

1 **Analysis of the potential of near ground measurements of**
2 **CO₂ and CH₄ in London, UK for the monitoring of city-scale**
3 **emissions using an atmospheric transport model.**

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5 **A. Boon¹, G. Broquet², D. J. Clifford¹, F. Chevallier², D. M. Butterfield³, I. Pison²,**
6 **M. Ramonet², J.D. Paris² and P. Ciais².**

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8 [1] Department of Meteorology, University of Reading, Reading, Berkshire RG6 6BB, UK

9 [2] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ,
10 UMR8212, IPSL, Gif-sur-Yvette, France

11 [3] National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

12 Correspondence to: A. Boon (alex.boon@reading.ac.uk)

13
14 **Abstract**

15 Carbon dioxide (CO₂) and methane (CH₄) mole fractions were measured at four near ground
16 sites located in and around London during the summer of 2012 in view to investigate the
17 potential of assimilating such measurements in an atmospheric inversion system for the
18 monitoring of the CO₂ and CH₄ emissions in the London area. These data were analysed and
19 compared with simulations using a modelling framework suited to building an inversion
20 system: a 2-km horizontal resolution South of England configuration of the transport model
21 CHIMERE driven by European Centre for Medium-Range Weather Forecasts (ECMWF)
22 meteorological forcing, coupled to a 1-km horizontal resolution emission inventory (the UK
23 National Atmospheric Emission Inventory). First comparisons reveal that local sources, that
24 cannot be represented in the model at a 2-km resolution, have a large impact on
25 measurements. We evaluate methods to filter out the impact of some of the other critical
26 sources of discrepancies between the measurements and the model simulation except that of
27 the errors in the emission inventory, which we attempt to isolate. Such a separation of the
28 impact of errors in the emission inventory should make it easier to identify the corrections
29 that should be applied to the inventory. Analysis is supported by observations from

1 meteorological sites around the city and a three-week period of atmospheric mixing layer
2 height estimations from lidar measurements. The difficulties of modelling the mixing layer
3 depth and thus CO₂ and CH₄ concentrations during the night, morning and late afternoon lead
4 to focus on the afternoon period for all further analyses. The discrepancies between
5 observations and model simulations are high for both CO₂ and CH₄ (i.e., their root mean
6 square (RMS) is between 8 and 12 parts per million (ppm) for CO₂ and between 30 and 55
7 parts per billion (ppb) for CH₄ at a given site). By analysing the gradients between the urban
8 sites and a suburban or rural reference site, we are able to decrease the impact of uncertainties
9 in the fluxes and transport outside the London area and in the model domain boundary
10 conditions. We are thus able to better focus attention on the signature of London urban CO₂
11 and CH₄ emissions in the atmospheric CO₂ and CH₄ concentrations. This considerably
12 improves the statistical agreement between the model and observations for CO₂ (with model–
13 data RMS discrepancies that are between 3 and 7 ppm) and to a lesser degree for CH₄ (with
14 model–data RMS discrepancies that are between 29 and 38 ppb). Between one of the urban
15 sites and either the rural or suburban reference site, selecting the gradients during periods
16 wherein the reference site is upwind of the urban site further decreases the statistics of the
17 discrepancies in general though not systematically. In a further attempt to focus on the
18 signature of the city anthropogenic emission in the mole fraction measurements, we use a
19 theoretical ratio of gradients of carbon monoxide (CO) to gradients of CO₂ from fossil fuel
20 emissions in the London area to diagnose observation based fossil fuel CO₂ gradients, and
21 compare them with the fossil fuel CO₂ gradients simulated with CHIMERE. This estimate
22 increases the consistency between the model and the measurements when considering only
23 one of the two urban sites, even though the two sites are relatively close to each other within
24 the city. While this study evaluates and highlights the merit of different approaches for
25 increasing the consistency between the mesoscale model and the near ground data, and while
26 it manages to decrease the random component of the analysed model–data discrepancies to an
27 extent that should not be prohibitive to extracting the signal from the London urban
28 emissions, large biases, the sign of which depends on the measurement sites, remain in the
29 final model–data discrepancies. Such biases are likely related to local emissions to which the
30 urban near ground sites are highly sensitive. This questions our current ability to exploit urban
31 near ground data for the atmospheric inversion of city emissions based on models at spatial
32 resolution coarser than 2-km. Several measurement and modelling concepts are discussed to
33 overcome this challenge.

1

2 **1 Introduction**

3 As major greenhouse gas (GHG) emitters, cities have an important part to play in national
4 GHG emission reporting. Over half of the world's population now live in cities, and the UN
5 estimate that the urban population will almost double from 3.4 to 6.3 billion by 2050 (United
6 Nations, 2012). In the face of this continued urban population increase, cities can expect
7 increased anthropogenic emissions unless measures are taken to reduce the impact of city life
8 on the atmosphere. The majority of anthropogenic carbon dioxide (CO₂) is released in the
9 combustion of fossil fuels for heating, electricity and transport, the latter of which is
10 particularly important in the urban environment. The major sources of methane (CH₄) in city
11 environments are leakage from natural gas infrastructure, landfill sites, wastewater treatment
12 and transport emissions (Lowry et al., 2001;Nakagawa et al., 2005;Townsend-Small et al.,
13 2012).

14 International agreements to limit GHG emissions make use of countries' self-reporting of
15 emissions using emission inventories. These inventories are based upon activity data and
16 corresponding emission factors and uncertainties can be substantial, particularly at the city
17 scale. Ciais et al. (2010a) showed uncertainties of 19% of the mean emissions at country scale
18 in the 25 EU Member States and up to 60% at scales less than 200-km. Currently there is no
19 legal obligation for individual cities to report their emissions; however, as environmental
20 awareness increases and actions are taken to reduce urban GHG emissions, monitoring of city
21 emissions to evaluate the success of emissions reduction schemes becomes an important
22 consideration.

23 Quantifying GHG emissions from cities using an atmospheric inversion approach (i.e., based
24 on gas mole fraction measurements, atmospheric transport modelling and statistical
25 inference), is a relatively new scientific endeavour (Levin et al., 2011;McKain et al.,
26 2012;Kort et al., 2013;Bréon et al., 2015;Henne et al., 2016;Staufer et al., 2016). Instruments
27 to measure urban GHG concentrations have been placed on tall masts or towers (at more than
28 50 m above the ground level, magl) or at near ground (at less than 20 magl) heights (Bréon et
29 al., 2015;Lac et al., 2013;McKain et al., 2012) with a preference generally given to higher
30 level measurement sites as these are expected to reduce variability due to local sources (Ciais
31 et al., 2010b). The city-scale inversion studies have mainly focused on the monitoring of CO₂
32 city emissions. However, McKain et al. (2015) have shown the potential of the city-scale

1 inversion approach to reduce uncertainties in CH₄ city emissions inventories, which can be
2 substantial in cities, such as Boston (Massachusetts), where the gas distribution network has a
3 high leakage level.

4 Near ground sites are cheaper and easier to install and maintain than tall towers. There are far
5 more choices of location for the placing of instrumentation near ground than on tall towers,
6 even within a city. The development of cheaper instruments could enable the deployment of
7 networks with numerous sites and this is likely to require placement of at least some sites on
8 near ground locations. If near ground sites can be used effectively they could be highly
9 complementary to the developing GHG observation networks. For their inversions of the
10 Paris emissions, Bréon et al. (2015) and Stauffer et al. (2016) used near ground measurements
11 taken in the suburban area of Paris but not in the city centre. They indicated that the capability
12 of exploiting urban measurements would strongly improve the monitoring of the city
13 emissions. Kort et al. (2013) evaluated (through Observing System Simulation Experiments,
14 which is a common practice in the data assimilation community, as detailed by Masutani et al.
15 (2010)) different configurations of surface station networks for monitoring emissions from
16 Los Angeles, and concluded that robust monitoring of megacities requires multiple in-city
17 surface sites (numbering at least eight stations for Los Angeles). McKain et al. (2012)
18 employed near ground sites in Salt Lake City, an urban area that is relatively small and
19 topographically confined. They concluded that surface stations could be used to detect
20 changes in GHG emissions at the monthly scale, but not to derive estimates of the absolute
21 emissions because of the inability of current models to simulate small scale atmospheric
22 processes.

23 Our study feeds such an investigation of the potential of city atmospheric inversion
24 frameworks using continuous measurements at near ground stations, including measurements
25 within the urban area. We focus our attention on the megacity of London, UK. Previous
26 studies of the GHG fluxes in London by the atmospheric community have largely focused on
27 direct measurements of local fluxes using the eddy covariance technique, and on high
28 resolution transport modelling to identify the emission (spatial) footprint associated with these
29 measurements (Helfter et al., 2011;Kotthaus and Grimmond, 2012;Ward et al., 2015). These
30 local eddy covariance measurements in London have been used to derive estimates of the
31 fluxes for specific boroughs or administrative areas (Helfter et al., 2011) and to compare the
32 typical fluxes for different types of land use (Ward et al., 2015).

1 The atmospheric inversion approach, which is based on different estimation concepts and
2 modelling scales to those of eddy covariance methods, has the potential to provide estimates
3 of the emissions for a far larger portion of the city, and ideally for the city as a whole. Rigby
4 et al. (2008) compared CO₂ concentration measurements from a central London site (Queen's
5 Tower, Imperial College) with near ground measurements at a more rural location (Royal
6 Holloway University of London) upstream of the city in the prevailing wind direction. They
7 thus characterised the CO₂ mole fraction enhancement as a result of the CO₂ emissions from
8 anthropogenic sources in the city. Hernandez-Paniagua et al. (2015) recently analysed the
9 long-term time series at the Royal Holloway site to study the long-term trends and seasonal
10 variation in CO₂ mole fractions, which are driven by the variations of the biological uptake
11 and of the anthropogenic activities underlying the city emissions. However, to our knowledge,
12 these data have not yet been exploited using the inversion approach to quantify the city
13 emissions. More recently, O'Shea et al. (2014) and Font et al. (2015) took airborne
14 measurements of CO₂ mole fractions over London and combined these with box models to
15 estimate vertical fluxes and a Lagrangian particle model to estimate the area ("footprints")
16 corresponding to these fluxes. O'Shea et al. (2014) compared the flux estimates with eddy
17 covariance flux measurements and the estimate of the city emissions from the 2009 UK
18 National Atmospheric Emissions Inventory (NAEI) (NAEI, 2013). In the course of their
19 analysis, Font et al. (2015) indicated that the uncertainties associated with footprint modelling
20 are high and that there is a need to improve their protocol to separate the natural and
21 anthropogenic CO₂ fluxes in their estimates, which is a traditional source of concern for the
22 monitoring of anthropogenic emissions of CO₂ (Bréon et al., 2015). Regular aircraft
23 campaigns could provide a good sampling of transitory city emissions but the continuous
24 monitoring of these emissions would likely have to rely on continuous measurements from
25 ground-based stations. To our knowledge, there have been few attempts to monitor the CH₄
26 emissions of the London area using atmospheric measurements (Lowry et al., 2001; O'Shea et
27 al., 2014).

28 In this context, we made quasi-continuous measurements of CO₂, CH₄ and CO during 2012 at
29 four sites in the London area (two inner city sites - Hackney and Poplar, one suburban site -
30 Teddington and one rural site outside the urban area - Detling) using sensors located at 10–15
31 m above ground level. We assess the ability of a km-resolution transport model driven by a
32 km-resolution emissions inventory to simulate these CO₂ and CH₄ measurements. The aim is
33 to understand whether such measurement sites are ultimately suitable for use in a flux

1 inversion scheme based on the km-resolution model. This study investigates the importance
2 of different sources of discrepancies between observed and simulated GHG mole fractions
3 (henceforth 'model–data discrepancies'). By decomposing the discrepancies depending on
4 their different sources, we attempt to isolate and exploit the part of the discrepancies that are
5 due to the errors in the estimates of the urban emissions. We focus on the following sources of
6 uncertainties and limitations when simulating the CO₂ and CH₄ measurements in the London
7 area with the model, which we can assume to be significant sources of model–data
8 discrepancies along with the errors in the estimate of the urban emissions:

- 9 (1) The differences of representativity in terms of spatial scale between the model and the
10 measurements: near ground sites could be highly sensitive to very local emissions, i.e., at
11 scales smaller than those represented by the model.
- 12 (2) Uncertainties in the modelled meteorological conditions, in particular in the wind speed
13 and direction and in the mixing layer height above the city.
- 14 (3) Uncertainties relating to both the conditions at the model domain boundaries and to the
15 modelling of the fluxes outside of the London area, which can influence the
16 concentrations in the London area.
- 17 (4) In the case of CO₂, uncertainties related to remote or near-field natural fluxes.

