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Key Points:
- Inflow and outflow from Greater London characterized using airborne measurements
- Mass balance approach used to determine area fluxes
- Comparisons made with surface and inventory estimates

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Area fluxes of carbon dioxide, methane, and carbon monoxide derived from airborne measurements around Greater London: A case study during summer 2012

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Abstract Airborne measurements of thermodynamic properties and carbon dioxide (CO_2), methane (CH_4), and carbon monoxide (CO) mole fractions were recorded on board the FAAM BAe-146 UK research aircraft and used to characterize the inflow and outflow from Greater London on 30 July 2012. All three trace gases were observed to be significantly enhanced downwind of Greater London with spatially resolved plumes of comparable extent and position. A mass budget calculation using a box model approach (and uncertainty propagation) was used to determine net regional fluxes of 21 ± 3 μmol CO_2 m^{-2} s^{-1}, 0.13 ± 0.02 μmol CH_4 m^{-2} s^{-1}, and 0.12 ± 0.02 μmol CO m^{-2} s^{-1} for Greater London. These fluxes are comparable with simultaneous surface observations and previous studies in urban environments. A comparison was made with the 2010 UK National Atmospheric Emissions Inventory (NAEI), and fluxes from this study are found to be factors 2.3 for CO_2 and 2.2 for CO larger than those estimated by the spatially disaggregated NAEI (2011) for Greater London. Fluxes of CH_4 were found to be a factor 3.4 larger than the UK NAEI (2009). The efficacy of this mass balance approach, in general, is also discussed in terms of key assumptions and uncertainties, and we offer advice for future studies on how uncertainties could be reduced.

1. Introduction

The importance of climate change has led to growing pressure on nation states to agree to reductions in greenhouse gas emissions (e.g., the Kyoto Protocol and the Copenhagen accord). Significant economic and political penalties may be imposed if these reductions are not met. The UK government in particular created the 2008 Climate Change Act to reduce CO_2 equivalent emissions to 80% of 1990 levels by 2050, having previously signed the Kyoto protocol agreeing to a 12.5% reduction of the 1990 baseline between 2008 and 2012.

Emissions of greenhouse gases and other pollutants can be estimated using an inventory or "bottom-up" approach, whereby activity rates and statistics for each source type (e.g., fuel burnt) are extrapolated to total emissions using emission factors (emission per unit activity) [*Gurney et al.*, 2009]. However, incomplete and imperfect monitoring of activity rates together with the associated interannual, seasonal, and even intraday variability in emission factors for each polluting activity can result in large total uncertainties [*van Leeuwen and van der Werf*, 2011]. These uncertainties have been calculated to be larger than the targeted emission reductions themselves [*Peylin et al.*, 2011; *Lindley et al.*, 2000].

Urban areas have been reported to be a significant net source of the major long-lived greenhouse gases. Source types in urban areas are diverse; for CO_2 and CO these are dominated by combustion sources due to energy production and transport, while for CH_4 in addition to combustion, natural gas infrastructure, landfills, and wastewater treatment, all cause significant emissions [*Grimmond et al.*, 2002; *Nemitz et al.*, 2002; *Moriwaki and Kanda*, 2004; *Vogt et al.*, 2006; *Famulari et al.*, 2010; *Helfter et al.*, 2011; *Peischl et al.*, 2013]. Despite only accounting for a small proportion of the Earth's surface, urban regions are estimated to account for approximately 70% of worldwide fossil fuel CO_2 emissions. And with the level of urbanization projected to rise with global population, city-scale emissions are of increasing global significance [*Duren and Miller*, 2012].

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A particular focus of scientific interest in recent years has been so-called megacities; these are cities with populations greater than 10 million and are some of the largest and densest sources of greenhouse gases and other pollutants [e.g., *Hopkins et al.*, 2009; *Molina et al.*, 2010; *Kort et al.*, 2012; *Lopez et al.*, 2013; *McMeeking et al.*, 2012]. The anthropogenic CO_2 source from these cities has been found to far outweigh any uptake from the local urban biosphere [*Newman et al.*, 2013]. As a result of the large number of strong anthropogenic sources within cities, these are areas that need to be especially targeted by "top-down" approaches. Top-down methods can provide an independent measurement constraint to inform and validate these inventories and emission reductions, whereby atmospheric observations are used to directly measure emissions [*Nisbet and Weiss*, 2010; *Polson et al.*, 2011; *Wennberg et al.*, 2012]. Cities are well suited to this approach because of the typically high density of sources they contain means that the resulting enhancement in greenhouse gases and other pollutants can usually be clearly identified over the local background.

A variety of measurement platforms have been employed to study emissions and thermodynamics in urban environments. These include ground-based [*McKain et al.*, 2012], tall tower [*Helfter et al.*, 2011], airborne [*Kalthoff et al.*, 2002; *Mays et al.*, 2009], and both ground- [*Wunch et al.*, 2009] and space-based remote sensing [*Kort et al.*, 2012]. These measurements can then be used to derive top-down fluxes using either tracer-tracer ratios [*Wennberg et al.*, 2012], the eddy covariance method [*Nemitz et al.*, 2002; *Nordbo et al.*, 2012], mass balance techniques (see section 2.3), or through inverse or adjoint modeling [*Brioude et al.*, 2012]. Each of these approaches has its own set of unique advantages and limitations (e.g., in spatial and/or temporal representivity), and the efficacy and accuracy of many of these methods remains the subject of scientific debate. Often, combinations of these methods can yield more robust constraint of uncertainty, but this often requires specialist field campaigns and tailored analysis. In summary, there is no singular or routine method from which to provide top-down evaluation of emissions at the urban scale at present. Such approaches have previously been used to verify national and regional inventories [*Biraud et al.*, 2000; *Schmidt et al.*, 2001; *van der Laan et al.*, 2009]. However, a number of studies have identified significant discrepancies when compared with inventories [*Bergamaschi et al.*, 2009; *Wunch et al.*, 2009; *Levin et al.*, 2010; *Peischl et al.*, 2012; *Karion et al.*, 2013]. Ideally, for a direct comparison with anthropogenic inventories, anthropogenic CO_2 needs to be spatially disaggregated from uptake by the biosphere. This remains challenging at the urban scale, and many of the measurement-led studies listed above necessarily report aggregate net emissions as a result.

