

Airborne determination of the temporo-spatial distribution of benzene, toluene, nitrogen oxides and ozone in the boundary layer across Greater London, UK

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Keywords

Airborne measurements, volatile organic compounds, benzene, toluene, nitrogen oxides, ozone, proton transfer reaction mass spectrometer, chemiluminescence detector, Automatic Hydrocarbon Network, Automatic Urban Rural Network, air quality, pollution, London.

Abstract

Highly spatially resolved mixing ratios of benzene and toluene, nitrogen oxides (NO_x) and ozone (O₃) were measured in the atmospheric boundary layer above Greater London during the period 24th June to 9th July 2013 using a Dornier 228 aircraft. Toluene and benzene were determined in-situ using a proton transfer reaction mass spectrometer (PTR-MS), NO_x by dual channel NO_x chemiluminescence and O₃ mixing ratios by UV absorption.

Average mixing ratios observed over inner London at 360±10 m a.g.l. were 0.20±0.05, 0.28±0.07, 13.2±8.6, 21.0±7.3 and 34.3±15.2 ppbv for benzene, toluene, NO, NO₂ and NO_x respectively. Linear regression analysis between NO₂, benzene and toluene mixing ratios yield a strong covariance indicating that these compounds predominantly share the same or co-located sources within the city.

Average mixing ratios measured at 360±10 m a.g.l. over outer London were always lower than over inner London. Where traffic densities were highest, the toluene/benzene (T/B)

1 concentration ratios were highest (average of 1.8 ± 0.5 ppbv ppbv⁻¹) indicative of strong local
2 sources. Daytime maxima in NO_x, benzene and toluene mixing ratios were observed in the
3 morning (~ 40 ppbv NO_x, ~350 pptv toluene and ~200 pptv benzene) and for ozone in the
4 mid-afternoon (~ 40 ppbv O₃) all at 360±10 m a.g.l.

5

6 **1 Introduction**

7 Ground level ozone (O₃) is a secondary pollutant, produced from photochemical reactions
8 involving volatile organic compounds (VOCs) and nitrogen oxides (NO_x = NO + NO₂).
9 Ozone has significant detrimental effects on human health and vegetation while NO₂ and
10 some VOCs also have, themselves, direct effects on health. Whilst the basic atmospheric
11 chemistry leading to O₃ formation is generally well understood, there are substantial
12 uncertainties associated with the magnitude and speciation of emissions of both VOCs and
13 NO_x from urban areas, leading to uncertainties in the detailed understanding of urban
14 photochemistry and air pollution.

15 In urban areas the dominant anthropogenic sources of VOCs are vehicular exhaust, fuel
16 evaporation and emissions from the commercial and industrial use of solvents (Karl et al.,
17 2009;Langford et al., 2010). Vehicular emissions are the predominant source of VOCs to the
18 atmosphere in urban and suburban areas, accounting for > 50% of the total (Watson et al.,
19 2001;Na et al., 2005;Kansal, 2009) with a wide range of VOCs emitted directly due to fuel
20 evaporation and from vehicular exhaust as unburnt fuel and as partially oxidized fuel
21 components. The dominant urban sources of NO_x are combustion processes, including
22 vehicles. In the UK as a whole, about 50% of NO_x is thought to be derived from vehicles,
23 although this percentage is larger in urban areas (Lee et al., 2015).

24

25 VOC and NO_x emissions from airports are also of importance, originating due to a
26 combination of emissions from aircraft exhaust, ground support equipment (GSE) exhaust
27 and evaporative losses during aircraft refuelling (Carslaw et al., 2006). High mixing ratios of
28 aromatic compounds, such as toluene and benzene, and low NO_x mixing ratios have been
29 previously observed in jet engine exhaust immediately after ignition, attributed to low engine
30 temperature causing incomplete combustion (Schürmann et al., 2007). Previous aircraft
31 exhaust studies have shown toluene/benzene (T/B) ratios observed during engine ignition are
32 up to 3.1 ppbv ppbv⁻¹, typical of kerosene fuel. At higher engine temperatures, i.e. during