18 We introduce the measurement sites and model configuration in Sect. 2. In Sect. 3 we first
19 consider issues of spatial representativity (Sect. 3.1) and then the ability of the model to
20 simulate the diurnal cycle of mixing layer height, CO₂ and CH₄ (Sect 3.2). In Sect. 3.3 we
21 compare winds simulated by the model with measurements at two surface meteorological
22 stations. In Sect. 3.4 we examine the day-to-day variations of measured and modelled CO₂
23 and CH₄. We attempt to remove the influence of the remote fluxes and conditions by
24 considering gradients in CO₂ and CH₄ across the city in Sect. 3.5, and then take the wind
25 direction into account when selecting the gradients (Sect. 3.6). Finally, we evaluate the
26 modelled fossil-fuel CO₂ using a simple method to estimate the anthropogenic component of
27 the observed CO₂ mole fractions based on the simultaneous CO measurements (Sect. 3.7). A
28 summary and discussion of the overall findings of the research is then given in Sect. 4.

29

1 **2 Methodology**

2 **2.1 London emissions inventory for CO₂ and CH₄**

3 As context for the location of the in situ measurements, and to provide an estimate of the
4 emissions applied within the model, we utilise the UK NAEI (NAEI, 2013), including a
5 mapping of CH₄ sources from Dragosits and Sutton (2011). The NAEI provides annual
6 gridded emission data for a wide range of atmospheric pollutants and GHGs with a sectorial
7 distribution by the main types of emitting activities: agricultural soil losses, domestic
8 (commercial, residential, institutional) combustion, energy production, industrial combustion,
9 industrial production processes, offshore own gas combustion, road transport, other transport,
10 solvent use, waste treatment and disposal and (for CH₄ only) agricultural emissions due to
11 livestock and natural emissions. Major CO₂ and CH₄ point sources (comprising large power
12 and combustion plants) are also listed and localised individually. Significant sources of all
13 these sectors apart from the offshore own gas combustion occur in the London urban area or
14 in its immediate vicinity. The methodology applied to derive these gridded maps is described
15 in Bush et al. (2010) and Dragosits and Sutton (2011).

16 The most up-to-date published emissions estimates available from NAEI at the time of this
17 study were for 2009. The CO₂ emissions for the region around London are shown at 2-km
18 resolution (the resolution of simulated transport; see Sect. 2.4) in Fig. 1 along with the
19 position of the measurement stations (Sect. 2.2). In the vicinity of London, nearly all point
20 sources of CO₂ are related to combustion processes with emissions from high stacks and
21 through warm plumes. The 10 largest emitters in the domain defined by Fig. 1 are power
22 stations, which represent nearly 27% of the emissions in this domain.

23 **2.2 GHG measurement site locations and characteristics**

24 The four measurement sites were located in and around London to sample air masses passing
25 over London at various levels of sensitivity to urban emissions (in the city centre, suburban
26 and rural areas). Note that no formal quantitative network design was applied beforehand to
27 select the optimal location of the stations for their ability to constrain the emissions of
28 London. The station locations were chosen based on the configuration of the emissions given
29 by the inventory maps and the availability of suitable locations for installation and
30 maintenance of the instruments.

1 The site locations are shown in Fig. 1 and were operational between June and September,
2 2012. The two urban sites of Hackney and Poplar were located in central London, 6 km apart
3 from each other and to the north-east of the main area of emissions (Hackney at $51^{\circ} 33'$
4 $31.45''$, $-0^{\circ} 3' 25.44''$; Poplar $51^{\circ} 30' 35.67''$, $-0^{\circ} 1' 11.33''$). The suburban site was located in
5 Teddington ($51^{\circ} 25' 13.63''$, $-0^{\circ} 20' 21.15''$), 17 km south-west of Central London. The
6 location of this site was chosen a priori to allow the analysis of the gradient due to the city
7 emissions when the wind blows from the south-west. This is usually the case and 52% of the
8 wind directions measured at Heathrow Airport (see Sect. 2.5) during the period July–
9 September 2012 (i.e., our study period) were from the south-west sector. The fourth site was
10 located in Detling, Kent ($51^{\circ} 18' 28.44''$, $0^{\circ} 34' 57.36''$), in a rural area approximately 50 km
11 from the inner city and was selected to help to detect the influence of remote fluxes on the
12 GHG mole fractions over the city.

13 The measurement stations at Hackney and Poplar were located on the rooftop of a college and
14 a primary education school, respectively. The inlets for each of these sensors were placed
15 approximately 10 m above street level and approximately 2 m above the rooftop level. The
16 NAEI emissions map (Fig. 1) shows substantial CO_2 sources west of the Poplar and Hackney
17 sites, relating to the city centre.

18 The site in Teddington was located on top of a building approximately 15 m from ground
19 level. Teddington is referred to in this study as a suburban site, due to its location in a
20 residential area beside Bushy Park. Bushy Park represents a large area of vegetation cover
21 surrounding the site to the east, south and west with residential and commercial land use
22 located to the north. The site in Detling was located on the top of a 10 m mast at an
23 established air quality measurement site in a pasture field approximately 2 km from the
24 nearest major roads.

25 **2.3 GHG measurements**

26 Continuous measurements of CO , CO_2 , CH_4 and water vapour were taken between 1st June
27 and 30th September 2012 for the Hackney, Poplar and Teddington sites and 5th July to 30th
28 September 2012 at Detling. Each site was instrumented with a G2401 Picarro cavity ring-
29 down spectroscopy (CRDS) instrument that logged data every 5 seconds and sent data files
30 each hour to a remote server.

1 All sensors across the network were manually calibrated on an approximately two-weekly
2 basis using the same gas standards, ensuring the consistency of the measurements from
3 different sites. The sensors were calibrated for linearity, repeatability of measurements (for
4 zero and span gases, i.e., respectively with concentrations zero and ambient concentration
5 gas) and drift in the field and in the laboratory prior to deployment. The synthetic standards
6 including the zero and span gases were prepared by National Physical Laboratory (NPL) as
7 described in Brewer et al. (2014) with mole fractions close to those of atmospheric ambient
8 air (379 ± 0.95 parts per million (ppm) for CO_2 and 1800 ± 5 parts per billion (ppb) for CH_4 ;
9 uncertainties being expressed as 1-sigma standard deviations, STD). A higher than ambient
10 concentration of CO was used as the standard gas (9.71 ± 0.015 ppm to be compared with the
11 CO measurements of this study which range between 0.1 and 0.9 ppb), because of the
12 unavailability of low CO standards at the time of the experiment, leading to high uncertainties
13 in CO measurements in ambient air. However, the linearity of the G4201 CRDS has been
14 evaluated by Zellweger et al. (2012) from 0 up to 20 ppm and their results show that the
15 CRDS analyser remains linear in this range of concentrations.

16 To quantify possible biases, and consistent with the recommendation from the World
17 Meteorological Organisation (WMO) Expert group, the design of the experiment should have
18 included regular measurements of a calibrated target gas. However, the fact that we were
19 using similar analysers at the four stations, operated with the same protocols and calibrated
20 with a single reference scale, reduced the risk of systematic biases between the sites. The high
21 1-sigma uncertainties in the molar fraction of the gases used for the calibration result in
22 unknown (positive or negative) biases that are common to all sites for the measurement period
23 since the same gas cylinders were used for all stations throughout the period (the calibration
24 error due to uncertainty in the calibration gas depends on the ambient concentration, but this
25 dependence is such that the resulting variability of the calibration error is negligible compared
26 with the variability of the concentrations in time or between sites). For this reason, the
27 calibration biases mostly cancel out when analysing gradients of ambient molar fractions
28 between the different sites of the network (this may not hold for higher molar fractions). This
29 bias precludes, however, the use of this network in combination with other stations that have a
30 different calibration standard.

31 In addition, the measurement error had a random component of STD 0.3 ppm for CO_2 , 8 ppb
32 for CH_4 and 15 ppb for CO. This error budget includes drifts and variability in readouts when

1 measuring zero and span gases, as well as the applied correction for water vapour on the CO₂
2 and CH₄ channels. Such a correction was applied because the airstream to the Picarro CRDS
3 was not dried. In practice, the measurements of CO₂ and CH₄ were taken from the dry channel
4 of these analysers to which a default correction had been applied for variability due to water
5 vapour (Rella et al., 2013). The uncertainty associated with applying the water vapour
6 correction to this type of instrument, for an H₂O content of 1.5%, was estimated to be 0.05
7 ppm for CO₂ and 1 ppb for CH₄ (Laurent et al., 2015). No water correction was applied for
8 CO. Expressed as a percentage of the mean measured concentration throughout the
9 measurement period, the total measurement uncertainties (root sum square, RSS, of the bias
10 and random errors) are 0.3%, 0.7% and 21% for CO₂, CH₄ and CO, respectively.

11 Data were calibrated using the standard gas cylinder values, and provided as 15-minute
12 averages by NPL. Calibration episodes were removed from the final dataset. The Teddington
13 sensor was inactive between 6th and 12th July due to sample pump failure and there were a
14 small number of missing days at Detling (due to power outage) and at Poplar (for unknown
15 reasons). There were few missing data at the Hackney site. The 15-minute data from the
16 measurement sites were aggregated by averaging into hourly time intervals for comparison
17 with the hourly output from the model. If fewer than four 15-minute data points were
18 available for any given hour (usually as a result of periodic data scan by the Picarro analyser
19 or return to functionality after a calibration event or instrument downtime), the corresponding
20 model and measurement hourly averages were removed from the analysis to maintain
21 consistency between the model and data hourly averaged values.

22 **2.4 Simulation of the atmospheric transport of CO₂ and CH₄**

23 To model the transport of CO₂ and CH₄ mole fractions over London, we used a “South of
24 England” configuration of the mesoscale atmospheric transport model CHIMERE (Schmidt et
25 al., 2001). This model has already been used for CO₂ transport and flux inversion at regional-
26 to-city scale (Aulagnier et al., 2010; Broquet et al., 2011; Bréon et al., 2015). The domain over
27 which CHIMERE was applied in this study (area ~ 49.9–53.2°N, –6.4–2.4°E) covers the
28 whole south of England to minimise the impact of defining model boundary conditions using
29 coarser model simulations close to the measurement sites. Additionally, the boundaries were
30 positioned as much as possible in the seas (instead of set across Southern England); in
31 particular, the western boundary from which the dominant winds flow over England.

1 However, the northern boundary crosses England and the south-eastern part of the domain
2 overlaps a small part of Northern France.

3 The model has a regular grid with 2-km horizontal resolution and 20 vertical levels from the
4 ground up to 500 hPa (with ~ 20 – 25 m vertical resolution close to the ground). CHIMERE is
5 driven by atmospheric mass fluxes from the operational analyses of the European Centre for
6 Medium-Range Weather Forecasts (ECMWF) at 3-hour temporal resolution and ~ 15 -km
7 horizontal resolution (which are interpolated linearly on the CHIMERE grid and every hour).
8 In this study, these mass fluxes were processed before their use in CHIMERE to account for
9 the increased roughness in cities and in particular in London: the surface wind speed was
10 decreased proportionally to the fraction of urban area in each model 2×2 km grid cell (i.e., it
11 is set to 0 for grid cells entirely covered by urban area, set to the value from ECMWF for grid
12 cells with no fraction of urban area, and, in a general way, set to the product of the fraction of
13 non-urban area in the grid cells times the value from ECMWF). The fraction of urban area
14 within each 2×2 km grid cell was derived from the land cover map of the Global Land Cover
15 Facility (GLCF) 1×1 km resolution database from the University of Maryland. This database
16 is based on the methodology of Hansen and Reed (2000) and Advanced Very High Resolution
17 Radiometer (AVHRR) data. The decreases in horizontal wind speed are balanced by an
18 increase of the vertical component of the wind. However, the current configuration does not
19 account for the urban heat island effect either in the ECMWF product or in the processing of
20 this product before its use by CHIMERE.

21 The simulations were initialised on 15th April, 2012. For the CO₂ simulations, the initial mole
22 fractions and the open boundary conditions (at the lateral and top boundaries of the model)
23 were imposed using simulated CO₂ from the Monitoring the Atmospheric Composition and
24 Climate Interim Implementation (MACC-II, 2012) forecasts at ~ 80 -km resolution globally
25 (Agustí-Panareda et al., 2014). The MACC-II forecast was initiated on 1st January, 2012 with
26 online net ecosystem exchange (NEE) from the CTESSEL model (see the description below
27 of the estimate of natural fluxes used for the CHIMERE simulations) and prescribed fossil
28 fuel CO₂ emissions and air-sea fluxes, and is not constrained by CO₂ observations. For the
29 CH₄ with CHIMERE, the initial and boundary conditions were imposed homogeneously in
30 space and time to be equal to 1.87 ppm, according to the typical mole fractions measured at
31 the Mace Head atmospheric measurement station in 2012 (NOAA., 2013). The top boundary
32 conditions were set to a smaller value: 1.67 ppm.