This paper presents a pilot study examining the efficacy of using airborne measurements to determine emissions from a megacity, for the purpose of constraining the uncertainties in emission inventories and the upscaling of surface observations. Airborne measurements were collected on board the UK's Facility for Airborne Atmospheric Measurement (FAAM) BAe-146 research aircraft on 30 July 2012 around the Greater London conurbation, UK. By applying a mass budget approach to measurements of the inflow and outflow from this region (and constraining with known uncertainties resulting from measurement error and assumptions implicit to box modeling), we are able to derive regional-scale fluxes of CO_2, CH_4, and CO from Greater London (and their corresponding uncertainties).

2. Methodology

Airborne measurements used in this study were recorded on board the FAAM BAe-146 research aircraft. We also make use of ground-based CO_2 and CH_4 eddy covariance flux measurements in Central London on the British Telecon (BT) Tower, recorded as part of the Clear Air for London (ClearfLo) campaign. This section describes instrumentation used (section 2.1) and provides a description of the 30 July 2012 flight (section 2.2) that has been used here to determine fluxes using the mass balance approach described in section 2.3.

2.1. Instrumentation

Measurements of CO_2 and CH_4 dry air mole fractions on board the FAAM BAe-146 were determined through cavity-enhanced absorption spectroscopy (Model RMT-200, Los Gatos Research Inc., USA). For a detailed description of this system and the associated experimental procedures see *O'Shea et al.* [2013]. In-flight calibrations were performed using "high" and "low" mole fraction gas standards, which are traceable to the WMO-X2007 and NOAA 2004 measurement scales for CO_2 and CH_4, respectively [*Dlugokencky et al.*, 2005; *Zhao and Tans*, 2006]. Uncertainty with reference to a "target" calibration gas standard was calculated at 0.17 ppm for CO_2 and 1.31 ppb for CH_4. At a 1 Hz sampling rate, 1σ repeatability was found to be ± 0.70 ppm for CO_2

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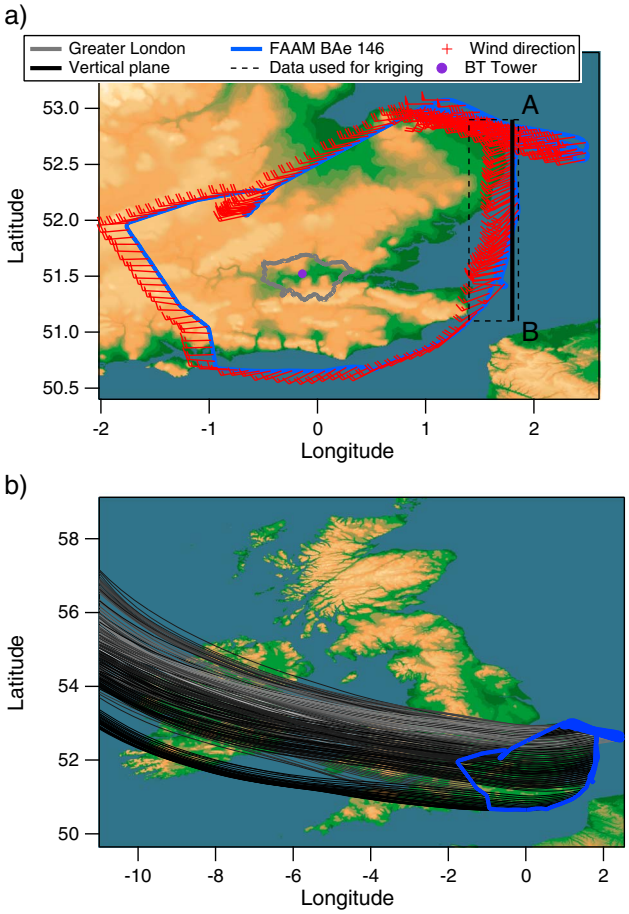

Figure 1. (a) The FAAM BAe-146's flight track around Greater London, UK, on the 30 July 2012 (8:55 to 13:34 GMT). Wind speed and direction are from the in situ measurements on the aircraft. Fluxes are calculated through the vertical plane that spans from point A to B (black line, 200 km) using the observations within the dashed box. (b) HYSPLIT back trajectories that are started at 60 s intervals along the FAAM BAe-146's flight track when it was below an altitude of 2000 m show a consistent westerly flow across Southern England.

and ± 2.37 ppb for CH_4 (for the period 20 July 2012 to 23 September 2013). Measurements of CO were made using vacuum ultraviolet florescence spectroscopy (AL5002, AeroLaser GmbH, Germany). The repeatability of the 1 Hz CO measured mole fraction was ± 1.5 ppb at 150 ppb, and the total instrumental uncertainty is estimated at 2% [*Gerbig et al.*, 1999]. Ambient temperature was measured using a Rosemount/Goodrich-type 102 total air temperature sensor, with uncertainty of 0.3 K. Ambient pressure was measured with uncertainty of 0.3 hPa, and the 3-D wind vectors were measured in situ using a five-hole turbulence probe mounted on the nose of the aircraft with uncertainty of 0.2 m s^{-1} [see *Petersen and Renfrew*, 2009; *Allen et al.*, 2011]. Eddy covariance and mole fraction measurements of CO_2 and CH_4 were also made in Central London at a height of 192 m on the BT Tower (51.5215°N, 0.1387°W) using a cavity ring down spectrometer (G2301-f, Picarro Inc., USA). The measurement height was approximately 22 times higher than the mean building height within the local area (10 km). The exception to this is Canary Wharf located 8–10 km east-south-east of the tower where there are buildings that are up to 235 m. For a complete description of the BT Tower measurement setup and local environment see *Helfter et al.* [2011, 2013].

2.2. The 30 July 2012 Flight

On the 30 July 2012 (Flight number B724) the FAAM BAe-146 conducted a flight out of Cranfield, UK, to determine fluxes of CO_2, CH_4, and CO from the Greater London metropolitan area in the buildup to the opening ceremony of the London 2012 Olympic Games. The flight formed two closed loops around Greater London (Figure 1a) taking off at 8:55 GMT and landing at 13:35 GMT. Sampling was predominantly within the planetary boundary layer (PBL) or immediately above to survey its vertical structure and extent. In situ measurements of the wind direction showed a consistent westerly airflow across the sampling domain (Figure 1a), at approximately 9 m s^{-1}. This is also shown by HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model [*Draxler and Rolph*, 2003] back trajectories, which were calculated at 60 s intervals along the FAAM BAe-146's flight track (Figure 1b), and show a 5 day maritime Atlantic air mass history for air arriving at the upwind measurement area. The consistency of this airflow, and its relatively well mixed and relatively clean (maritime) air mass history, over the measurement domain and over the UK mainland, lends itself well to a case study using a mass budget approach (see section 2.3).

