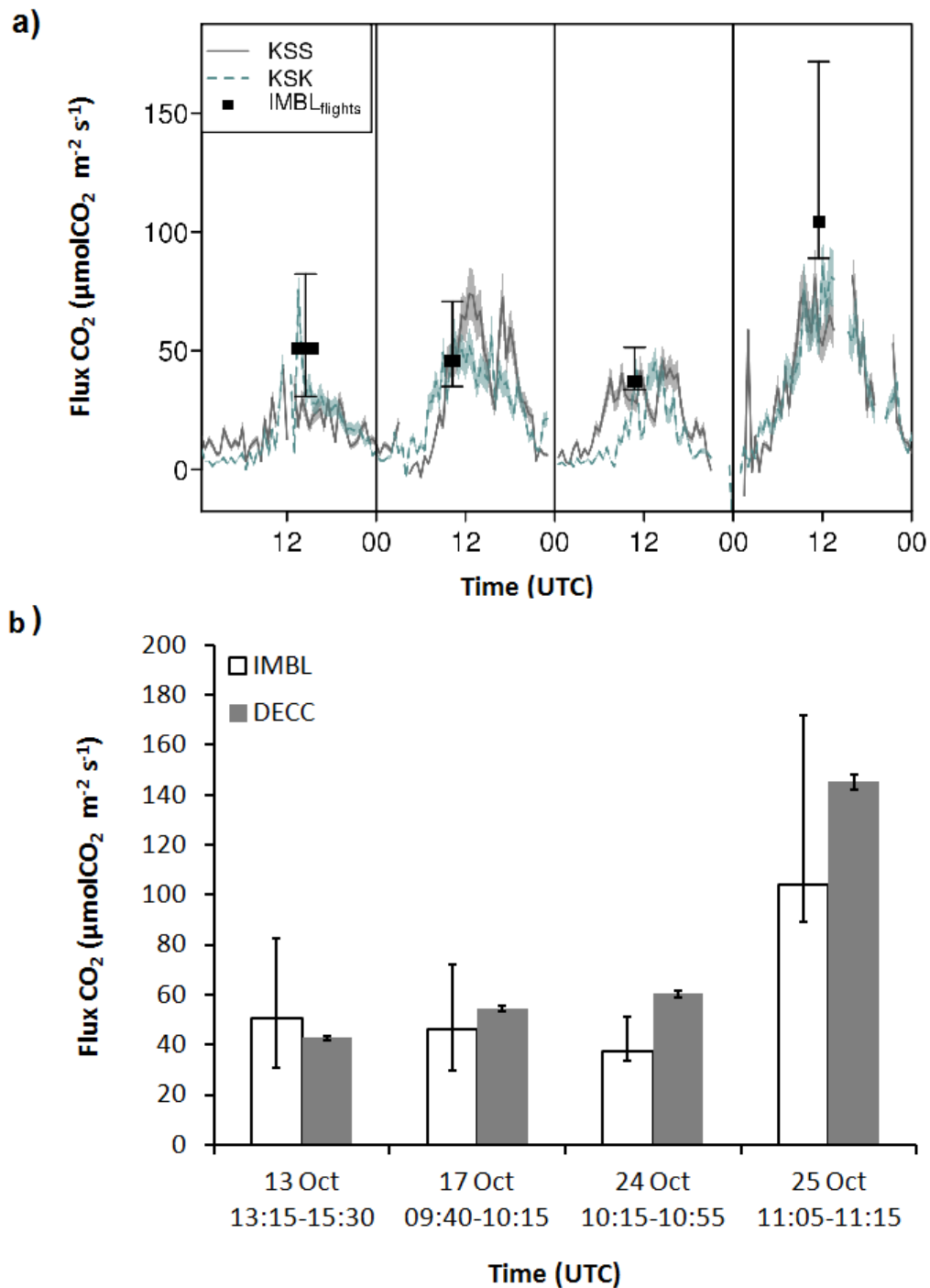
299 Our sensitivity analysis suggests that horizontal variability of the  $CO_2$  field in the UBL, observed here  
300 by transects, is the most critical factor affecting  $F_{CO_2,IMBL}$ . The determination of the BL height and vertical wind  
301 speed has more impact on  $F_{CO_2,IMBL}$  from upwind-downwind profiles.

302

### 303 3.2.4 $CO_2$ surface fluxes in Greater London

304 Aircraft-based  $F_{CO_2,IMBL}$  and tower-based  $F_{CO_2,EC}$  have complementary spatial and temporal resolutions  
305 and limitations (Lloyd et al. 2007; Desai et al. 2011). With two EC systems in central London, the intra-site  
306 variability in the  $F_{CO_2,EC}$  could be assessed (Fig 4a). The lower KSK site (smaller source area) is expected to be  
307 dominated by processes at the building-scale, while the taller KSS site is representative of the neighbourhood-  
308 scale (Kotthaus and Grimmond, 2013b) and  $F_{CO_2,IMBL}$  represent a larger area ( $10^2$ - $10^4$  km<sup>2</sup>) and integrate  
309 processes at the city-scale.