1 Anthropogenic emissions of CO₂ and CH₄ were prescribed to CHIMERE within its domain
2 using the NAEI emission inventory described in Sect. 2.1. Three-dimensional hourly
3 emissions for CO₂ and CH₄ were interpolated from this inventory on the 2-km horizontal
4 resolution model grid. The derivation of the emissions for the UK based on the NAEI
5 inventory included injection heights for major point sources and temporal profiles (see below
6 for details on the definition of injection heights and temporal profiles). The CO₂ emissions for
7 the small part of France appearing in the domain were derived from the Emission Database
8 for Global Atmospheric Research (EDGAR, 2014) at 0.1° horizontal resolution for the year
9 2008. Injection heights and temporal variations were ignored for this part of France, which is
10 assumed to have little impact on the simulation of CO₂ in London because of the distance
11 between these two areas and since the dominant wind blows from the southwest.

12 The definition of injection heights can have a large impact when modelling the transport of
13 CO₂ mole fractions from combustion point sources (Bieser et al., 2011). Many parameters
14 underlying the effective injection heights for each source are not available (e.g., the stack
15 heights, the flow rate and the temperature in the stacks). Furthermore, this study focuses on
16 data during summer, and, as indicated later, during the afternoon when the troposphere is
17 well-mixed, so that the impact of the injection heights is minimum. Therefore, we derived
18 approximate values for these heights as a function of the sectors associated with the point
19 sources only, and based on the typical estimates by sector for nitrogen oxide gases (NO_x), CO
20 and SO₂ (and for neutral atmospheric temperature conditions) from Pregger and Friedrich
21 (2009). The resulting injection heights for the emissions listed as point sources by the NAEI
22 inventory (other emissions were prescribed at ground level) ranged from the second vertical
23 CHIMERE level (~ 25 to 55 magl) for the smallest industrial and commercial combustion
24 plants to the 8th vertical CHIMERE level (~ 390 to 490 magl) for the power stations. All CH₄
25 emissions sources were prescribed at ground level.

26 The variations of CO₂ and CH₄ in time are strongly driven by those of the emissions at the
27 hourly to the seasonal scale (Reis et al., 2009). In the modelling framework of this study,
28 temporal profiles were derived for the three sectors of CO₂ emissions with the largest
29 variations in time: road transport, power generation in large combustion plants, and residential
30 and commercial combustion. They were based on Reis et al. (2009) using data from 2004 to
31 2008. These sectorial profiles were applied homogeneously in space for the whole South of
32 England. For road transport, the temporal profiles were based on the product of monthly

1 weights for a typical year, daily weights for a typical week and hourly weights for each day of
2 the week (with two maxima during week days and one maximum for Saturdays and Sundays)
3 derived from statistical data about the variations of traffic flows in the UK. For the power
4 generation and residential and commercial combustion, only monthly variations were
5 considered based on the consumption for typical years. Previous studies have diagnosed some
6 seasonality for CH₄ emissions (Lowry et al., 2001;McKain et al., 2015). As examples of the
7 potential explanations for this phenomenon, the seasonality of the gas consumption for
8 heating (with large consumption for lower temperatures, especially in winter) could drive
9 seasonal variations in the gas leakage (Jeong et al., 2012), and the seasonal variations of the
10 meteorology (pressure, humidity, temperature) could impact the decomposition and release of
11 CH₄, and thus the emissions, from the waste storage and waste treatment sector (Börjesson
12 and Svensson, 1997;Masuda et al., 2015;Abushammala et al., 2016). However, characterizing
13 such seasonal variations is a difficult task, which may vary substantially depending on the
14 sectors and cities. To our knowledge, there are no studies on which we could build reliable
15 temporal profiles for the CH₄ emissions in London, and we thus did not attempt to derive
16 them. Instead, we set the CH₄ emissions constant in time.

17 Natural fluxes of CO₂ were taken from the 15-km resolution NEE product from ECMWF
18 (Boussetta et al., 2013), which is calculated online by the CTESSEL land surface model
19 coupled with the ECMWF numerical weather prediction model. The CTESSEL model does
20 not have a specific implementation for urban ecosystems and due to its moderate 15-km
21 horizontal resolution, we cannot expect this model to provide a precise representation of the
22 role of ecosystems within London.

23 Ocean fluxes for both gases within the domain were ignored because they are assumed to be
24 negligible at the timescales considered in this study (Jones et al., 2012). At the spatial and
25 temporal scales considered in this study, the loss of CH₄ through chemical reactions is also
26 negligible and was thus ignored here.

27 The model tracks the transport of the total CO₂, but also of its different components
28 separately: CO₂ from the boundaries (BC-CO₂), from the NEE (BIO-CO₂) and from fossil-
29 fuel emissions (FF-CO₂). The model does not track CO mole fractions; however, the CO
30 measurements are used to evaluate the FF-CO₂ in Sect. 3.7.

31 The 15-km resolution of the ECMWF analyses, used as meteorological forcing for
32 CHIMERE, yields relatively uniform wind speed and direction at the city scale. The

1 interpolation of this product on the 2-km CHIMERE grid is compared with the observations
2 from surface meteorological sites located in and around London in Sect. 3.3.

3 **2.5 Meteorological measurements**

4 An important contribution to model–data discrepancies can arise from errors in the
5 representation of meteorological conditions; particularly wind speed and direction, and
6 mixing layer height. To evaluate the errors in the meteorological forcing of CHIMERE,
7 hourly observations of wind speed and direction were collected from the UK Met Office
8 Integrated Data Archive System (MIDAS) (UK Meteorological Office, 2012). The measured
9 wind data were obtained for 10 magl at Heathrow Airport, London ($51^{\circ} 28' 43.32''$, $-0^{\circ} 26'$
10 $56.54''$) and East Malling, Kent ($51^{\circ} 17' 15.36''$, $0^{\circ} 26' 54.24''$). East Malling is located 6 km
11 from the Detling site and Heathrow is located 7 km from the Teddington site and 18 km from
12 the Hackney and Poplar sites. The locations of the meteorological sites are shown in Fig. 1.

13 Observed winds at East Malling were compared with winds from ECMWF (interpolated on
14 the CHIMERE grid) at the lowest level (0–25 m) and at the corresponding horizontal location
15 of the CHIMERE grid. Observed winds at Heathrow were compared with the next CHIMERE
16 level up (25–50 m) because the urban roughness correction had been applied to the lowest
17 level. This avoids strong biases in the model–data comparison that would arise because the
18 urban roughness correction was necessarily applied in a homogenous way for the
19 corresponding model grid cell, while, in reality the site is not located within the urban canopy.

20 Hourly mean mixing height measurements were collected from a Doppler lidar that was
21 located on the grounds of a school in North Kensington ($51^{\circ} 31' 13.97''$, $-0^{\circ} 12' 50.85''$) as
22 part of the Clearflo project (Bohnenstengel et al., 2014). The limited sampling rate of the lidar
23 was accounted for using a spectral correction method described in Barlow et al. (2014) and
24 Hogan et al. (2009). Mixing heights were calculated based on a threshold value of the vertical
25 velocity variance, which was perturbed between 0.080 and 0.121 $\text{m}^2 \text{s}^{-1}$, to check the
26 sensitivity of calculated mixing heights to the threshold, which is an approximate parameter
27 for this computation. Mean, median, 5th and 95th percentile values were calculated for each
28 hour based on these perturbations, and account for both measurement and method
29 uncertainties (Barlow et al., 2014;Bohnenstengel et al., 2014). Based on the 5th and 95th
30 percentile data averaged across all data for each hour, estimated measurement and method
31 uncertainty was between 53 and 299 m throughout the daily cycle, with the highest

1 uncertainties usually overnight. These measurement uncertainties are small when compared
2 with the amplitude of the observed diurnal cycle shown in Fig. 3a. Lidar data were available
3 for the period between 23rd July, 2012 and 17th August, 2012 and were compared with the
4 modelled boundary layer height (diagnosed in the ECMWF forecast using a critical value of
5 0.25 for the bulk Richardson number) at North Kensington during this period.

6

7 **3 Results and discussion**

8 The data used for all statistical diagnostics of the model–data discrepancies in this section
9 (including the wind roses and mean diurnal cycles in Fig. 2 and 3) are for the period 5th July
10 to 30th September, 2012 since data were available at all GHG sites during this period. The
11 analyses of model–data discrepancies in GHG mole fractions utilise the hourly average of the
12 15-minute aggregate measurements (Sect. 2.3) and the analyses of meteorological
13 measurements relate to hourly data for the same period. However, some of the figures with
14 time series of the GHG concentrations display the GHG available data in June 2012 to
15 provide indications that the behaviour of the model is similar between June and the following
16 months. Hereafter, we use the term “signature” to refer to the positive or negative amount of
17 atmospheric gas mole fraction (and to its spatial and temporal variations) due to a given flux
18 (natural or anthropogenic surface source or sink over a given area and over a given time
19 period, or advection of an air mass from a remote area).

20 **3.1 First insights on the influence of local sources on urban GHG** 21 **measurements**

22 We first consider the representativity of the CO₂ and CO at the urban sites by analysing them
23 as a function of wind speed and direction. In particular, we try to give a first assessment of the
24 weight in the measurements of “local” sources. By local sources, we refer to sources that are
25 located at distances from the measurement sites that are shorter than the distances over which
26 we can simulate the transport from these sources at the spatial resolution of our Eulerian
27 model. This includes sources at less than 1–5 km from the measurement sites since the model
28 has a 2-km horizontal resolution. Figure 2 shows wind roses at Hackney and Poplar for
29 measured CO and CO₂, and modelled CO₂, alongside aerial images of the site locations. To
30 reduce the influence of boundary layer variation on the measured and modelled mole

1 fractions, and to anticipate the data selection on which the study will focus, we include
2 measured and modelled data for the afternoon period only (see Sect. 3.2).

3 At Hackney there is an increase in measured CO and CO₂ mole fractions during periods of
4 south-easterly wind (Fig. 2a and b). A busy roundabout is located approximately 10 m to the
5 south-east of the Hackney site with an A-road running from north to south to the east of the
6 sensor location (Fig 2d). There is no increase for south-easterly winds when analysing
7 modelled CO₂ (Fig. 2c) suggesting that the observed increase in the measurements could be
8 related to the roundabout whose specific influence cannot be represented at the 2-km
9 resolution in the model.

10 At Poplar, the measured CO and CO₂ is more uniform than at Hackney (Figs. 2e and f). It is
11 still higher in the east but there is no visible signature of the busy roads to the north and south
12 of the site (Fig. 2h). The modelled CO₂ at Poplar (Fig. 2h) is very similar to that of Hackney
13 (Fig. 2c), which can be explained by the proximity between the two corresponding model grid
14 cells (Fig. 1). This supports the earlier assumption that the high mole fractions obtained at
15 Hackney for south-easterly winds are related to a local source. These analyses also raise a
16 more general assumption that while the model simulates the signature of emissions at a
17 relatively large scale (due to handling emissions and transport at 2-km resolution and with
18 significant numerical diffusion) in the area of these 2 sites, there are likely local scale
19 unresolved emissions strongly influencing observed CO₂ at both urban sites.

20 At both urban sites the observed CH₄ wind roses are very similar, showing increased mole
21 fractions towards the east of the sites (data not shown); however, mole fractions are greater in
22 magnitude at Poplar than at Hackney. Similarly to CO₂, the model simulates lower CH₄ mole
23 fractions than observed, with a similar distribution at both sites. The stronger similarity
24 between the wind roses at the two sites when considering CH₄ measurements than when
25 considering CO₂ measurements could be explained by the absence of strong CH₄ local
26 sources in the vicinity of the measurement sites. The NAEI inventory does not locate any
27 major waste treatment facility at less than 5 km from these sites and it assigns a level of
28 emissions from the other sectors (which are characterised by diffuse sources in the inventory)
29 for this vicinity that is similar to the general level of CH₄ emissions in the London urban area.
30 Local CH₄ leaks from the gas distribution could occur and impact the measurements but this
31 analysis does not highlight such local sources.

1 Despite the potential influence of local sources that are unresolved by the transport model, we
2 attempt, in the following sections, to understand and decompose the large discrepancies
3 between the model and the measurements illustrated in Fig. 2. The objective is to analyse
4 whether one can identify the discrepancies due to errors in the emissions at scales larger than
5 $2 \times 2 \text{ km}^2$ which should give insights on the potential for applying atmospheric inversion.

6

7 **3.2 CO₂, CH₄ and mixing layer mean diurnal cycles**

8 The mean observed and modelled diurnal cycles of the CO, CO₂ and CH₄ mole fractions at
9 the four GHG measurement sites and the mixing layer height at North Kensington (see Sect.
10 2.5) are presented in Fig. 3. The amplitude of the mean diurnal cycle in mixing layer height
11 (Fig. 3a) is approximately 1500 m, typical of summer convective conditions in an urban area
12 (Barlow et al., 2014).