Meteorological conditions during the flight were characterized by high pressure over continental Europe and low pressure centered to the northwest of the UK, giving rise to the observed westerly airflow across Southern England. Frontal systems and precipitation associated with the low-pressure center did not reach the UK mainland during the flight, and the weather during the flight was characterized by predominantly

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clear skies with little fair weather cumulus due to the presence of a strong capping inversion. Some high-level cirrus ahead of the frontal systems was noted on the western leg of the flight track shown in Figure 1. Ground-based ceilometer measurements were made at three locations, spanning from Detling (51.2833°N, 0.5833°E) to North Kensington (51.4833°N, 0.1667°W) in Central London to Chilbolton (51.1569°N, 1.4387°W), which is approximately 150 km to the west. These measurements suggest that throughout the 31 July 2012, the PBL depth was generally between 500 and 750 m (not shown) (S. Grimmond, personal communication, 2013).

2.3. Mass Balance Approach

The relatively large-surface footprint of the FAAM BAe-146 measurements (in terms of the last point of surface contact of air sampled aloft) can allow net fluxes for the whole of Greater London to be determined with careful characterization of the measurement environment and the measurements themselves. To derive regional-scale fluxes from the airborne measurements, we employ a mass budget approach. Such methods have previously been applied to determine emissions from both points [*Ryerson et al*., 1998; *Karion et al*., 2013] and diffuse sources, such as from urban centers [*White et al*., 1976; *Kalthoff et al*., 2002; *Hopkins et al*., 2009; *Mays et al*., 2009].

For mass budget methods to be applicable, the spatial extent of the urban plume needs to be measured and characterized as it is advected through a vertical plane perpendicular to the prevailing wind. To be useful, the approach requires dense, rapid, or repeated sampling throughout this vertical plane from which to build a sample to enable accurate contouring of trace gas mole fractions. Also, implicit in this technique are accurate measurements of wind through the plane from which to derive a planar flux and good characterization of the background mole fraction (i.e., the mole fraction upwind of the source region) from which to derive the representative atmospheric enhancement as air passes over the source region. A similar method to that used in this study has been applied to determine CO_2 and CH_4 fluxes from Indianapolis [*Mays et al*., 2009; *Cambaliza et al*., 2013]. The method does not necessarily require the species of interest to be well mixed vertically throughout the PBL (so long as there is sufficient sampling as is the case here), as is often assumed when applying mass budget approaches [e.g., *Ryerson et al*., 1998; *Karion et al*., 2013; *Hopkins et al*., 2009; *White et al*., 1976].

Crosswind legs were performed downwind (east) of London at different altitudes to sample the horizontal and vertical extent of the London plume. These transects below a height of 1600 m were projected onto a vertical-latitudinal plane approximately perpendicular to the prevailing wind vector (westerly). This plane is shown in Figure 1a as line A (1.80°E, 52.90°N) to B (1.80°E, 51.10°N). The projection is performed using the point of closest approach to the line AB [*Kalthoff et al*., 2002]. All measurements projected onto this plane were made within the dashed box in Figure 1a; Figure 2a shows the flight tracks projected onto this plane.

The discrete data points are then interpolated onto a regular grid, with each grid box 10 km and 50 m in horizontal and vertical extent, respectively (Figure 2b). The interpolation method is performed using the kriging methodology described in detail and applied by *Mays et al*. [2009] using the MATLAB "EasyKrig3.0" program [*Chu*, 2004]. In situ measurements on the FAAM BAe-146 of CO_2, CH_4, CO, pressure, temperature, and the 3-D wind vector are all interpolated in this manner. The flux (mol s^{-1}) of a species S through AB can then be found using

$$\text{Flux} = \int_0^z \int_A^B \left(S_{ij} - S_0\right).n_{ij} U_{\perp ij}\, \mathrm{d}x\, \mathrm{d}z \tag{1}$$

where S_{ij} is the mole fraction (mol mol^{-1}) of species S for each coordinate on the vertical plane AB (Figure 1a). S_0 is the background, which is calculated as the mean mole fraction west of London below 1600 m (upwind). This assumes a well-mixed homogeneous background that is representative of all downwind measurements. The n_{ij} term is the kriged mole density of air (mol m^{-3}), which is determined using an ideal gas assumption and the kriged pressure and temperature measurements on the FAAM BAe-146. The $U_{\perp ij}$ (m s^{-1}) term is the kriged wind speed perpendicular to AB. Fluxes are then integrated over the vertical (the surface to 1600 m altitude) and horizontal (AB) extent of the plane to calculate a total flux through this plane.

3. Results and Discussion

As might be expected, CO_2, CH_4, and CO were all enhanced downwind of London compared to their respective upwind background. This is shown in Figure 2 for CO_2, where there is a peak mole fraction of 399.1 ppm compared to a mean background (term S_0 in equation (1)) of 385.8 (±1.4 at 1σ) ppm, an enhancement of ~3%. Similar behavior

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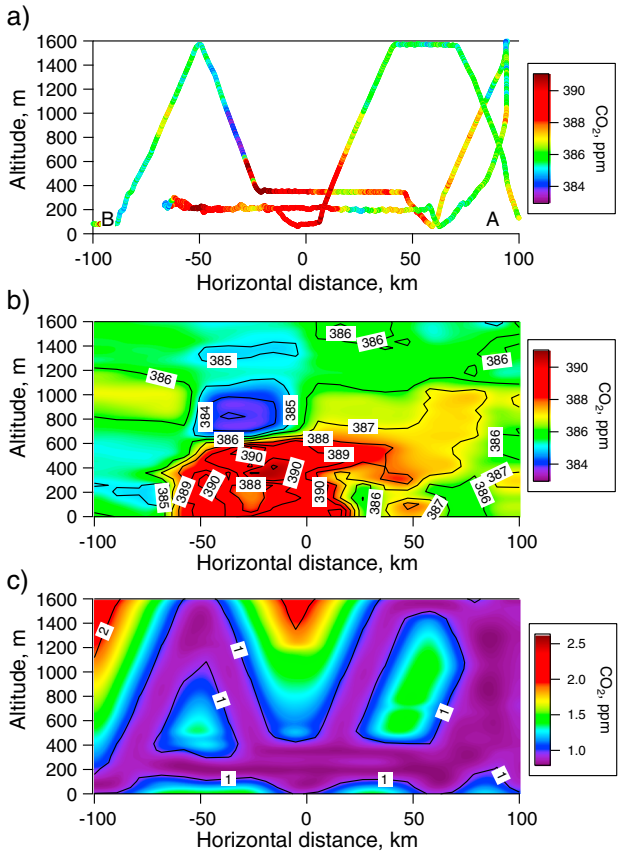