1 taxiing, higher aromatics tend to crack leading to a reduced amount of these species, but
2 increasing amounts of benzene. Thus for aircraft taxiing, a T/B ratio of ~ 0.5 ppbv ppbv⁻¹ was
3 previously observed (Spicer et al., 1994). Similarly higher NO_x mixing ratios are observed
4 due to higher engine combustion. As well as the contribution from aircraft, additional
5 emissions from airport environments occur during the handling of aircraft with GSE. The
6 GSE vehicles are mostly diesel powered, leading to relatively high emission rates of the
7 oxides of nitrogen. During aircraft refuelling, gaseous air-fuel mixtures are released from the
8 aircraft tanks through fuel vents which can be discriminated by the observed T/B ratio, since
9 kerosene fuel tends to have an enhanced amount of aromatic compounds. VOC emissions
10 during engine refuelling were previously found to account for 2.7% of the total VOC
11 emissions of Zurich airport (Schürmann et al., 2007).

12
13 Background and peak UK VOCs, O₃ and NO₂ mixing ratios are determined hourly by the
14 national monitoring networks such as the Automatic Hydrocarbon Network (AHN) and the
15 Automatic Urban and Rural Network (AURN), both operated by the Department of
16 Environment, Food and Rural Affairs). Hourly mixing ratios of NO_x species are currently
17 measured at 130 network sites with selected VOCs measured at 4 sites. Within Greater
18 London these sites form part of the London Air Quality Network (LAQN). However,
19 measurements from these networks suffer from the limitations of being made at relatively
20 few sites and so may not be representative of mixing ratios over larger spatial scales.

21
22 The development of fast-response analytical instruments for NO_x and VOCs means that the
23 mixing ratios of these analytes can now be measured at high spatial resolution from low-
24 flying aircraft. The advantages of in-situ aircraft measurements are that they provide
25 information on the horizontal and vertical distributions of air pollutants over a large spatial
26 area allowing continuous gradients of mixing ratios to be observed across cities and their
27 surrounding rural areas.

28
29 In this study, we investigate the mixing ratios of O₃, benzene, toluene, NO, NO₂ and NO_x
30 across the Greater London region during several flights using the Natural Environment
31 Research Council (NERC) Atmospheric Research and Survey Facility Dornier 228 aircraft
32 between 24th June and 9th July 2013. The aim of this work was to (i) quantitatively determine
33 the vertical, horizontal spatial and temporal distribution of VOCs, NO_x and ozone mixing

1 ratios across London from an airborne platform, with a view to identify dominant emission
2 sources in the region using measured T/B concentration ratios and (ii) wherever possible,
3 compare these fast response airborne measurements with hourly ground-level measurements
4 made by the national monitoring networks.

5 6 **2 Method**

7 **2.1 NERC Dornier 228**

8 The NERC Dornier 228 is a twin-engine turbo-prop powered, non-pressurised aircraft
9 operated by the Airborne Research and Survey Facility (ARSF) based at Gloucester airport in
10 central England. The aircraft has a cabin volume of 14 m³ and operated with a crew of 2
11 pilots and 4 scientists for the duration of the flights. The aircraft has a minimum and
12 maximum airspeed of 65 and 95 m/s respectively producing a maximum range of 2400 km.
13 The aircraft has a maximum payload of 5970 kg including fuel, with a maximum operational
14 altitude for science of 4500 m.

15 16 **2.2 Flight description**

17 Six research flights (RF) totalling 15 hours in duration were conducted between the hours of
18 8:30 – 17:20 UTC (table 1). Figure 1a shows all flight legs conducted during the project,
19 overlaid on a transport map of SE England. Here we will focus on data obtained in transects
20 across London. Figure 1b shows a map of Greater London on which typical repeated south-
21 westerly to north-easterly flight legs of ~50 km are plotted. Identical flight legs across
22 Greater London were chosen due to tight air traffic regulations and to allow data analysis in
23 both a temporal and spatial domain. The grey area represents the Greater London boundary,
24 the black area the inner London boundary and the blue area London's congestion charging
25 zone (CCZ) in which road traffic is heavily regulated and subject to financial charging.
26 Airspeed and altitude were fixed during the flights across Greater London with mean values
27 of $73 \pm 3 \text{ m s}^{-1}$ and $360 \pm 10 \text{ m a.g.l}$ respectively (table 1).