13 Observed CO₂ mole fractions at all sites follow a typical mean diurnal cycle (Fig. 3) with
14 maximum mole fractions in the early morning (approx. 05:00, UTC being used hereafter) and
15 minimum mole fractions during the afternoon (approx. 15:00), which can be related to the
16 typical variation in mixing height (Fig. 3a), and in vegetation CO₂ exchanges (with
17 photosynthesis and a CO₂ sink during daytime but CO₂ emissions during night-time) during a
18 daily cycle. The early morning peak in CO₂ mole fractions occurs on average an hour later at
19 the inner city sites (06:00) compared with the rural and suburban sites (05:00) as shown in
20 Figs. 3c and 3e. This may be due to the signature of working-week urban emissions with a
21 peak in traffic around 06:00 to 09:00. This is supported by large observed CO mole fractions
22 at the urban sites with substantial early morning and evening peaks (Fig. 3b). The peak in CH₄
23 measured mole fractions occurs at around 06:00 at all sites (Figs. 3d and 3e).

24 At all sites the model underestimates by 1 to 5% (by 5 to 9 ppm for CO₂ and by 13 to 29 ppb
25 for CH₄) the mean observed CO₂ and CH₄ mole fraction during the afternoon hours (12:00 to
26 17:00), with the highest biases at Hackney for CO₂ and at Poplar for CH₄ (see the model–data
27 biases for this period in Table 1). This underestimation is consistently larger than the
28 confidence intervals for the averaging (associated with the limited time sampling) indicated
29 throughout Fig. 3. The underestimation continues throughout the diurnal cycle at Detling and
30 Teddington (Figs. 3c and d); however, at the urban sites (Figs. 3e and f), the night-time (00:00
31 to 05:00) CO₂ and CH₄ mole fractions are considerably larger in the model than in the

1 observations. This leads to excessively strong diurnal variations at the urban sites, with the
2 exception of CH₄ at Poplar (Fig. 3f).

3 On average, mixing layer height is underestimated in the model at North Kensington by
4 approximately 13% (46 m) of the equivalent lidar measurement during the night and 33%
5 (583 m) during the afternoon (Fig. 3a). There is a high daily variability in the mixing layer
6 height model–lidar measurement discrepancies (with a 454 m STD in the 12:00–17:00 period
7 and a 394 m STD in the 00:00 to 05:00 period) and thus this underestimation is not systematic
8 (see Sect. 3.4). However, this may still explain the overestimation of mole fractions at the
9 urban sites during night-time but cannot explain the underestimation of CO₂ and CH₄ mole
10 fractions during the afternoon.

11 Accurate modelling of the boundary layer height in meteorological models is an on-going
12 concern, particularly in urban areas (Gerbig et al., 2008; Lac et al., 2013) and description of
13 nocturnal stratification is weak in atmospheric transport models (Geels et al., 2007). During
14 the night there can be a considerable urban heat island in London as shown for North
15 Kensington and rural Chilbolton by Bohnenstengel et al. (2014). The model used in our study
16 does not currently have an urban land-surface scheme capable of reproducing the urban heat
17 island effects on atmospheric transport (Sect. 2.4). This may explain the different sign of the
18 model–data discrepancies during night-time between the urban sites and the other sites. We
19 thus restrict the remaining analyses in this paper to the period between 12:00 and 17:00,
20 wherein we can expect the boundary layer to be well developed, to have a stable height and to
21 exert minimum influence on the variations in gas mole fractions (Geels et al., 2007; Göckede
22 et al., 2010).

23 **3.3 Comparison between modelled and measured winds**

24 This section focuses on the horizontal wind, which is a critical driver of day to day variations
25 in GHG mole fractions. We aim to validate the model wind forcing through comparison with
26 meteorological sites described in Sect. 2.5. The analyses (using hourly data) of measured and
27 modelled wind are restricted to between 12:00 and 17:00 because all further GHG analyses
28 are focused on this afternoon period (Sect. 3.2).

29 At East Malling, on average, the model underestimates wind speed by 0.50 m s⁻¹ (12% of the
30 observation mean) and wind direction by 6.90° (defining positive angles clockwise hereafter).
31 The RMS of the hourly model–data discrepancies is 1.10 m s⁻¹ for wind speed and 26° for

1 wind direction. At Heathrow Airport, there is an average positive bias of 0.37 m s^{-1} (7% of
2 observation mean) and 5° for wind speed and direction respectively (RMS model–data
3 discrepancies of 1.27 m s^{-1} and 2.24° for wind speed and direction respectively). Some of this
4 discrepancy may arise from the necessity of comparing the 25–50 m average wind data from
5 the model to the 10 m height measurements at the Heathrow meteorological station.

6 It is highly difficult to translate such statistics of the errors on the wind into typical errors on
7 the simulation of the GHG concentrations at the GHG measurement sites since there is a
8 complex relationship between them, which strongly depends on the specification of the local
9 to remote emissions, and on the spatial distribution of the errors in the meteorological
10 parameters or in these emission estimates at the local to larger scales. The overestimation of
11 the wind speed in the urban area, unlike the underestimation of the mixing layer height, could
12 partly explain the underestimation of the afternoon GHG concentrations at the urban sites
13 since it should lead, on average, to an underestimation of the signature of the urban emissions.
14 However, such an impact of the 7% overestimation of the urban wind speed cannot explain,
15 by itself, the 5 to 9 ppm (21 to 29 ppb) underestimation of the urban CO_2 (CH_4) afternoon
16 concentrations since the average differences between the urban and rural or suburban
17 concentrations during the afternoon do not exceed 10 ppm and 30 ppb according to both the
18 model and the measurements (Fig. 3).

19 Lac et al. (2013) employed the Meso-NH meteorological model at 2-km horizontal resolution
20 with an urban surface scheme that models specific energy fluxes between urban areas and the
21 atmosphere. Their modelled meteorology was compared with hourly meteorological
22 measurements in the Paris region. They showed a typical bias of 0.8 m s^{-1} for wind speed and
23 20° for wind direction, which is larger than the agreement obtained here with the ECMWF
24 winds driving CHIMERE at a native resolution of 15-km. Nehr Korn et al. (2013) found a
25 wind speed bias of between -1 and 2.5 m s^{-1} and RMS of between 1 and 4 m s^{-1} when
26 comparing the WRF model at 1.33-km resolution over Salt Lake City, US, with an urban land
27 surface scheme, to local hourly wind measurements. Therefore, the choice of a 15-km wind
28 field to force the CHIMERE transport model over London does not seem to raise typical wind
29 errors larger than when using a state of the art meteorological model at typically 1 to 3-km
30 resolution.

1 3.4 Daily CO₂ and CH₄ mole fractions during the mid-afternoon

2 The average CO₂ and CH₄ mole fractions for the afternoon of each day throughout the
3 analysis period are presented in Figs. 4 and 5. Some data have been excluded from these
4 analyses; we ignore hereafter, at a given site, any hour during which either modelled or
5 measured data were not available. We have also excluded data from 29th August and 23rd to
6 24th September since the model simulated very large GHG peaks on these days which do not
7 occur in the data. Data from June have been excluded from the statistical analysis to maintain
8 comparability with Detling at which data were not available during this month.

9 According to both the measurements and the model, there is an increase in both the mean
10 value (typically by 7 ppm and 26 ppb according to the measurements) and variability
11 (typically by 1 ppm and 16 ppb according to the measurements) of CO₂ and CH₄ mole
12 fractions, from the rural and suburban Detling and Teddington sites (Figs 4a, 4d, 5a and 5d) to
13 the urban sites Hackney and Poplar (Figs. 4b, 4c, 5b and 5c). This can be explained by their
14 relative distance to the main area of anthropogenic emission in the centre of London (Fig. 1)
15 and due to the location of Teddington (Detling) to the south-west (south-east) of the London
16 area while the dominant wind directions are from the west. According to the model, in
17 general, modelled CO₂ is lower than the signature of the MACC-II boundary conditions (BC-
18 CO₂ in Fig. 4) at Detling and Teddington (by ~ 3 ppm on average) since the negative
19 signature of the CO₂ NEE is larger than the positive signature of the anthropogenic emissions
20 between the model boundaries and these sites (see Fig. 4a) and d)). The London emissions
21 between Detling or Teddington and Hackney or Poplar compensate for this decrease (see Fig.
22 4b) and c)) in such a way that CO₂ at Hackney and Poplar is generally similar to BC-CO₂
23 (with less than 1 ppm difference on average over July–August), except in September when it
24 is higher (by ~ 5 ppm on average) because of the NEE being weaker in this month than during
25 the previous months. Furthermore, the NEE and the anthropogenic emissions do not strongly
26 alter the CO₂ variability from the boundary conditions and the correlation (*R* value) between
27 the variations of modelled hourly CO₂ and those of hourly BC-CO₂ is high (between 0.75 and
28 0.85, depending on the site) even at urban sites. The modelled CH₄ time series, which uses a
29 constant value at the boundaries, cannot show such a dependency on the model boundary
30 conditions (Fig. 5).

31 Statistical comparisons between modelled and measured hourly CO₂ and CH₄ mole fractions
32 are given in Table 1. While the magnitude of the STD of the model–data discrepancies is

1 similar to that of the bias for CO₂, it is far larger than the bias for CH₄. The RMS of CO₂
2 model–data discrepancies is highest at Hackney (12 ppm) but similar at the other three sites (8
3 to 9 ppm, Table 1). Higher RMS of CH₄ model–data discrepancies are found at Poplar and
4 Hackney (48 and 55 ppb) than at Teddington and Detling (32 and 33 ppb) (Table 1). The
5 model–data discrepancies are substantially larger than measurement errors for both CO₂ and
6 CH₄ (Table 1) so we can exclude measurement error as a key source of the discrepancies. The
7 discrepancies should thus mainly be associated with representation errors (Sect. 3.1), transport
8 errors (Sect. 3.3), errors in the domain boundary-conditions and in the prescribed fluxes
9 within the domain and outside the London area, or with errors in the emissions prescribed in
10 the London area (based on NAEI data, see Sect. 2.1). The model–data CO₂ or CH₄ hourly
11 discrepancies at the urban sites during the afternoon are not significantly correlated (*R* values
12 are between 0 and 0.2 for all cases) with the mixing layer height model–lidar measurement
13 discrepancies at North Kensington (Sect. 3.2) or with the wind speed or direction model–data
14 discrepancies at Heathrow Airport (Sect 3.3).

15 Model–data correlations are significantly higher for hourly CH₄ (*R* values between 0.4 and
16 0.6, depending on the sites) than for hourly CO₂ (between 0. and 0.1). However, the
17 amplitude of the variations of hourly CH₄ is strongly different between the model (whose
18 STD is of 15.5 to 18.5 ppb depending on the sites) and the measurements (whose STD is of
19 32.8 to 51.5 ppb), which explains the very large model–data discrepancies given in Table 1.
20 The potential impact of local CH₄ sources near the urban sites (see Sect. 3.1) cannot explain
21 that these discrepancies are very high at Teddington and Detling even though they can explain
22 that they are significantly larger at Hackney and Poplar. This suggests that the actual CH₄
23 conditions on the boundaries of the modelling domain may have a strong influence on the
24 variations of measured CH₄, as for CO₂, but we miss it through the use of constant CH₄
25 boundary conditions in the model.

26 **3.5 CO₂ and CH₄ gradients between pairs of sites**

27 An increasing number of studies on the atmospheric monitoring of the city emissions focus on
28 analysing and assimilating measurement gradients (Bréon et al., 2015;McKain et al.,
29 2015;Turnbull et al., 2015;Wu et al., 2015;Staufner et al., 2016) rather than measurements at
30 individual sites since it reduces the influence of the GHG fluxes that are outside the city of
31 interest (of the model boundary conditions and of the fluxes that are outside the city but
32 within the model domain when analysing model simulations). This approach assumes that

1 such an influence has a large spatial and temporal scale and is therefore similar for different
2 measurement sites in and around the city (Bréon et al., 2015). Here, the strong influence of
3 boundary conditions on the modelled CO₂, and the potential issue raised by using a constant
4 boundary condition for the CH₄ simulations, leads us to assume that uncertainties in both of
5 the CO₂ or CH₄ boundary conditions can explain a large part of the substantial discrepancies
6 between observed and modelled GHGs that are diagnosed at the four measurement sites. We
7 thus analyse the CO₂ or CH₄ gradient between the urban sites and the rural or suburban sites.
8 Because of this computation, the rural and suburban sites are called hereafter “reference
9 sites”. This analysis requires data at both the urban and the reference sites for a given hour
10 and thus adds a new criterion to the data time selection already described and applied in Sect.
11 3.4. The gradients are henceforth described as follows; Hackney and Detling (HAC–DET),
12 Hackney and Teddington (HAC–TED), Poplar and Detling (POP–DET) and Poplar and
13 Teddington (POP–TED).