310 Although direct comparison of  $F_{CO_2,EC}$  and  $F_{CO_2,IMBL}$  is not necessarily warranted given the lack of  
311 immediate correspondence, Levy et al. (1999) argue that results should be within the same range and show  
312 similar variation day-to-day. On 17 and 24 October,  $F_{CO_2,EC}$  and  $F_{CO_2,IMBL}$  have similar magnitude at the times  
313 when IMBL were calculated (Figure 4a), while the  $F_{CO_2,IMBL}$  is higher than the observed surface flux on 13  
314 October and even more clearly so (by at least  $20 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) on 25 October. These discrepancies may be  
315 explained partly by the uncertainties inherent in the IMBL method (Table 3), but the EC measurements may also  
316 underestimate the turbulent flux (as noted by Kotthaus and Grimmond 2013b). In terms of day-to-day variations,  
317 the EC and IMBL method both indicate similarly strong fluxes on 13, 17 and 24 October and also agree in  
318 estimating the largest fluxes on the 25 October.



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Figure 4 (a) Time series of turbulent fluxes of CO<sub>2</sub> as observed at eddy covariance sites KSS and KSK in central London (lines) and estimates from the aircraft observations (rectangles). The EC errors are shaded assuming  $\pm 15\%$  error on the 30 mins fluxes based on Euster et al. (1997), Dragoni et al. (2007) and Richardson et al. (2012) (b) Comparison of the surface fluxes calculated from aircraft observations (IMBL) against spatially integrated emissions as calculated from the DECC emissions inventory. Error bars on IMBL fluxes denote maximum and minimum values.

327 The annual CO<sub>2</sub> emissions for GL in 2011 were 18.3 μmolCO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> (DECC, 2014). Scaling the  
328 footprint area for temporal variations of the emissions, IMBL fluxes are within -37% (24 October) and 19% (13  
329 October) of the DECC emissions. The differences between the  $F_{CO_2,IMBL}$  and  $F_{CO_2,inv}$  on 24 October may relate to  
330 the  $F_{CO_2,IMBL}$  footprint area encompassing large areas outside GL (Fig. 3e) and/or the uncertainty in the temporal  
331 scaling.

332 Day-to-day differences in  $F_{CO_2,IMBL}$  are partly attributed to variations in the flux source area given that  
333 IMBL fluxes were calculated for similar times (except for 13 October). The DECC annual  $F_{CO_2,inv}$  has a  
334 concentric pattern: central GL boroughs have emissions of 50-350 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>, surrounding centre  
335 boroughs 25-50 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>, and outer boroughs <25 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>. The highest  $F_{CO_2,IMBL}$  (October 25)  
336 was found when the footprint area encompassed the high emission central boroughs. Although the 17 October  
337 footprint also sampled central London, the calculated air residence times were shorter (10-30 s, Fig. 3c,d) (25  
338 October, 70-140 s, Fig. 3f) and the probable footprint included the lower emission area of south-west GL. On 24  
339 October the probable footprint extended over the outer boroughs to the west and south-west of GL (average  
340 annual emissions <25 μmolCO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>).

341

#### 342 **4 Discussion and conclusions**

343 Here we have presented four airborne surveys that measured CO<sub>2</sub> mixing ratios in the UBL of GL in  
344 October 2011 that were used to estimate urban-scale emissions by quantifying boundary layer growth,  
345 entrainment processes and horizontal transport. The top-down inverse IMBL method infers temporally and  
346 spatially integrated fluxes that can be used to evaluate emissions inventories at policy-relevant scales such as  
347 cities, megacities, and oil and gas fields. Previously, this approach has been used to infer nocturnal fluxes of  
348 GHG with a single ground-level measurement site (Zimnoch et al. 2010), but inclusion of anthropogenic  
349 emissions for critical daytime activities was missing. Entrainment and advection fluxes are usually not  
350 considered in the calculations based on ground-level observations due to a lack of measurements at the top of  
351 the BL and the spatial gradient of CO<sub>2</sub>. However, as shown in this study, the entrainment term (13 October) and  
352 advection (17 October) terms can be large fractions of the urban carbon budget. Observations from light aircraft  
353 characterize different parts of the budget to permit calculation of integrated regional surface CO<sub>2</sub> fluxes at larger  
354 scales than ground-level observations. Complementary aircraft surveys characterizing entrainment, vertical  
355 mixing and spatial heterogeneity in the UBL add value to continuous measurements at ground-level (Strong et

356 al., 2011). However, aircraft observations are time-limited (e.g. plane time, flight path access) and weather-  
357 biased, so represent case studies.