28
29 A north-westerly wind direction was observed during the flights, perpendicular to the flight
30 transects. (table 1). Perpendicular wind directions are useful in providing a cross section of
31 pollutant mixing ratios across London. RF 1 focussed on vertically profiling the PBL above
32 London. Boundary layer (BL) height determinations were made from a combination of
33 airborne observations and ground based measurements. Approximately hourly lower cloud
34 base altitude determinations were made from Heathrow airport using laser cloud based

1 recorder (LCBR) observations. The lowest observed cloud base was interpreted as BL height.
2 Where cloud based observations were not available (during clear skies), temporally
3 interpolated BL height determinations from aircraft observations were used. Briefly, before
4 commencing the city transects, a spiral descent from 2500 to 350 m a.g.l was performed 70
5 km south of London (position BL 1, figure 1b). Similarly, immediately after completing the
6 city transects, a spiral ascent from 350 to 2500 m was performed directly north of London
7 (position BL 2, figure 1b). These manoeuvres were performed to determine the height of the
8 BL before and after the flights.

9

10 **2.3 Meteorological and GPS sampling**

11 Core equipment on the aircraft consisted of an Aircraft Integrated Meteorological
12 Measurement System (AIMMS-20) turbulence probe (Aventech Research Inc.) mounted in
13 an underwing PMS type pylon. The instrument is capable of precisely defining the aircraft
14 altitude and velocity to within fractions of one metre per second with a temperature and
15 humidity measurement precision of approximately 1%. This information is combined with
16 fully compensated air-data measurements to compute wind speed with an accuracy of 0.5
17 knot and wind direction accuracy of 5 – 10 degrees (Beswick et al., 2008). The 3D position of
18 the aircraft was measured using an IPAS 20 (Leica) inertial position and altitude system at an
19 accuracy of 0.05 – 0.3 metres. All variables were acquired at a data acquisition rate of 20 Hz.

20

21 **2.4 NO_x sampling**

22 NO_x was measured from the aircraft using a fast time resolution (10Hz), high sensitivity NO_x
23 chemiluminescence system built by Air Quality Design, Inc. The instrument has a dual
24 channel architecture for independent quantification of NO and NO₂. Each channel has a
25 sample flow of 1.5 L min⁻¹ to ensure the required fast response time. Both sample flows are
26 continually humidified to ensure that any changes in ambient humidity do not change the
27 instrument sensitivity due to quenching of the chemiluminescence by water vapour. A
28 detailed review of a similar system was described by (Lee et al., 2009), being a single
29 channel instrument which operates using the same principles at the Cape Verde Atmospheric
30 Observatory. NO₂ was quantified in a second channel by photolytic conversion to NO using
31 blue light LED diodes centred at 395nm. The 395nm wavelength has a specific affinity for
32 NO₂ photolytic conversion to NO, giving high analyte selectivity within the channel. Recent
33 work (Pollack et al., 2010) evaluated the relative high NO₂ affinity for conversion of NO₂ to
34 NO using 395nm blue light LED's. They highlighted the low probability of other species

1 within the gaseous chemical matrices such as nitrous acid (HONO), being affected by the
2 395nm light, so in turn reducing possible non NO₂ species interfering with the measurement.
3 NO_x was then quantified by ozonation of the subsequent total NO present in the reaction
4 vessel after conversion with NO₂ derived from the difference between NO_x and NO mixing
5 ratios.

6 The instrument was calibrated by adding a small flow (5 sccm) of a known NO concentration
7 (5 ppmv – Air Liquide) in the ambient sample flow, resulting in around 10ppbv of NO. The
8 conversion efficiency of the NO₂ converter was measured during each calibration by gas
9 phase titration of the NO to NO₂ by addition of O₃. NO₂ mixing ratio data is corrected for
10 using the measured 90% photolytic conversion efficiency. In flight calibrations were always
11 carried out above the boundary layer, thus ensuring low and stable background levels of NO_x.
12 Typically calibrations are carried out at the beginning and end of a flight, with sensitivities
13 and conversion efficiency interpolated between the two and applied to all data. In this work,
14 the 10Hz data has been averaged to 1Hz, with detection limits for the 1Hz data being ~75pptv
15 for NO and 100pptv for NO₂ with approximate total errors at 1ppbv being 10 and 15% for
16 NO and NO₂ respectively.