14 Figure 6 presents the daily afternoon mean gradients of measured and modelled CO₂ and CH₄
15 mole fractions (ΔCO_2 and ΔCH_4) alongside the daily afternoon mean gradient of modelled
16 fossil fuel CO₂ (FF-CO₂) and NEE (BIO-CO₂) components ($\Delta\text{FF-CO}_2$ and $\Delta\text{BIO-CO}_2$) from
17 the model simulation. One can see from Fig. 6 that the modelled ΔCO_2 closely tracks
18 modelled $\Delta\text{FF-CO}_2$ (with *R* values of 0.80–0.95 depending on the selected pair of sites), while
19 $\Delta\text{BIO-CO}_2$ (the average of which is smaller than 0.9 ppm in absolute value between all pairs
20 of sites) and the influence of the boundary conditions on these gradients (the average of which
21 is smaller than 0.1 ppm in absolute value between all pairs of sites) are relatively small,
22 compared with $\Delta\text{FF-CO}_2$, particularly when Teddington is used as the reference site (Fig. 6).
23 This strongly supports the assumption that the signature of boundary conditions and fluxes
24 outside the London area operates on a large spatial and temporal scale and is therefore similar
25 between different sites within the London area, even though this cannot be directly verified
26 from the measurements. We thus expect that both the modelled and measured gradients
27 between the urban and the reference sites bear a clear signature of the anthropogenic
28 emissions from the London area.

29 The largest hourly ΔCO_2 are observed on the HAC–DET gradient with a mean (\pm STD) of 8.2
30 ± 5.3 ppm. The hourly POP–DET gradients have a mean (\pm STD) of 5.6 ± 4.6 ppm. These are
31 much larger than the gradients observed between an 87 m tower in central London at less than

1 11 km from Hackney and Poplar, and a rural location, at less than 15 km from Teddington, by
2 Rigby et al. (2008).

3 The bias, STD and consequently RMS of the model–data discrepancies between modelled and
4 measured gradients of both CO₂ and CH₄ (Table 2) are much reduced compared with the
5 same metrics at individual urban sites (Table 1). The RMS of the model–data discrepancies is
6 roughly halved for ΔCO₂ compared with CO₂ at a single urban site (from 9.0 or 11.7 ppm for
7 the urban sites to 3.6–6.3 ppm for the gradients depending on the corresponding pairs of
8 sites). There is also a small improvement in correlation between observed and modelled ΔCO₂
9 compared with correlation between observed and modelled CO₂ at individual urban sites
10 (from between 0.02 and 0.13 to between 0.20 and 0.35), but model–data correlations for
11 ΔCH₄ are reduced compared with those for CH₄ at the individual urban sites (from between
12 0.42 and 0.58 to between 0.20 and 0.30).

13 The measurements at each site are affected by a constant calibration bias (see Sect. 2.3),
14 therefore the decrease in model–data biases after the gradient computation partially comes
15 from the cancellation of this systematic error. However, this systematic error (typically ±1
16 ppm and ±5 ppb for CO₂ and CH₄ respectively; Table 1) is much smaller than the difference
17 between the model–data biases when considering the analysis of mole fractions at individual
18 sites (Table 1) and those when considering gradients between these sites (Table 2).
19 Furthermore, the random measurement error should be larger for gradients than at individual
20 sites (since the STD of the measurement error for the difference between two data at
21 individual sites is the RSS of the STD of the independent measurement errors for these data).
22 Therefore, the main driver of the strong decrease of model–data discrepancies when analysing
23 gradients instead of mole fractions at individual sites should be the strong reduction of the
24 large scale errors from the boundary conditions and remote fluxes.

25 The random component of the measurement errors should be uncorrelated between different
26 sites, and thus the STD of the gradient measurement error should be $\sqrt{2}$ times the STD of the
27 measurement error at individual sites. Therefore, the gradient measurement error should
28 remain much smaller (typically equal to 0.4 ppm and 11 ppb for CO₂ and CH₄ respectively)
29 than the gradient model–data discrepancies (Table 2). The gradient model–data discrepancies
30 should thus mainly be related to model (transport and representation) errors and errors in the
31 estimate of fluxes in the London area, unless a significant influence of the remote fluxes

1 remains in the measured gradients even though this section has shown that such an influence
2 is negligible in the modelled gradients.

3 **3.6 CO₂ and CH₄ gradients with wind direction filtering**

4 Figure 6 shows that the fit between the modelled ΔCO_2 and $\Delta\text{FF-CO}_2$ is better for gradients to
5 Teddington than to Detling. Potential explanations could be that Teddington is far closer to
6 London's centre than Detling (Fig. 1), and that Teddington is more frequently upwind of the
7 city than Detling. The signature of fluxes outside the urban area can be assumed to be more
8 homogeneous along the wind direction than over the whole urban area (Bréon et al.,
9 2015;Staufer et al., 2016), in particular for the measurements (for the model, the boundary
10 conditions and fluxes outside London are prescribed with relatively coarse resolution
11 products, see Sect. 2.4; so this signature is homogeneous over larger spatial scales in the
12 model than in the measurements). Bréon et al. (2015) decreased the signature of the fluxes
13 outside the Paris urban area by considering gradients between two sites along the wind
14 direction rather than by considering all gradients irrespective of the wind condition. Applying
15 this general concept to our study, we expect the gradients to Teddington to be representative
16 of the London urban emissions more often than the gradients to Detling. Measured gradients
17 calculated without considering the wind direction, particularly gradients to Detling, could
18 retain a significant influence of the boundary conditions and fluxes outside the London area
19 (even though this does not occur in the model). In extreme cases, the signature of remote
20 fluxes can be far lower at the urban sites than at Detling (e.g., if Detling, unlike the urban
21 sites, sees anthropogenic emissions from the continent) so that the signature of the
22 anthropogenic emissions at the urban sites could not compensate for it; this would explain
23 why the measured gradients sometimes reach negative values (e.g., -20.9 ppm for CO_2 on
24 Sept 9, while the wind blows from the south southwest) even though they were computed to
25 isolate the signature of the London emissions (Fig. 6).

26 Therefore, to reduce the influence of remote fluxes and increase the signature of the London
27 urban emission when analysing both the measured and simulated gradients, we next select
28 gradients for hours in which the corresponding reference site is upwind of the corresponding
29 urban site. In practice, we select the hourly gradient between an urban site and the reference
30 site when the wind direction measured at Heathrow (if the reference site is Teddington) or
31 East Malling (if the reference site is Detling) is within a $\pm 20^\circ$ range around the direction from
32 the reference site to the urban site (which corresponds to the pink shading on Fig. 6). The

1 selected gradients correspond to 22% (101 over 452) of the available HAC–TED afternoon
2 gradients and 22% (93 over 431) of the POP–TED available afternoon gradients for either
3 CO₂ or CH₄. There are only 17 hourly (CO₂ or CH₄) gradients to Detling (3% of all available
4 afternoon gradients to Detling) recorded wherein Detling was positioned upwind of the urban
5 sites. Because of this low number of selected observations, gradients to Detling are ignored in
6 the remainder of the analyses.

7 The statistics of the model–data discrepancies for gradients to Teddington when this site is
8 upwind the urban sites are presented in Table 2. Filtering for wind direction reduced the
9 negative bias and the RMS of discrepancies for ΔCO_2 HAC–TED gradients, but slightly
10 increased the RMS of discrepancies and increased the positive bias on the ΔCO_2 POP–TED
11 gradient relative to the statistics on the discrepancies without wind filtering. The resulting
12 STD of the discrepancies has values (approximately 2.5–3.5 ppm) that correspond to the
13 typical observation and model transport errors identified by other inverse modelling studies,
14 e.g., Bréon et al. (2015) diagnose a 3 ppm STD of the observation error for gradients in the
15 Paris area. However, the bias in ΔCO_2 for both HAC–TED and POP–TED after wind filtering
16 is within the range of 1 to 2 ppm which remains relatively high compared with the average of
17 these gradients both in the model and in the measurements. There is an underestimation of
18 ΔCO_2 at Hackney and an overestimation of ΔCO_2 at Poplar. Regarding ΔCH_4 , all the statistics
19 of the model–data discrepancies after wind filtering are improved substantially, resulting in
20 the RMS discrepancies being roughly halved (from ~ 37 ppb to ~ 15 ppb) when comparing
21 the statistics with and without wind filtering.

22 To increase the number of selected gradients and thus the robustness of the statistics, we next
23 conduct a test wherein the constraint on the wind direction is relaxed to $\pm 40^\circ$ around the
24 direction from the suburban to the urban site. The resulting bias and RMS of model–data
25 discrepancies for ΔCO_2 are very similar for HAC–TED to those with a range of $\pm 20^\circ$ around
26 the direction from the suburban to the urban site (with bias of -1.8 ppm and RMS of the
27 discrepancies of 3.4 ppm). However, the $\pm 40^\circ$ wind direction improves the statistics at Poplar
28 (with bias of 0.9 ppm and RMS of model–data discrepancies of 3.1 ppm). While this option
29 yields better results in general, it diverges from the principle of monitoring the gradients of
30 concentration along the transport direction only.

31 Since local sources have been identified as a potential major source of model–data
32 discrepancies, a further analysis of the gradients when the wind direction is within a $\pm 20^\circ$

1 range around the direction from the suburban to the urban site is conducted by selecting only
2 gradients to Teddington when both the hourly mean wind speed measured at Heathrow and
3 modelled at Teddington are above 3 ms^{-1} . Such a threshold is assumed to decrease the
4 influence of local sources on the variations of the GHG mole fractions (Bréon et al., 2015).
5 However, the sensitivity to this selection is relatively weak and it only slightly improves the
6 results for ΔCO_2 and ΔCH_4 for HAC–TED (i.e., decreases the RMS discrepancies by 0.3 ppm
7 for ΔCO_2 and 2.1 ppb for ΔCH_4) and ΔCH_4 for POP–TED (i.e., decreases the RMS
8 discrepancies by 0.4 ppb) and slightly increases the discrepancies for ΔCO_2 for POP–TED
9 (i.e., increases their RMS by 0.2 ppm), while further decreasing the number of observations
10 (to 82 POP–TED gradients and 87 HAC–TED gradients for either CO_2 or CH_4) and thus
11 reducing the robustness of the statistics.

12 **3.7 Estimation of the fossil fuel component of the CO_2 mole fractions**

13 While the signature of the fossil fuel emissions dominates and the contribution of the natural
14 fluxes is weak in the modelled gradient between urban and suburban CO_2 , especially when
15 considering POP–TED and HAC–TED gradients filtered according to the wind direction
16 (Sect. 3.6 and Fig. 6b) and d)), the contribution of the natural fluxes can be significant even
17 when applying the wind direction filtering for HAC–DET or POP–DET CO_2 gradients (Fig.
18 6a) and c)). Furthermore, the CTESSEL model used to simulate the CO_2 NEE does not
19 correctly represent the NEE in the London area (see Sect 2.4) while the natural fluxes within
20 urban areas can be significant compared with the anthropogenic emissions (Nordbo et al.,
21 2012). These points, the discussions in Sect. 3.6, and the residual discrepancies when
22 comparing measured and modelled gradients question the validity of the assumption that the
23 signature of the natural fluxes is not significant compared with that of the fossil fuel
24 emissions in the measured gradient with or without wind direction filtering.

25 In this section we thus attempt to improve the focus on the signature of the urban emissions
26 by deriving a CO_2 fossil fuel component from both the modelled and the measured gradients.
27 While the model directly provides the fossil fuel CO_2 gradient ($\Delta\text{FF-CO}_2$) values, we use an
28 empirical method based on the continuous CO measurements to extract an observation based
29 estimate of $\Delta\text{FF-CO}_2$ between the measurement sites, since CO and CO_2 are co-emitted when
30 fossil fuels are burnt. We focus the analysis on HAC–TED and POP–TED when Teddington
31 is located upwind of the urban sites (with a $\pm 20^\circ$ margin for the selection of the

1 corresponding wind direction), given that such a choice increases the consistency between the
2 model and the data (Sect. 3.6).

3 The ratio of CO to FF-CO₂ (henceforth R_{co/co_2}) varies depending on the different type of
4 sources (e.g., traffic, industry) whose relative influence at the measurement sites can vary in
5 time due to changing traffic and meteorological conditions. However, we assume that these
6 relative influences on HAC–TED and POP–TED gradients are constant in time during the
7 afternoon when Teddington is upwind of the urban sites. We also assume that CO acts as a
8 conservative tracer and does not interact with the surrounding environment during its
9 transport throughout the London urban area (Gamnitzer et al., 2006). Consequently, we
10 assume that R_{co/co_2} resulting from the combination of all sources is constant for gradients
11 between two given sites. Using CO gradients and this ratio, one can derive the observation
12 based $\Delta FF-CO_2$ using the following equation (Eq. 1):

$$13 \quad \Delta FF - CO_2 = \frac{CO_{urb} - CO_{suburb}}{R_{co/co_2}}, \quad (1)$$

14 where CO_{urb} is the observed CO mole fractions at the urban site and CO_{suburb} is the observed
15 CO mole fractions at the suburban Teddington site.