358 The IMBL fluxes had similar day-to-day variability to both the central London eddy-covariance  
359 observations and the scaled (temporal, spatial) emissions inventory data. The IMBL fluxes are the same order as  
360 the eddy-covariance observations and within -37% to 19% of the emissions inventory. Thus the IMBL method  
361 appears to provide an additional independent estimate of city-scale fluxes to complement neighbourhood-scale  
362 eddy-covariance fluxes and emissions inventory data.

363 The sensitivity tests undertaken suggest differences of the order of 100% in  $F_{CO_2,IMBL}$  consistent with  
364 other city-scale fluxes derived from aircraft measurements using mass-balance approaches (e.g. for GHG Mays  
365 et al. 2009; Turnbull et al. 2011, NO<sub>x</sub> emissions Trainer et al. 1995). However, changes in UBL CO<sub>2</sub>  
366 concentration along large city transects may challenge city-wide emission quantification as this was the main  
367 source of uncertainty for IMBL fluxes. Atmospheric transport and surface exchange are continuous, creating a  
368 dynamic, complex picture in large cities that can hardly be resolved in short-term airborne campaigns (Gioli et  
369 al. 2014). This suggests that in a megacity such as London it may be necessary to consider internal boundary  
370 layers (IBL) within the city. The atmosphere above the outer boroughs, which are more extensive and typically  
371 have shorter roughness elements (e.g. buildings), may be well mixed, but over the central business district areas  
372 where the buildings are much taller the BL at the flight height may be the IBL for that area rather than the fully  
373 mixed UBL. Thus more detailed knowledge of the BL dynamics over urban areas is critical. Moreover, the rate  
374 of emission along a transect may temporally vary producing spatial variations of CO<sub>2</sub> within the UBL.

375 Downwind [CO<sub>2</sub>] enhancements above the background concentration are more representative of the  
376 mix of emissions taking place in the urban environment. A single pair of upwind-downwind profiles does not  
377 sample the entire urban area (Fig. 3e,f). In order to overcome this, multiple downwind profiles should be  
378 sampled in future surveys.

379 Footprint analysis allows identification of the areas potentially contributing to CO<sub>2</sub> concentrations in  
380 the UBL. Emissions from the inventory have been scaled for the footprint of airborne measurements and it  
381 might be a source of uncertainty. For better comparison of emissions and IMBL fluxes, meso-scale modelling  
382 such as the proposed by Brioude et al. (2013) could enhance better spatial scaling of the fluxes.

383 Anthropogenic and biogenic fluxes are inherently included in  $F_{CO_2,EC}$  and  $F_{CO_2,IMBL}$ , whereas biogenic  
384 fluxes are missing from the  $F_{CO_2,inv}$  fluxes. The role of vegetation varies with amount (e.g. Helfter et al. 2011),  
385 but generally in urban areas it plays a small role in the CO<sub>2</sub> budget (Crawford et al. 2011, Strong et al. 2011;

386 Newman et al. 2013). In London the vegetation varies by size (age) and type across the city (Lindberg and  
387 Grimmond 2011). By October the role of vegetation is likely small during the daytime relative to urban sources  
388 even in suburban areas with a large amount of vegetation (Ward et al. 2013). To distinguish the anthropogenic  
389 signal, fast-response measurements of urban pollutants (e.g. NO<sub>x</sub>, CO) as tracers of traffic-related emission and  
390 isotopic analysis of carbon (e.g. <sup>13</sup>C/<sup>12</sup>C-CO<sub>2</sub>, Δ<sup>14</sup>CO<sub>2</sub>) would aid interpretation. An emissions ratio approach  
391 (e.g. Turnbull et al. 2011) would allow apportionment and identification of the sectors emitting more CO<sub>2</sub> into  
392 the atmosphere and thus facilitate evaluation of policy effectiveness to reduce the contribution of GHG  
393 emissions from urban areas.

394

### 395 **Acknowledgements**

396 The flights were undertaken as part of the ClearLo project funded by the Natural Environment  
397 Research Council (NERC) and coordinated by the National Centre for Atmospheric Science (NCAS). The  
398 flights surveys were supported by the NERC-ARSF grant (GB11-05). We would like to thank the crew and the  
399 operations team of the ARSF team. We extend our thanks to Rebecca Fisher at Royal Holloway University of  
400 London (RHUL) for the calibration to the NOAA standards of the references used for the surface monitoring  
401 sites. We are grateful to the Lab of the Atmosphere and the Oceans from the Institut Català de Ciències del  
402 Clima (LAO-IC3) for the airborne CO<sub>2</sub> instrument and in-flight standards and the insightful comments of  
403 reviewers which improved the paper. The research was supported by the National Institute for Health Research  
404 (NIHR) Biomedical Research Centre based at Guy's and St Thomas' NHS Foundation Trust and King's College  
405 London and NERC ClearLo (NE/H003231/1).