Figure 2. CO_2 measurements downwind of London on the vertical plane AB (shown in Figure 1). (a) The discrete flight tracks shown have been interpolated over the two-dimensional plane using a kriging methodology. (b) The total CO_2 flux through this plane can be determined using equation (1). (c) The sum in quadrature of both the kriging uncertainty (1σ) and the analytical uncertainty.

is exhibited in CH_4 (Figure 3) with a peak enhancement of 73 ppb (~4%) over a mean background of 1883 (±8 at 1σ) ppb, and in CO (Figure 4), which was up to 30 ppb (~31%) greater than a mean background of 96 (±5 at 1σ) ppb. These peak mole fractions are comparable with those observed in Central London; mean mole fractions on the BT Tower for the 30 July 2012 were 391.7 ppm (range 381.4 ppm to 401.3 ppm) for CO_2 and 1911 ppb (range 1866 ppb to 1975 ppb) for CH_4 (Table 1).

The kriged downwind data for all three trace gases define a plume of comparable extent and location, centered at approximately 51.82°N (−20 km horizontal distance, Figures 2–4), with ~50 km horizontal extent and largely below a height of 700 m. Correlation coefficients calculated for the fluxes through each grid cell for all three species were found to be strongly positively correlated (CO_2:CH_4 $R^2 = 0.82$, CO_2:CO $R^2 = 0.85$, and CH_4:CO $R^2 = 0.75$). This may be because they share common source types (e.g., combustion) or may be a result of mixing from various source types during transport from broadly colocated sources [e.g., *Crounse et al.*, 2009]. The integrated fluxes through the plane AB were found to be 38,453 ± 3346 mol CO_2 s^{-1}, 264 ± 16 mol CH_4 s^{-1}, and 253 ± 11 mol CO s^{-1} (Table 2). A discussion of the uncertainties in these fluxes will be given in section 3.2.

3.1. Air Mass History

The sampling of the London plume occurred during two periods: 10:00 to 10:30 GMT and 12:00 to 13:00 GMT. On both occasions the plume was estimated to be between 4 and 5 h old (assuming Central London was the source) calculated using the wind measurements on the FAAM BAe-146. This is further supported by HYSPLIT back trajectories, where a plume age of 3 to 5 h was found. This would suggest that during the first loop around London, the plume may have originated just before typical rush hour (07:00 to 09:00 GMT), while for the second loop it originated during rush hour proper (07:00 to 10:00 GMT). However, there were no significant differences in observed mole fractions between the two periods. We are therefore not able to deconvolve intraday variability and assume constant fluxes throughout the measurement period. For future studies, the plume should ideally be sampled closer to source when it is less dispersed, resulting in a shorter measurement period. This was not possible for this study due to strict air traffic restrictions in force for the London 2012 Olympics.

To examine the spatial extent of the London plume on this date and the characteristic history of air sampled by the FAAM BAE-146, we employ the UK Met Office's Numerical Atmospheric-dispersion Modeling Environment (NAME) [*Jones et al.*, 2007]. The model uses meteorological data from the Met Office's Unified Model (at 25 km resolution) to simulate the forward or backward movement of tracer particles according to atmospheric conditions and turbulence. To take into account the uncertainty and

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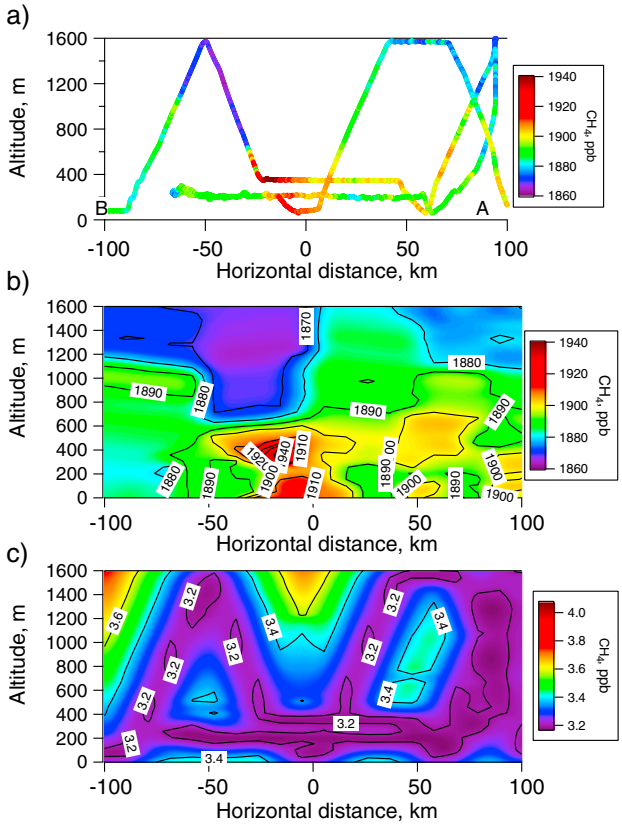

Figure 3. Same as Figure 2 but for CH_4 measurements downwind of London.

nature of the turbulence, 10,000 fluid particles are released, and the spread of the particles with time shows the most likely pathways of the air masses. The units in Figures 5 and 6 are a combination of the number of these particles appearing in a volume of air over a particular grid box and are related to the residence time.

The plume was simulated in forward mode whereby particles were released from the surface (10 m) within the Greater London metropolitan area (grey line Figure 1) and tracked forward in time in the elevation ranges of 0–1500 m. The model counts the number of particles in each 0.05° × 0.05° box every 15 min and sums these values over the model run time (3 to 9 h). Several runs were performed with release times chosen to span the range of possible plume ages sampled by the FAAM aircraft. A representative plume is shown in Figure 5 at 12:00 GMT (30 July 2013) where particles were released from Central London at 07:00 GMT. These NAME plumes show that only a small amount of lateral dispersion (perpendicular to wind) occurs before the 07:00 plume reaches the AB plane and also shows that the FAAM BAe-146 sampled across the core of this plume. The vast majority of the London plume was predicted by NAME to have passed through AB at or below 1500 m, validating the vertical extent defined for the kriging plane.