16 We can assume a traffic-dominated value of R_{co/co_2} during summer as we can anticipate lower
17 energy consumption due to natural gas burning in the surrounding area (Vogel et al., 2010).
18 Examination of the diurnal cycle of CO at the urban sites revealed the typical traffic-based
19 variability of increased mole fractions in the early morning and late afternoon and larger CO
20 mole fractions during the day than overnight (Sect. 3.2, Fig. 3b). A value of 0.011 is given to
21 R_{co/co_2} based on the literature that has evaluated traffic dominated values of R_{co/co_2} in urban
22 areas (in Western areas of the world) using the ¹⁴C isotope (Wunch et al., 2009; Vogel et al.,
23 2010; Newman et al., 2013). We further assume that the errors in observation based $\Delta FF-CO_2$
24 are smaller than the model or actual $\Delta FF-CO_2$ variations.

25 Modelled $\Delta FF-CO_2$ is on average slightly larger than observation-based $\Delta FF-CO_2$ on the
26 HAC–TED gradient (observed-based mean $\Delta FF-CO_2 \pm STD$ of 6.2 ± 2.3 ppm and modelled
27 mean $\Delta FF-CO_2 \pm STD$ of 5.8 ± 3.8 ppm). On the POP–TED gradient, observation-based $\Delta FF-$
28 CO_2 is considerably lower than the modelled $\Delta FF-CO_2$ (observation-based mean $\Delta FF-CO_2 \pm$
29 STD of 3.5 ± 1.0 ppm and modelled mean $\Delta FF-CO_2 \pm STD$ of 6.3 ± 2.9 ppm). Statistical
30 comparisons between modelled and observation-based $\Delta FF-CO_2$ mole fractions are given in
31 Table 3. Compared with ΔCO_2 (Table 2), we see a very strong reduction in bias and RMS on

1 the HAC–TED gradient when considering the fossil fuel component only. However, the POP–
2 TED gradients model–data bias is significantly increased when comparing results for Δ FF–
3 CO₂ to those for Δ CO₂ (Tables 2 and 3).

4

5 **4 Concluding remarks**

6 **4.1 Summary and discussions**

7 In this study we compared observed CO₂ and CH₄ mole fractions from four near ground
8 measurement sites in and around London to the simulations from a mesoscale transport model
9 driven by temporally and spatially varying emissions estimates. We aimed to determine
10 whether these near ground sites would be amenable to the atmospheric inversion of the
11 London city scale emissions using such an atmospheric transport model. The measurements
12 and model simulation applied to the period June–September 2012. Given the initial diagnostic
13 of very large model–data discrepancies at the different measurement sites, this study
14 attempted to remove or characterise the influence of some of the underlying sources of
15 uncertainty and to isolate, in both the model and the measurements, the signal that
16 corresponds to the London anthropogenic emissions, which would be targeted by the
17 inversion.

18 Focusing the analysis on afternoon data limited the impact of the model’s inability to
19 correctly predict the transitions of the mixing layer depth in morning and evening. This
20 problem was acknowledged in other GHG transport studies (Denning et al., 1999; Geels et al.,
21 2007; Lac et al., 2013). It is possible that this is exacerbated here because of the London urban
22 heat island, which is significant overnight (Barlow et al., 2014; Bohnenstengel et al., 2014),
23 while the model meteorological forcing did not include an urban parameterisation of the heat
24 fluxes.

25 Focusing the analysis on gradients between the urban sites and the reference sites, especially
26 when selecting them for periods when the suburban reference site was upwind of the urban
27 sites, strongly reduced the impact of errors from the boundary conditions and fluxes outside
28 of the London area in the modelling configuration. Since these boundary conditions and
29 remote fluxes were shown to strongly drive the time variations of the mole fractions in the
30 London area, this focus yielded a relatively low time-varying component of the model–data
31 discrepancies. According to the model, this gradient computation also allowed isolating the

1 signature of the London anthropogenic emissions from that of the natural fluxes in the area.
2 The very good fit between the modelled fossil fuel CO₂ gradient between Hackney and
3 Teddington (when Teddington is upwind of Hackney) and the CO measurement based
4 estimate of this gradient (even though this estimate relied on crude assumptions regarding the
5 correlation between CO and fossil fuel CO₂) could further support the assumption that the
6 urban to suburban along-wind gradient bears a very strong signature of the London emissions
7 that is consistent between the model and the measurements.

8 However, there are large biases between the modelled fossil fuel CO₂ gradient between Poplar
9 and Teddington (when Teddington is upwind of Poplar) and the CO measurement-based
10 estimate of this gradient, and between the modelled and measured CO₂ gradients between the
11 urban and reference sites (filtering or not by the wind direction so that the reference site is
12 upwind of the urban site). These biases could be related to biases in the estimate of
13 anthropogenic emissions in the model. However, there is a clear difference between the
14 measured gradients from Hackney to Teddington and those from Poplar to Teddington, while
15 the model predicts similar gradients when considering either urban site, either when
16 considering the average, or the daily variations of the afternoon gradients (Fig. 6b and d). In
17 particular, this results in model–data biases with opposite signs depending on the urban site
18 considered. This indicates that such biases and much of the variations in the gradient model–
19 data discrepancies are likely related to local sources that cannot be represented with the 2-km
20 resolution model rather than to errors in the city scale estimate of the anthropogenic emissions
21 in the model. Local traffic sources, identified southeast of the Hackney site in Sect. 3.1,
22 should not influence the gradients between Hackney and Teddington when the wind blows
23 from Teddington (on the west) to Hackney (on the east). However, other smaller CO₂ sources
24 are likely to occur nearby to the urban sites.

25 For CH₄ there is greater similarity between observations and between the model simulations
26 at the two urban sites. This suggests that there are no CH₄ local sources near these sites. This
27 seems reasonable because the major CH₄ point sources in urban environments are mainly
28 related to a limited number of specific waste processing sites, none of which are located near
29 the measurement sites by the NAEI inventory, or to points of leakage in the gas distribution
30 network, which only represent 20% of the CH₄ emissions in the London area according to
31 Lowry (2001). This, and the poorer representation of the boundary conditions for CH₄ in the
32 model, can explain why the CH₄ discrepancies were reduced more successfully than the CO₂

1 discrepancies when switching from the analysis of data at individual sites to the analysis of
2 gradients.

3 The errors in the meteorological forcing could also contribute to the model–data CO₂ or CH₄
4 discrepancies even though the analysis did not identify a direct link between them and the
5 model–data wind or mixing layer height discrepancies. The biases between this forcing and
6 measured wind in terms of biases in wind speed (0.37 m s⁻¹ i.e., 7% of observation mean) and
7 in terms of biases in wind direction (5°, where positive is clockwise) were smaller than
8 reported by other studies (Lac et al., 2013), but could be highly problematic in a urban
9 environment with highly heterogeneous sources in the vicinity of the measurement sites
10 (Bréon et al., 2015). Our analysis also showed that the meteorological forcing used in this
11 study underestimated the mixing layer depth during the afternoon.

12 Furthermore, we assessed measurement error as a potential source of model–data
13 discrepancies throughout our analyses in this study. Practical constraints for this short
14 measurement campaign did not allow us to design it in such a way that the measurements can
15 be compared with each other or with other measurements within 0.1 ppm, as recommended by
16 WMO for the northern hemisphere (WMO, 2012). The random measurement error at
17 individual sites was smaller than the model–data discrepancies by an order of magnitude so
18 was considered to be negligible. However, the systematic measurement error is large enough
19 not to be neglected in the raw discrepancies, even though it does not dominate. By definition,
20 the unknown offset in our network vanishes when inter-site gradients are considered, but only
21 because a unique calibration cylinder was used for all sites and for the whole measurement
22 period, which is not a robust solution for larger and longer-lasting local networks. This
23 unknown offset hampers any comparison with other measurement sites in the UK or other
24 places in the world that can therefore not be assimilated in the same inverse modelling system
25 as our London city measurements.

26 **4.2 Conclusion regarding the potential of near ground measurements for the** 27 **monitoring of the city-scale emissions**

28 As a result, the amplitude of the model–data discrepancies in the gradients is often as large as
29 that of the measured gradients, in particular for CH₄, which is not optimistic regarding the
30 ability to adjust the estimate of the London urban emissions. McKain et al. (2015) were able
31 to conduct a city-scale assessment of the emissions of Boston, but this relied on the fact that

1 the fugitive CH₄ emissions from the gas distribution network are high in large cities in the US
2 (Philipps et al. 2013). As indicated above, Lowry et al. (2001) showed that such emissions are
3 far lower for a city like London and similar conclusions were raised by recent CH₄ monitoring
4 campaigns in Paris and Rotterdam within the KIC Climate Carbocount-city project
5 (<http://www.climate-kic.org/projects/carbon-emissions-from-cities/>). In many cities, including
6 London, the major CH₄ emissions do not seem to be spread or significant enough in the urban
7 environment to be monitored using a city-scale atmospheric inversion approach. Monitoring
8 individually (using local-scale inversion techniques, (Yver Kwok et al., 2015)) the specific
9 CH₄ point sources dominating the city emissions and which are often located outside the
10 central urban area (landfills, waste water treatment plants and gas compression sites) may thus
11 prove to be more suitable than the city-scale approach in these cities.

12 For CO₂, the fact that the model–data discrepancies in the gradients, which mainly consist of
13 biases, do not occur at large scale and are likely strongly driven by local sources that cannot
14 be represented with the 2-km resolution transport model raises strong challenges for the
15 inversion of the CO₂ emissions using such a transport model. The location of the
16 measurement sites in the core of the urban area (where the building and traffic is very dense
17 and the topography is made complex by the urban canopy) close to the ground (at less than 15
18 magl), where the sensitivity to local sources is very high, may be responsible for such an
19 issue. Therefore, this study strongly questions the current ability to exploit a GHG network
20 with near ground urban measurement sites alongside a state of the art atmospheric inversion
21 system with kilometre-scale atmospheric transport models and ignoring the sub-grid scale
22 variability of such models.

23 **4.3 Perspectives**

24 Bréon et al. (2015) and Stauffer et al (2016) showed that near ground CO₂ measurements at
25 less than 20 magl, and located in suburban areas at opposite edges of the urban area, can be
26 used for city-scale CO₂ inversions assimilating cross-city upwind–downwind gradients.
27 Exploiting CO₂ measurements at more than 20 magl in the core of the urban area could
28 remain a challenge due to local transport processes and sources, as shown by the analysis of
29 Bréon et al. 2015 for the measurements at the top of the Eiffel Tower in Paris. This challenge
30 may be addressed using networks with different types of urban measurements (e.g. integrated
31 column measurements, Hase et al. (2015)), or averaging data from sufficiently dense

1 sampling to obtain information about the spatial scales relevant to the model. Several
2 conceptual improvements of the inversion methodology could also support the exploitation of
3 urban measurements and to determine where, under which conditions and/or how the large-
4 scale signal can be filtered from the measurements so that it could be well represented by the
5 kilometre-scale models. This would require the analysis of the representativity of potential
6 location of the urban measurement sites and of the CO₂ atmospheric variability at very high
7 resolution using e.g. local high resolution model simulations, mobile measurements, or a very
8 dense array of measurements in a small area. All these measurements and modelling concepts
9 remain to be deployed and tested but this still leaves some potential for the exploitation of
10 near ground urban measurements within city-scale inversion frameworks.

11 Even though this study mainly highlighted the challenges of using near ground urban
12 measurements, it still strengthened the confidence in specific inversion techniques. The
13 assimilation of measurement gradients along the wind direction instead of individual
14 measurements is increasingly used for city-scale activities. However, it is barely used for
15 larger scale inversion activities. Alternative approaches are used to limit the impact of the
16 uncertainties in the model boundary conditions, such as controlling the signature of these
17 conditions at the different measurements site by the inversion (Lauvaux et al., 2012; Henne et
18 al., 2016). The improvement brought by the gradient analysis and the issues encountered with
19 urban measurement strongly supports the potential of this “gradient approach” and
20 encourages the design of city networks where most stations are located at the edge of the
21 urban area rather than spread evenly in the core of this area. Finally, the improvement of the
22 model–data statistics obtained with a simple approach for deriving observation-based fossil
23 fuel CO₂ gradients from CO gradients demonstrates the need for accurate partitioning of the
24 natural and anthropogenic atmospheric signals even in a city like London. This increases
25 confidence in the idea that the joint assimilation of CO and CO₂ data could strengthen the
26 potential of the inversion for monitoring the anthropogenic emissions, even though some
27 recent studies highlight the challenge for deriving precise estimates of the (variable) CO/CO₂
28 anthropogenic emission ratio (Ammoura et al., 2014).