17

18 **2.5 Ozone sampling**

19 Ozone was quantified in-situ, using a Thermo Scientific 49i UV absorption instrument
20 generating data every 4 seconds. A mercury lamp emitting UV light was used,
21 with absorption at 254 nm being proportional to O₃ concentration. The
22 measurement uncertainty was estimated to be ±0.8 ppbv.

23

24 **2.6 VOC sampling**

25 Benzene and toluene mixing ratios were determined simultaneously using an Ionicon
26 (Innsbruck, Austria) high sensitivity proton transfer reaction mass spectrometer (PTR-MS)
27 fitted with a stainless steel ringed drift tube (9.6 cm) and three Pfeiffer turbo-molecular
28 pumps. This instrument has been described in detail elsewhere (Karl et al., 2009;de Gouw
29 and Warneke, 2007;Hewitt et al., 2003;Hayward et al., 2002). Therefore only instrument
30 setup, operation and flight modifications are outlined here. The instrument, normally housed
31 in one cabinet, had been re-engineered by the manufacturers into two racks suitable for
32 mounting into the aircraft. To mitigate shock and vibration to the PTR-MS during flight, the
33 instrument racks, mass spectrometer and MD4 diaphragm pump were individually shock

1 mounted using stainless steel spring mountings (vibrachoc). A pressure controller was added
2 (Bronkhorst) which regulates the inlet flow (50-500 sccm), such that pressure upstream of
3 the controller is maintained at a constant value. As a result the PTR-MS drift tube pressure is
4 independent of fluctuations in ambient pressure caused by varying flight altitude. Ambient
5 sample air was only exposed to heated (70°C) Teflon and stainless steel tubing, minimizing
6 memory effects, inlet losses and the build-up of impurities in the inlet system. Considerable
7 efforts were made to prevent VOC contamination of the PTR-MS inlet during operation on
8 the ground and during take-off. On the ground the PTR-MS inlet remained closed (and all
9 sample tubing capped). Approximately 3 hours before each flight the instrument voltages
10 were switched on to allow for primary ion count stabilisation and instrument calibration.
11 During this time dry zero grade air (BOC) was purged through the zero air generator and
12 PTR-MS inlet in series to minimise instrument background and to prevent the build-up of
13 contaminants. Immediately prior to take off, the sample flow was instantaneously switched to
14 dry zero grade air contained in a 1L silica coated stainless-steel can (Thames Restek, UK)
15 within the aircraft, which was then continuously sampled until the aircraft had reached an
16 altitude of 2500m, allowing the PTR-MS to be fully operational during take-off.

17
18 VOC measurements were obtained at a sampling rate of 5 Hz and a repetition rate of ~2 Hz.
19 In this work, the 2Hz mixing ratios data has been averaged to 1Hz for analysis. The target
20 protonated masses and likely contributing compounds were m/z 79 (benzene) and m/z 93
21 (toluene). Additionally, both the primary ion count m/z 21 ($\text{H}_3^{18}\text{O}^+$), its first water cluster
22 ($\text{H}_3^{18}\text{O H}_2^{18}\text{O}^+$) at m/z 39 and O_2^+ at m/z 32 were determined. PTR-MS drift tube pressure,
23 temperature and voltage were held constant at 2.0 mbar, 40°C and 480 V respectively,
24 maintaining an E/N ratio of approximately 110 Td. For flights at ~360 m a.g.l, the m/z 21
25 primary ion count ranged between $(4 - 7) \times 10^7$ ion counts per second (cps) with an average
26 of 6×10^7 . Ion counts of m/z 32 ranged between $(0.8 - 3) \times 10^6$ cps, with an average of $2 \times$
27 10^6 cps, which represented 3% of the primary ion signal. Ion counts of m/z 39 ranged
28 between $(1 - 5) \times 10^6$ cps with an average of 3×10^6 cps, which represented 6% of the
29 primary ion signal.