Retroplumes were also calculated by releasing particles at 30 s intervals along the FAAM BAe-146's flight track and running NAME backward in time for 6 h. By counting the number of particles that have originated over London (grey line Figure 1) at surface level (0–100 m) for each 1 min start point, it is possible to qualitatively characterize how strongly London emissions have influenced the sampled air. This is shown in Figure 6—the region of greatest London influence compares well with the plume identified by enhanced CO_2, CH_4, and CO (Figures 2–4). Air masses at the top and latitudinal edges of the AB-kriged plane do not show any influence from Greater London, supporting our assumption that all emissions from Greater London pass fully through the kriged plane.

We now also recalculate the flux through AB using only those grid cells that have been influenced by Greater London, between −47 km and 58 km horizontal distances and 0 to 1250 m altitude (Figure 2). These air masses were found to be responsible for 93%, 90%, and 87% of the total flux through the plane AB of CO_2, CH_4, and CO, respectively. For comparison with previous studies, we convert the derived flux from these air masses to μmol m^{-2} s^{-1} assuming that the Greater London region (1738 km^2) is solely responsible for the flux (Table 3). The limitations of such assumption will be discussed in section 3.2. Area fluxes are found to be 21 ± 3 μmol CO_2 m^{-2} s^{-1}, 0.13 ± 0.02 μmol CH_4 m^{-2} s^{-1}, and 0.12 ± 0.02 μmol CO m^{-2} s^{-1}.

3.2. Uncertainties

The uncertainties impacting the determinant of equation (1) can be grouped into three categories: (1) the instrument uncertainties associated with the measurements of mole fraction, temperature pressure, and the wind vector (these are given in section 2.1); (2) natural variability (heterogeneity) in the background (S_0) (this is taken as 1σ of the upwind measurements); and (3) uncertainty in interpolating the discrete flight onto the plane AB tracks (i.e., incomplete sampling). In the latter, we use the standard deviation of the kriging as output from

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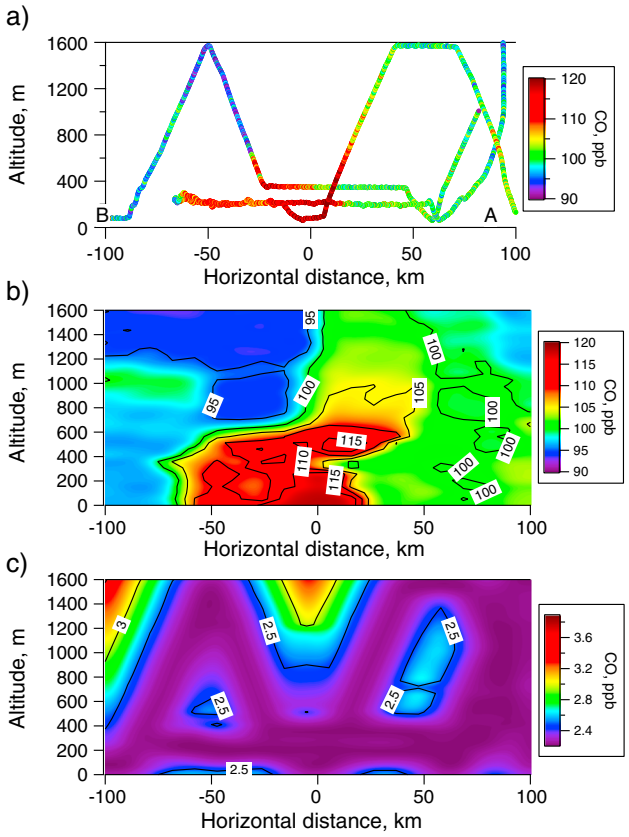

Figure 4. Same as Figures 2 and 3 but for CO measurements downwind of London.

the MATLAB "EasyKrig3.0" program [*Chu*, 2004]. The sum in quadrature of the kriging uncertainty and the analytical uncertainty is shown in Figures 2c, 3c, and 4c. As expected, uncertainty increases with distance from the flight tracks. The total uncertainty for the calculated fluxes (Table 2) can be found by propagating the uncertainties associated with the individual terms in equation (1) using the error propagation method described by *Bevington and Robinson* [1992].

We now examine the uncertainties that are implicit in the surface flux calculation, which uses the planar (AB) flux from equation (1). These are associated with model transport error and/or assumptive constraints about the surface flux footprint. If the total London emission (plume) does not pass through the plane AB, the magnitude of the total flux will be commensurately underestimated. The dimensions of the plane were chosen to reflect the length of the downwind transects and the altitude range that was most densely sampled by the FAAM BAe-146 aircraft. Both the ground-based ceilometer measurements and airborne vertical thermodynamic profiles suggest that between 07:00 and 12:00 GMT on the 30 July 2012, the PBL depth was less than 750 m; as such, the resultant plume from London that day was dynamically constrained to below this altitude. This is much less than the 1600 m vertical extent of AB, confirming that we have fully captured its vertical extent. Figure 2 shows a distinct plume at the center of the plane with mole fractions tending to approximately background values elsewhere. This is further supported by both forward (Figure 5) and backward (Figure 6) NAME trajectories.

A sensitivity test was performed whereby the fluxes through AB were recalculated while the flux integration height (z in equation (1)) was varied from 1600 m to 600 m. Within 5% for both CO_2 and CO, the calculated fluxes do not change down to an integration height of 800 m, after which the flux drops as would be expected should we not have captured the whole plume. CH_4 shows greater complexity; a higher flux (+20%) is calculated with a 1200 m integration height compared with that at 1600 m. This may be a result of a (unexpectedly large and unlikely) sink term in the flux footprint. However, since the measurements did not occur purely in the Lagrangian frame, it is not possible to identify whether or not this was due to a small potential change in the background, though we expect that this is more likely. An additional 20% uncertainty in the total flux may therefore be a more realistic uncertainty to include here, which could be improved in future case studies by careful flight design and sampling optimized for a Lagrangian frame; for megacities such as London with strict airspace rules, this may require the use of multiple measurement platforms.