29

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5

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1 Table 1: Summary of systematic and random errors of hourly measurements (see Sect. 2.3)
 2 and of the hourly model–data discrepancies using data between 12:00 and 17:00 UTC during
 3 July to September 2012. Values are given for CO₂ (CH₄ in brackets) in parts per million
 4 (ppm) and parts per billion (ppb) for CH₄. STD denotes standard deviation; RMS denotes root
 5 mean square.
 6

Error Type	Measurement error	Model–data discrepancies			
		Detling	Hackney	Poplar	Teddington
Bias	STD of bias: 1.0 (5)	−5.3 (−19.0)	−9.1 (−20.7)	−5.5 (−28.6)	−5.7 (−13.3)
STD	0.3 (8)	6.5 (27.4)	7.3 (43.2)	7.1 (46.9)	7.1 (29.3)
RMS	-	8.4 (33.3)	11.7 (47.9)	9.0 (54.9)	9.1 (32.2)

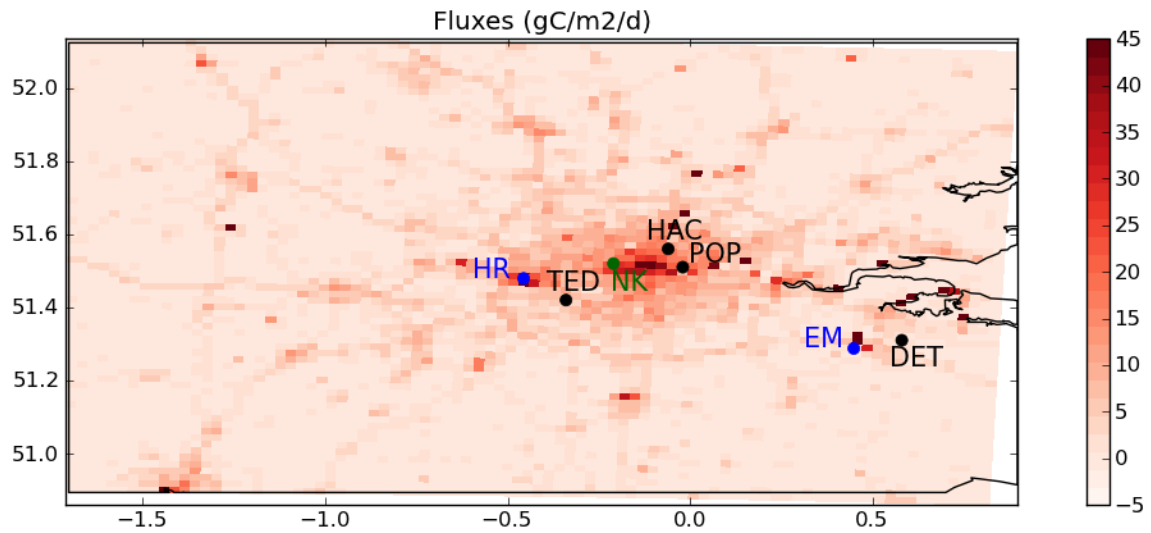
1 Table 2: Summary of systematic and random errors of hourly measured gradients (see Sect.
2 3.5, the standard deviation of the measurement error for gradients is computed as $\sqrt{2}$ times the
3 value of Table 1, assuming null correlation of this error between different sites) and of the
4 hourly gradient model–data discrepancies using data between 12:00 and 17:00 UTC during
5 July to September 2012. Values are given for ΔCO_2 (ΔCH_4 in brackets) in parts per million
6 (ppm) and parts per billion (ppb) for CH_4 . The two last columns present discrepancies for
7 afternoon gradients to Teddington wherein Heathrow measured wind direction places
8 Teddington upwind of each urban site (for angles between the wind direction and the
9 direction between Teddington and a given urban site smaller than 20° , see Sect. 3.6). STD
10 denotes standard deviation; RMS denotes root mean square.

	Gradient measurement error	All afternoon discrepancies				Teddington upwind discrepancies only	
		HAC–DET	POP–DET	HAC–TED	POP–TED	HAC–TED	POP–TED
Bias	STD of bias: 0.0 (0)	–3.8 (–2.6)	–0.2 (–9.7)	–2.9 (–7.1)	0.6 (–16.1)	–1.4 (–3.5)	1.7 (–10.8)
STD	0.4 (11)	5.1 (34.4)	4.4 (36.6)	4.2 (28.3)	3.6 (32.2)	2.9 (14.5)	3.4 (11.0)
RMS	-	6.3 (34.4)	5.1 (29.2)	4.4 (37.8)	3.6 (36.0)	3.2 (14.8)	3.7 (15.3)

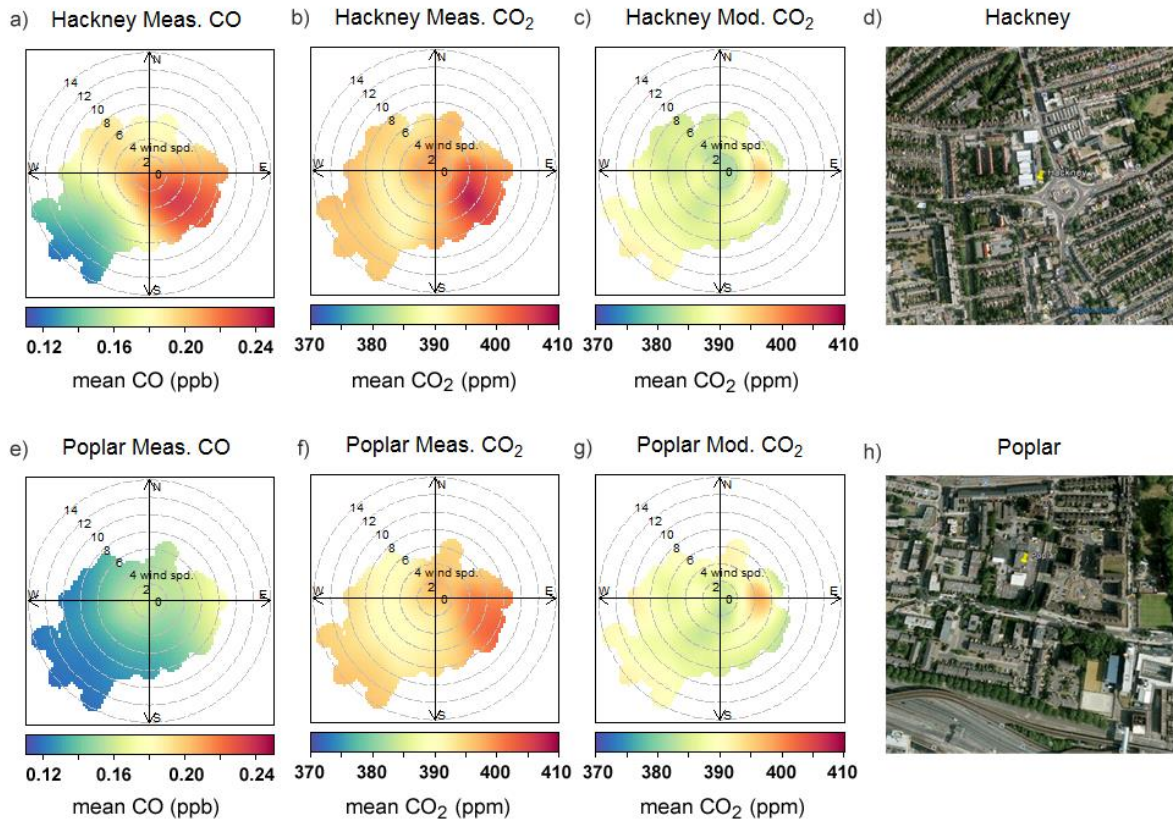
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1 Table 3: Statistics of the hourly difference between modelled and observationally based fossil
 2 fuel CO₂ gradients ($\Delta\text{FF-CO}_2$) in parts per million (ppm) for HAC–TED and POP–TED
 3 during the afternoon periods (12:00 to 17:00 UTC) between July and September, when
 4 Heathrow measured wind direction places Teddington upwind of each urban site (for angles
 5 between the wind direction and the direction between Teddington and a given urban site
 6 smaller than 20°, see Sect. 3.6). RMS denotes root mean square.

Error Type	HAC–TED	POP–TED
Bias	–0.4	2.8
RMS	2.5	3.6

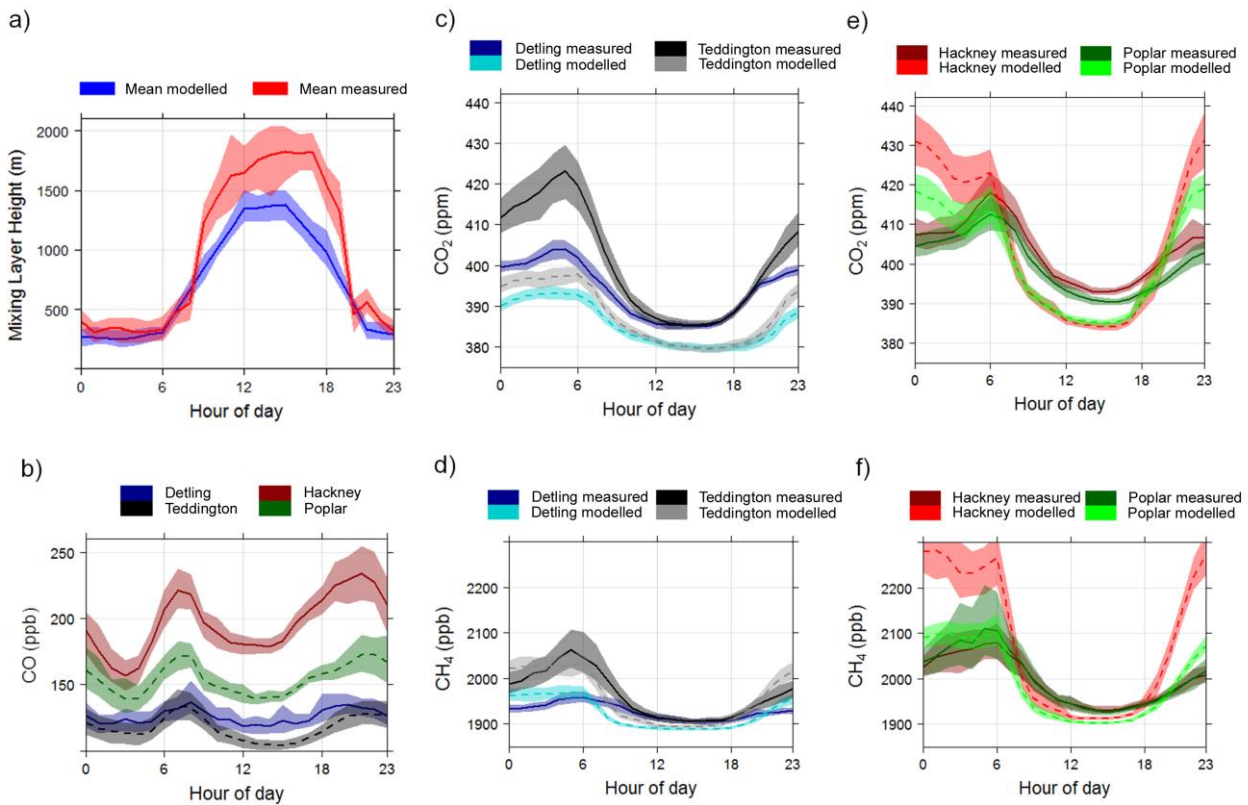


1
 2 Figure 1: Map of the spatially derived (at 2-km resolution) CO₂ fossil fuel emissions
 3 inventories (gC m⁻² d⁻¹) for the London section of the model domain, indicating the location
 4 of the four GHG measurement stations (black), the two meteorological sites Heathrow (HR)
 5 and East Malling (EM) (blue) and the North Kensington LIDAR site (NK, green). Dark red
 6 corresponds to relatively high CO₂ values (upper limit of 45 gC m⁻² d⁻¹) and light pink to
 7 relatively low (uptake) CO₂ values (lower limit of -5 gC m⁻² d⁻¹).
 8