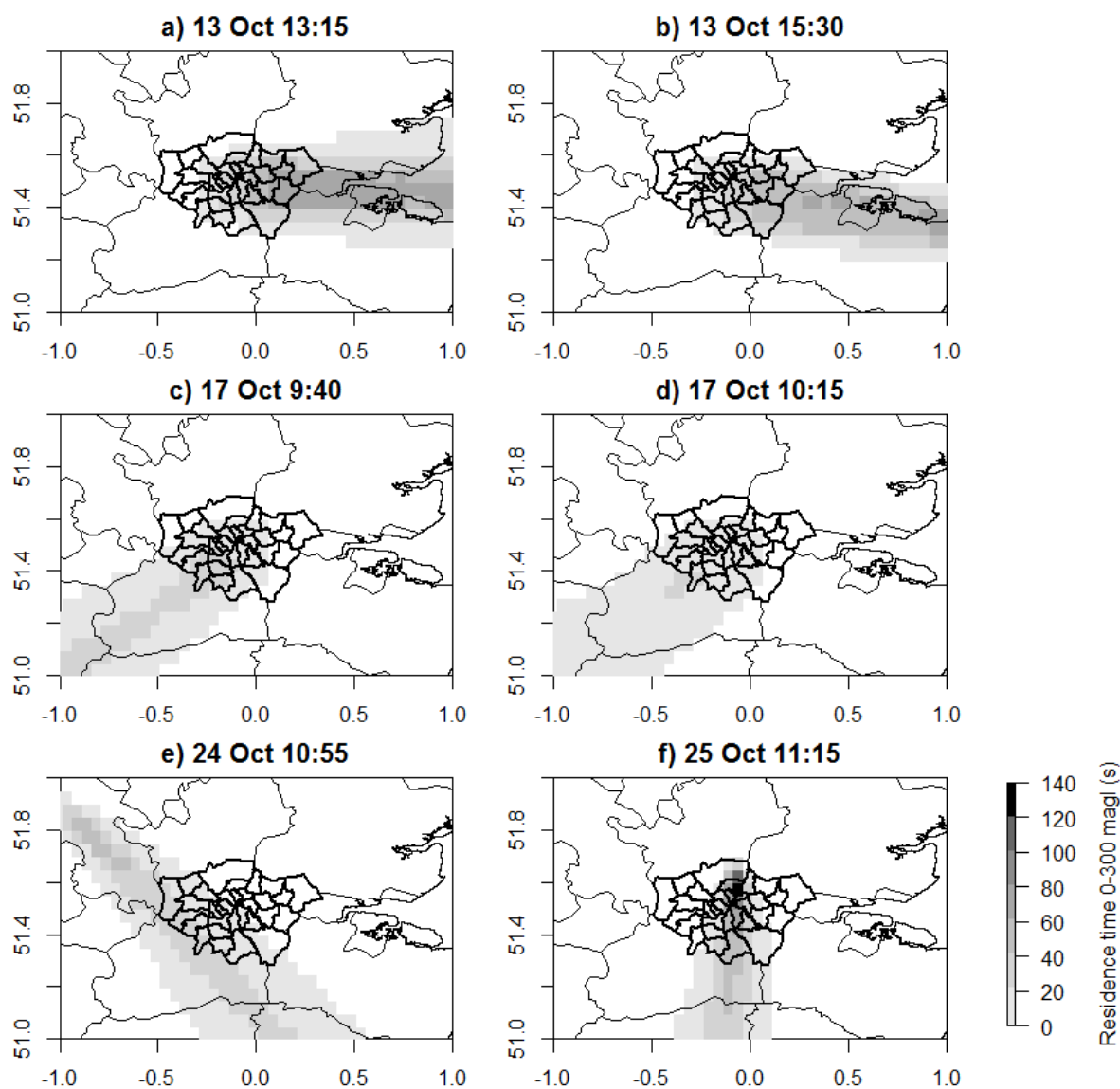
### 406 **Figures**

407 Fig. 1: B&W (print version)

408 Fig. 2: B&W (print version)

409 Fig. 3: B&W (print version), Colour (web version)

410 Fig. 4: B&W (print and web version)



411

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Figure 3 in B&W for print version

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