As a result of the nature of using discrete point measurements to determine the 3-D extent of the London plume, there is the possibility the FAAM BAe-146 either oversampled or undersampled the plume, resulting in a proportional error in the total flux. Similarly, if the plume moved significantly, the latitudinal or vertical

Table 1. A Summary of the Observations by the FAAM BAe-146 on the 30 July 2012

	CO_2	CH_4	CO
Background	385.8 ± 1.4 ppm	1883 ± 8 ppb	96 ± 5 ppb
Peak enhancement	13.3 ppm (3%)	73 ppb (4%)	30 ppb (31%)

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Table 2. Fluxes Determined Using Observations by the FAAM BAe-146 on the 30 July 2012[a]

	CO_2	CH_4	CO
Flux AB (mol s^{-1})	38,453 ± 3346	264 ± 16	253 ± 11
Flux AB London air mass (mol s^{-1})	35,861 ± 2553	238 ± 12	219 ± 8
NAEI enclosed by flight track (mol s^{-1})	67,904	n/a	462
NAEI Greater London (mol s^{-1})	15,294	71	98

[a]Fluxes through the plane AB (Figure 1) were determined using a mass budget approach, and air masses that originated from Greater London were isolated using the NAME (Numerical Atmospheric-dispersion Modeling Environment) model. See section 3.4 for a description of the uncertainties. A comparison is made with the UK National Atmospheric Emissions Inventory (NAEI). For CO_2 and CO the inventory used in the comparison is for the year 2011, and for CH_4 it is for 2009.

position derived when sampling its dimensions could either be underestimated or overestimated. However, this was suggested not to be the case by the NAME trajectories.

The largest uncertainty present is in converting the flux through the plane AB to a corresponding emissions footprint and surface flux from Greater London. We have used the NAME model to guide this, and the fact the simulated London plume is shown at a similar location and with comparable dimensions supports the assumptions. However, it does not rule out the potential for emission from outside of Greater London contributing to the measured flux. As such, it is possible that surface fluxes in this study may possibly overestimate the true value (by up to a maximum of ~95%) though we would expect sources within the bounds of the flight track to be weighted within the London conurbation due to the greater density of sources. As mentioned previously, for future studies it would be beneficial to sample the plume closer to source, which would significantly reduce this uncertainty.

3.3. Comparison With Surface Observations and Previous Studies

As a result of the heterogeneous nature of the urban environment, methods that spatially integrate the urban flux provide a useful addition to those with smaller footprints such as eddy covariance. Figure 7 shows the CH_4 and CO_2 flux measurements at the BT Tower on 30 July 2012. The plume sampled by the FAAM BAe-146 is expected to have originated between either 6:00 and 9:00 GMT if calculated using wind measurements on the FAAM BAe-146 or 5:00 and 10:00 if calculated using HYSPLIT trajectories. During these periods mean fluxes at the BT Tower were found to be 43 ± 28 μmol s^{-1} m^{-2} and 35 ± 26 μmol s^{-1} m^{-2}, respectively. The flux determined using the airborne measurements (22 and 14 μmol s^{-1} m^{-2} lower, respectively) is within 1σ of these values. Fluxes of CH_4 are also found to be within 1σ of the mean of those measured at the BT Tower, which were 0.23 ± 0.19 μmol s^{-1} m^{-2} for 6:00 to 9:00 GMT and 0.18 ± 0.17 μmol s^{-1} m^{-2} for 5:00 to 10:00 GMT. The mean CO_2 and CH_4 fluxes on the BT Tower in Central London were 25 ± 20 μmol s^{-1} m^{-2} and 0.14 ± 0.11 μmol s^{-1} m^{-2}, respectively, on 30 July 2012. No CO fluxes were measured at the BT Tower on the 30 July 2012.

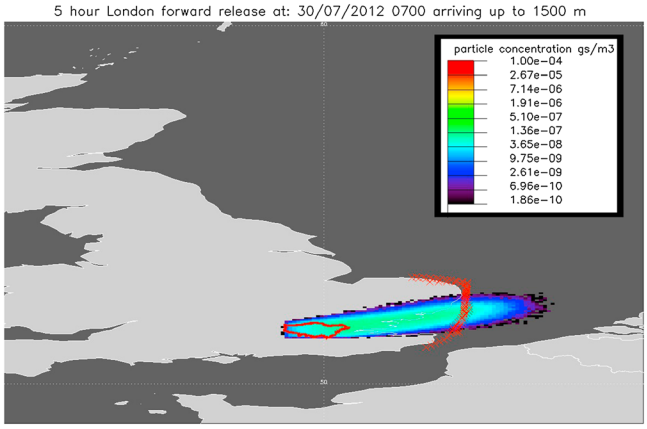

Figure 5. NAME (Numerical Atmospheric-dispersion Modeling Environment) dispersion model simulation of 5 h forward plume extent at 12:00 GMT (30 July 2013) from Central London surface (red contour) air released at 07:00 GMT. One minute averaged flight track is shown by red crosses.

Table 3 shows a comparison between this study and other similar flux measurements in urban areas. This study is the first that directly observes the total integrated CO_2, CH_4, and CO fluxes from the Greater London area. However, several previous studies have examined CO_2 fluxes: *Rigby et al.* [2008] determined a CO_2 flux of 18 ± 28 μmol s^{-1} m^{-2} for a Central London location during winter 2006 and 2007. *Helfter et al.* [2011] made CO_2 eddy covariance measurements from the BT Tower in Central London

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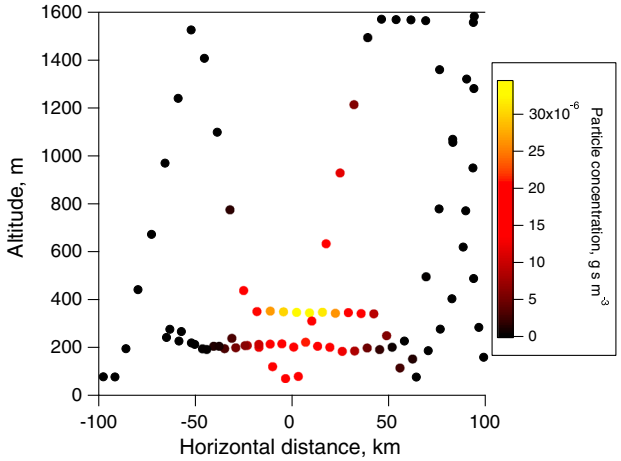

Figure 6. The influence of London emissions on the air masses sampled by the FAAM aircraft, on the plane AB, as determined using backward NAME model runs for 10,000 tracer particles released backward in time from the GPS position of the FAAM aircraft. Only those particles at the surface (0–100 m) within the grey box in Figure 1 are shown highlight locations of London surface emissions reaching the flight elevations. Warm colors show regions of greater air mass influence from London and vice versa for darker colors.

between 2006 and 2008 where averaged diurnal cycle ranged between 7 and 47 μmol s^{-1} m^{-2}. The CO_2 flux from this study is comparable with these studies. However, *Font et al.* [2013] used aircraft measurements over Central London on 4 days during October 2011 to derive fluxes that were over a factor of 2 larger, ranging between 37 and 104 μmol s^{-1} m^{-2}, than those determined by the airborne measurements, but within the range measured at the BT Tower.