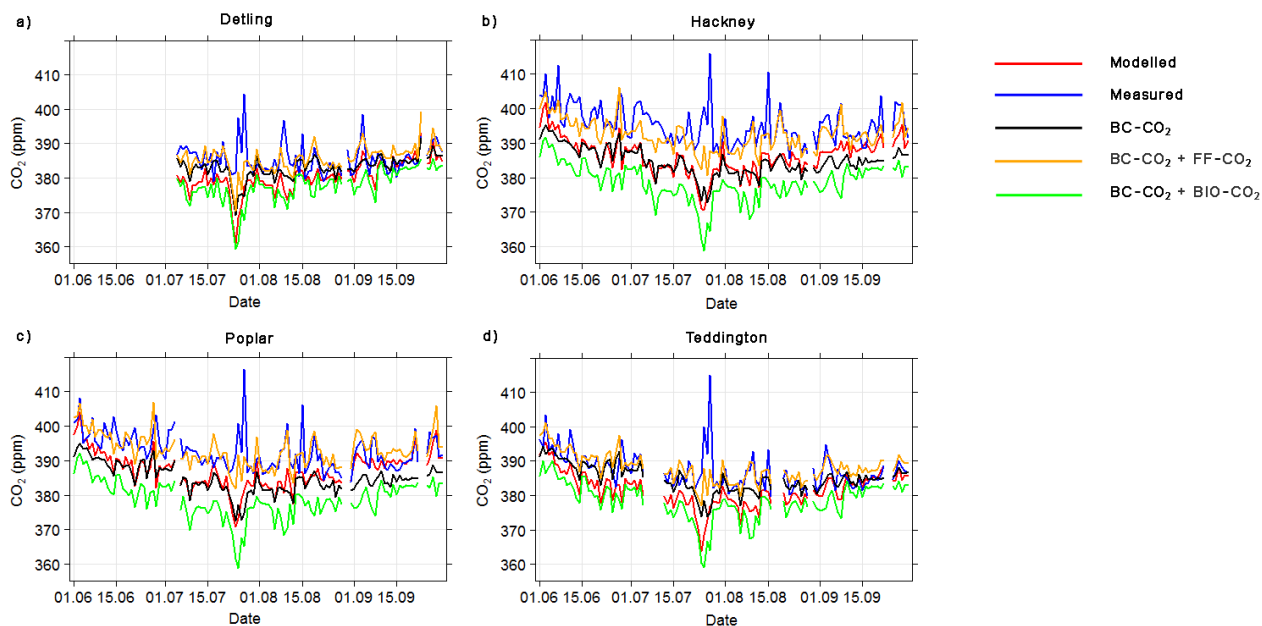
1
2 Figure 2: Wind roses for each urban measurement site incorporating hourly data for wind
3 speed, wind direction (Heathrow measured data) and CO₂ mole fraction between the hours
4 12:00 and 17:00 UTC for a) observed CO mole fractions at Hackney, b) observed CO₂ mole
5 fractions at Hackney, c) modelled CO₂ mole fractions at Hackney, d) a map (© 2012 Google-
6 Imagery and Bluesky, the GeoInformation group) of the immediate vicinity of the Hackney
7 site, e) observed CO mole fractions at Poplar, f) observed CO₂ mole fractions at Poplar, g)
8 modelled CO₂ mole fractions at Poplar and h) a map (© 2012 Google-Imagery and Bluesky,
9 the GeoInformation group) of the immediate vicinity of the Poplar site. The colours on the
10 wind roses show the gas mole fraction (parts per million, ppm) with the radius corresponding
11 to the magnitude of the windspeed (m s⁻¹) and the azimuthal angle to the wind direction (°N).
12 Red corresponds to relatively high concentrations and blue to relatively low concentrations
13 within the given scale of each gas (min = 0.11 parts per billion (ppb) and max = 0.25 ppb for
14 CO, and min = 370 ppm, max = 410 ppm for CO₂).

15

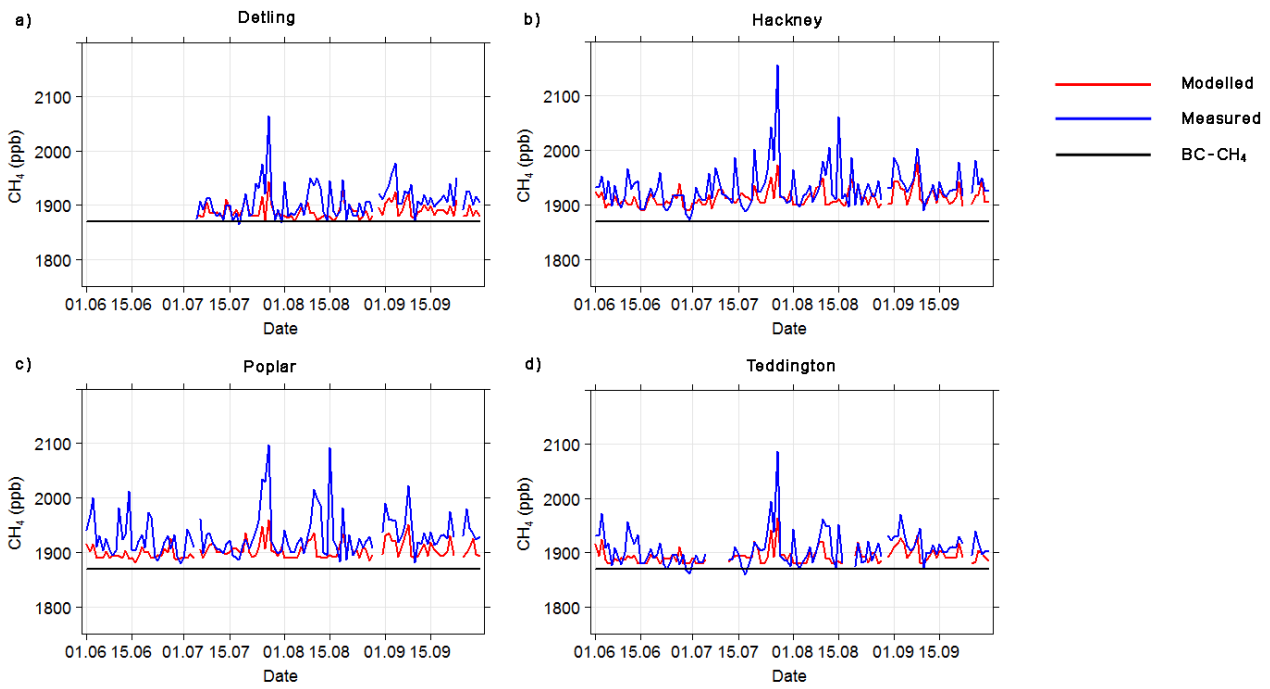


1
 2 Figure 3: Mean diurnal cycles of a) modelled (blue) and measured (red) boundary layer height
 3 and measured mean mixing layer height at North Kensington based on the spectral correction
 4 method described in Sect. 2.5, b) measured CO mole fractions at the rural (Detling, blue),
 5 suburban (Teddington, black), and urban sites (Hackney, red and Poplar, green), c) modelled
 6 (light shade) and measured (dark shade) CO₂ mole fractions at the rural (Detling, blue) and
 7 suburban (Teddington, black) sites, d) modelled and measured (dark shade) CH₄ mole
 8 fractions at the rural (Detling, blue) and suburban (Teddington, black) sites d) modelled (light
 9 shade) and measured (dark shade) CO₂ mole fractions at the urban (Hackney, red and Poplar,
 10 green) sites and f) modelled and measured CH₄ mole fractions at the urban (Hackney, red and
 11 Poplar, green) sites. June data are excluded due to unavailability of data during this period at
 12 Detling. Shading represents an estimate of the 95% confidence interval in the mean, related to
 13 the limitation of the sampling of the daily values at a given hour, assuming these values are
 14 independent (based on the division of two times their temporal standard deviation by the
 15 square root of the number of values).

16



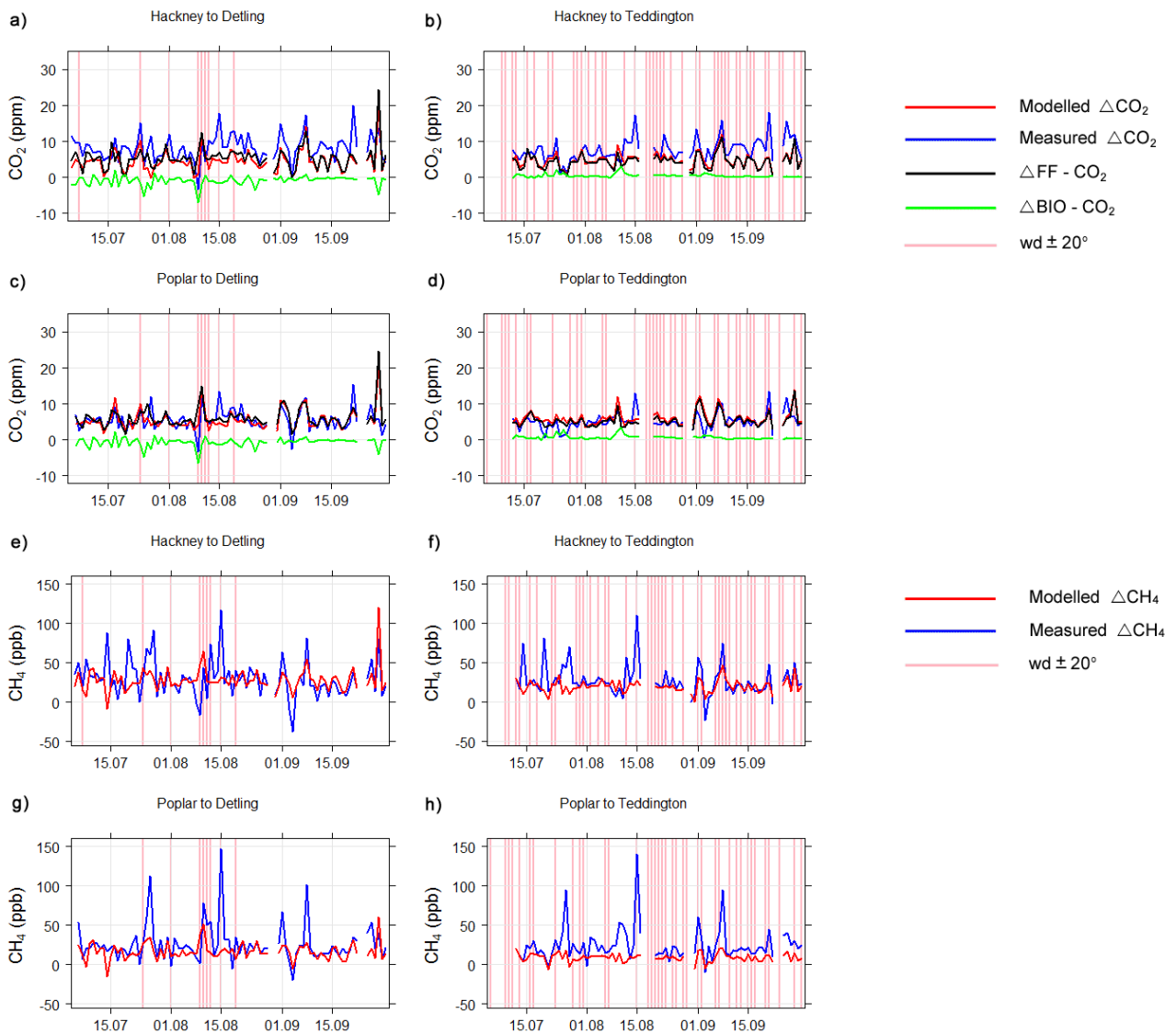
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 2 Figure 4: Time series of averages for the afternoon period (12:00 to 17:00 UTC) each day of
 3 modelled CO₂ mole fractions (red), measured CO₂ mole fractions (blue), modelled signature
 4 of the CO₂ boundary condition mole fractions from MACC-II (BC-CO₂, black), the modelled
 5 signature of the CO₂ fossil fuel emissions added to that of the boundary conditions (BC-CO₂
 6 + FF-CO₂, orange) and the modelled signature of the CO₂ NEE added to that of the boundary
 7 conditions (BC-CO₂ + BIO-CO₂, green) at a) Detling, b) Hackney, c) Poplar and d)
 8 Teddington.
 9



1

2 Figure 5: Time series of averages for the afternoon period (12:00 to 17:00) each day of
 3 measured CH₄ mole fractions (blue), modelled CH₄ mole fractions (red) and the constant
 4 signature of the modelled CH₄ boundary conditions (BC-CH₄, black) at a) Detling, b)
 5 Hackney, c) Poplar and d) Teddington.

6



1
2 Figure 6: Time series of averages for the afternoon period (12:00 to 17:00) each day of
3 measured ΔCO_2 (blue), modelled ΔCO_2 (red), modelled signature of the fossil fuel CO_2
4 emissions ($\Delta\text{FF}-\text{CO}_2$) (black) and modelled signature of the CO_2 NEE ($\Delta\text{BIO}-\text{CO}_2$) (green)
5 between a) Hackney and Detling, b) Hackney and Teddington, c) Poplar and Detling and d)
6 Poplar and Teddington. Time series of averages for the afternoon period (12:00 to 17:00) of
7 measured (dark and light blue) or measured (red and orange) ΔCH_4 between e) Hackney or f)
8 Poplar and Detling (dark blue and red) or g) Hackney and h) Poplar and Teddington (light
9 blue or orange). Vertical pink lines indicate days during which at least one hourly afternoon
10 wind direction is within a $\pm 20^\circ$ range around the direct line from the reference site to the
11 urban site according to the wind measurements at Heathrow (if the reference site is
12 Teddington) or East Malling (if the reference site is Detling).