The CH_4 fluxes in urban locations have not been as extensively studied as CO_2, partly because reliable fast response CH_4 sensors have become available only recently. However, we find this study to give a result similar to studies conducted in Indianapolis [*Mays et al.*, 2009] and Florence [*Gioli et al.*, 2012]. In contrast, *Kuc et al.* [2003] report fluxes over a factor 2 larger for Krakow, while *Zimnoch et al.* [2010] determine a mean CH_4 flux a factor 4 smaller than this study, though for only nighttime observations.

For the 30 July 2012 flight, we find a CH_4:CO_2 flux ratio of 6.9 ± 0.7 mmol CH_4 (mol CO_2)$^{-1}$ (Table 4). This is similar to flux measurements from the BT Tower (Table 3), which for the period 6:00 and 9:00 GMT on the 30 July 2012 the mean ratio was 5.0 ± 1.2 mmol CH_4 (mol CO_2)$^{-1}$. Both these studies for London are also comparable to other urban locations such as 8.9 ± 7.9 mmol CH_4 (mol CO_2)$^{-1}$ for Indianapolis [*Mays et al.*, 2009] and 6.70 ± 0.01 mol CH_4 (mol CO_2)$^{-1}$ for the Los Angeles (LA) Basin [*Peischl et al.*, 2013]. Based on their respective emission ratios, both of these previous studies attributed the majority of CH_4 emissions to noncombustion sources. Combustion sources typically produce proportionally more CO_2, such as vehicles,

Table 3. Determined Area Fluxes From Both Mass Balance and Eddy Covariance Techniques From This Study and Other Similar Studies in Urban Environments[a]

				Flux (μmol m^{-2} s^{-1})		
	Location	Year	Season	CO_2	CH_4	CO
This study (mass balance)	London, UK	2012	Summer	21 ± 3	0.13 ± 0.02	0.12 ± 0.02
This study (eddy covariance)[b]	London, UK	2012	Summer	1 to 83 (25 ± 20)	0.01 to 0.37 (0.14 ± 0.11)	
Font et al. [2013][c]	London, UK	2011	Autumn	37 to 104		
Helfter et al. [2011][d]	London, UK	2007	Year round	7 to 47		
Harrison et al. [2012][e]	London, UK	2007/08	Autumn			0.25/0.17
Rigby et al. [2008][f]	London, UK	2006	Year round	18 ± 28		
Famulari et al. [2010][g]	Edinburgh, UK	2005	Autumn	−100 to 100		0.08 to 1.7
Nemitz et al. [2002][h]	Edinburgh, UK	2000	Autumn (day)	35.4		
NAEI [2011][i]	London, UK	2011	Year round	8.9	0.041	0.056

[a]NAEI is the emissions estimate for Greater London from the National Atmospheric emissions inventory (see section 3.4 for the uncertainties in the NAEI).
[b]Range of the daily averaged fluxes at the BT Tower for summer 2012 (numbers in brackets show fluxes for 30 September 2012).
[c]*Font et al.* [2013] used a mass balance approach using airborne measurements from four flights; the range of measured fluxes is shown.
[d]*Helfter et al.* [2011] used eddy covariance (EC); the range of fluxes is shown.
[e]*Harrison et al.* [2012] used EC. Means for two autumn periods are shown.
[f]*Rigby et al.* [2008] used a boundary layer model; given is the average emission rate for the winter measurement period.
[g]*Famulari et al.* [2010] used the EC technique; given is the range of fluxes.
[h]*Nemitz et al.* [2002] used EC; given is the mean daytime flux.
[i]The National Atmospheric Emissions Inventory, CO_2 and CO are for 2011, while CH_4 is for 2009.

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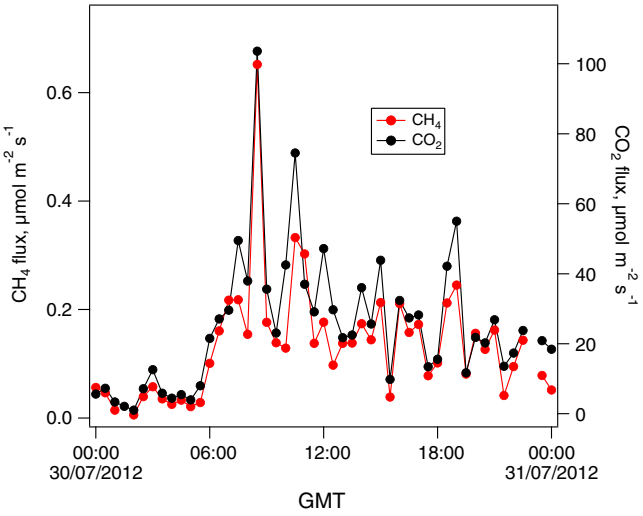

Figure 7. Time series of CO_2 and CH_4 fluxes on 30 July 2012 measured at the BT Tower, London, using the eddy covariance technique.

which have a ratio of 0.14 ± 0.01 mmol CH_4 (mol CO_2)$^{-1}$ [*Nam et al.*, 2004], or coal combustion with a ratio of 0.3 mmol CH_4 (mol CO_2)$^{-1}$ [*Babbitt and Lindner*, 2005]. Large landfills are present in the LA Basin, which are thought to account for a significant proportion of emissions [*Peischl et al.*, 2013]. This is not the case for Greater London. It is generally expected that the most significant CH_4 source in Greater London is leakage from the natural gas distribution network. However, this leakage might be expected to be constant over the day (the supply pressure is relatively constant), while ground-based measurements during ClearfLo indicate larger diurnal variability [*Helfter et al.*, 2013].

A second-round London flight of the FAAM BAe-146 was conducted on 9 August 2012 (B725). Assuming a Central London source, the plume during this flight was estimated to have originated between 3:30 and 4:30 GMT. The London plume was not sampled as extensively, preventing the same mass budget calculation from being applicable. However, the chemical species were correlated during the downwind measurements. The CH_4:CO_2 flux ratio of 3.90 ± 0.02 mmol CH_4 (mol CO_2)$^{-1}$ (R^2 = 0.79) is 43% lower than the previous flight, suggesting significant intraday and/or interday variability in fluxes. The urban CH_4 variability on the other hand is expected to be driven mainly by leaks from the gas distribution network, which may show smaller diurnal and seasonal changes [*Gioli et al.*, 2012]. The BT Tower flux measurements showed both large diurnal changes in both the magnitude of the CH_4:CO_2 flux ratio and also the degree of correlation between the two species [*Helfter et al.*, 2013]. This is most likely due to different source dynamics over the course of the day/night, which illustrates, at least qualitatively, that there are a variety of common and independent sources of CH_4 and CO_2 present.

Few direct flux measurements exist of CO fluxes above urban areas. *Famulari et al.* [2010] previously measured a CO:CO_2 flux ratio of 21.4 mmol CO (mol CO_2)$^{-1}$ above Edinburgh, with ratios of 8.7 and 5.1 mmol CO (mol CO_2)$^{-1}$ for two autumn periods over London from the BT Tower [*Harrison et al.*, 2012]. Previous studies have found the urban CO_2, CH_4, and CO fluxes to vary by over 100% day to day [*Mays et al.*, 2009; *Font et al.*, 2013], with CO_2 and CO intraday variability correlating strongly with vehicle activity and seasonal variability mainly due to changes in heating related emissions [*Nemitz et al.*, 2002; *Helfter et al.*, 2011].

3.4. Comparison With the National Atmospheric Emissions Inventory

The UK National Atmospheric Emissions Inventory (NAEI) reports anthropogenic annual emission estimates at a 1 km^2 spatial resolution for CO_2 and CO [*NAEI*, 2011]. The most recent year publically available is 2011. The inventory does not include human respiration nor uptake by the biosphere; however, for Central London these are estimated to be small in magnitude and opposite in effect, resulting in a negligible net flux [*Helfter et al.*, 2011]. However, this may not be the case for the extremities of the sampling domain outside London. Uncertainties are not provided by the NAEI for the spatially disaggregated emission maps. However, for the UK total emissions uncertainties are given as 2%, 17%, and 30% for CO_2, CH_4, and CO, respectively [*NAEI*, 2011].

Table 4. Flux Ratios Between Chemical Species Downwind of London for Flights on the 30 July 2012 and 9 August 2012[a]

Flux Ratio (mmol mol^{-1})	30 July 2012	9 August 2012
CO: CO_2	6.6 ± 0.7 (R^2 = 0.85)	1.92 ± 0.01 (R^2 = 0.50)
CO: CH_4 (mol mol^{-1})	1.04 ± 0.08 (R^2 = 0.75)	1.75 ± 0.01 (R^2 = 0.72)
CH_4: CO_2	6.9 ± 0.7 (R^2 = 0.82)	3.90 ± 0.02 (R^2 = 0.79)

[a]Orthogonal distance regressions were used to determine all regression slopes.

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For comparison with the airborne measurements, we determine the total source both enclosed by the FAAM BAe-146's flight track and also only that from Greater London (Table 2), i.e., assuming that sources are entirely weighted to the London conurbation. The CO_2 and CO planar fluxes through AB determined for the 30 July 2012 are found to be between the two surface fluxes calculated from the spatially resolved inventory for these two regions. When only the flux from the London influenced air masses are considered, CO_2 and CO are found to be factors of 2.3 and 2.2 larger than the London emission according to the NAEI, respectively. Previous airborne studies have also measured fluxes that were similarly larger than those reported by inventories [e.g., *Peischl et al*., 2012] (for the LA basin), while the eddy covariance flux measurements of *Helfter et al*. [2011] agreed well with the NAEI for CO_2 for London.

As a result of their very high uncertainty, UK emission maps for CH_4 are no longer made publically available by the NAEI. Therefore, this study provides an important top-down constraint for future work in this area. However, CH_4 emission estimates for years previous to 2009 are available. The 2009 NAEI estimates a total emission of 71 mol s^{-1} for Greater London, a factor 3.4 smaller than suggested by this work.

Though the aircraft and the eddy covariance fluxes show good agreement on the 30 July 2012, *Helfter et al*. [2011, 2013] report good agreement between there CO_2 eddy covariance measurements and the NAEI when their entire data set is used. However, similarly large positively biased disagreement was found for CH_4, which were a factor 2 to 3 larger than the inventory [*Helfter et al*., 2013].

However, for all species, results from a single flight alone cannot be used to provide a comprehensive climatological assessment of an annual emissions inventory, especially one that is not for the current year. The determined fluxes in this study are representative of a near rush hour period, during the buildup to the 2012 London Olympic Games. Further measurements would be needed to identify the necessary diurnal and seasonal variation in fluxes, which this work has shown to be significant. However, this broad comparison is still instructive for placing the derived fluxes in context.

4. Conclusions

On the 30 July 2012, airborne observations of CO_2, CH_4, and CO were made upwind and downwind of London. All species were found to be significantly enhanced during the downwind transects, showing a plume of comparable location and extent. Regional net fluxes were determined by performing a mass budget, these were found to be $38{,}453 \pm 3346$ mol CO_2 s^{-1}, 264 ± 16 mol CH_4 s^{-1}, and 253 ± 11 mol CO s^{-1}. For this method to be applied, it is essential to have a consistent airflow and a well-mixed background upwind of the source, both of which were present on the 30 July 2012. When only air masses that originated from Central London are included, area fluxes are found to be 21 ± 3 μmol CO_2 m^{-2} s^{-1}, 0.13 ± 0.02 μmol CH_4 m^{-2} s^{-1}, and 0.12 ± 0.02 μmol CO m^{-2} s^{-1}, which is comparable with previous studies in urban environments and a factor 2.3 and 2.2 larger than estimated by the *NAEI* [2011] for CO_2 and CO, respectively. Fluxes of CH_4 were found to be a factor 3.4 larger than those estimated by the *NAEI* [2009]. Eddy covariance flux measurements made at the BT Tower also suggest that the NAEI underestimates the CH_4 emission by a similar extent (a factor 2 to 3) [*Helfter et al*., 2013].

Further seasonal measurements would be necessary to determine the consistency of these results and for a more direct comparison with the annual NAEI emissions inventory. However, this study highlights the unique ability of aircraft to routinely characterize emissions from area sources such as cities and points to future missions to target localized hot spots and distributed point sources.

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