30
31 Toluene and benzene calibrations were carried out approximately 2 hours prior to each flight
32 using an in-house built dynamic dilution calibration system. This involved the dynamic
33 dilution of a 500 ppbv certified gas standard (Apel, Riemer) with humidity controlled zero
34 grade air (BOC gases) to mixing ratios near typically observed levels. Zero air humidity was

1 calibrated over 20 -80% RH in triplicate to assess humidity effects on sensitivity during the
2 campaign. Benzene and toluene do not react with the hydrated hydronium ions generated at
3 higher ambient air humidity within the PTRMS drift tube (Warneke et al., 2001). To account
4 for this humidity dependent PTRMS sensitivity toward benzene and toluene, these
5 compounds were normalised against the hydronium ion counts only. Typical instrument
6 sensitivities observed during the campaign ranged between 380 – 480 icps ppbv⁻¹, 6 – 8
7 normalised ion counts per second (ncps), and 400 – 600 icps ppbv⁻¹, 6 – 9 ncps, for benzene
8 and toluene respectively. Instrument uncertainties were 16±5 and 21±9 % for benzene and
9 toluene respectively, calculated using the standard deviation of linear regression (Sm) of pre-
10 flight calibrations. Instrument limits of detection (LoDs) for 1Hz averaged data were
11 determined by the method outlined by Taipale and colleagues (Taipale et al., 2008) and were
12 13±8 and 18±11 pptv for benzene and toluene respectively.

13
14 During flights, ambient air was sampled from the forward facing stainless steel isokinetic
15 inlet along a heated (70°C) 5 m ¼” Teflon tube (0.21” ID) pumped by a stainless steel
16 diaphragm pump (Millipore) at a flow-rate of 22L min⁻¹. A portion of this ambient air (~300
17 sccm) was diverted into the pressure controlled inlet of the PTR-MS instrument such that the
18 overall delay time was < 3 s. To determine blank VOC mixing ratios, the remaining ambient
19 air was purged into a custom built zero air generator which consisted of a 3/8” stainless steel
20 tube packed with 1g of platinum coated quartz wool (Elemental Microanalysis) which
21 efficiently removes VOCs (de Gouw et al., 2004). The zero air generator was operated at
22 350°C and 30 psi for the duration of the flights to maintain optimal operating conditions. The
23 catalytic converter does not remove water vapour from the sample stream, which is of
24 particular importance as the instrument response from background impurities may depend
25 upon sample air humidity. During flights, zero air was periodically back-flushed through the
26 inlet system to determine instrument background.

27

28 **2.7 LAQN ground monitoring sites**

29 Data were obtained from three LAQN ground level monitoring sites for comparative purposes. These
30 were:

31 (i) Marylebone Road (Westminster), an urban kerbside site in a street canyon, situated 1.5 m
32 from the kerb of a frequently congested 6 lane road, the A501 (51.5225°N, 0.1546°W).

1 (ii) Horseferry Road (Westminster), an urban background monitoring station located within
2 an area of mixed commercial and residential buildings (51.4947°N, 0.1319°W). The nearest
3 road is the B323 Horseferry Road approximately 17 m north of the station.

4 (iii) Greenwich-Eltham (Eltham), a suburban background site situated in Greenwich within
5 an education centre (51.4526°N, 0.0708°E). The site is approximately 25 m from the nearest
6 road, the A210 Bexley Road. The surrounding area consists of trees, grassland, recreational
7 areas and suburban housing.

8
9 These sites all monitor NO, NO₂ and NO_x at hourly resolution and O₃ at 15 minute resolution.
10 However, only the Westminster-Marylebone Road and Greenwich-Eltham monitoring sites
11 monitor benzene and toluene at hourly resolution. The locations are shown in figure S-1.

12 13 **3 Results**

14 **3.1 Intercomparison of WAS TD-GCFID and PTR-MS**

15 To compare the volume mixing ratios obtained with the on-board PTR-MS with those
16 measured by gas chromatography with flame ionisation detection (GC-FID), whole air
17 canister sampling (WAS) was conducted twice per flight using silica coated stainless steel
18 cans (Thames Restek, UK) with subsequent GC-FID analysis for benzene and toluene
19 (Hopkins et al., 2009; Hopkins et al., 2003). The WAS system avoids possible artefact
20 formation or analyte loss that may occur on adsorbents if a pre-concentration sampling
21 system is used (Cao and Hewitt, 1993, 1994a, b). Previous ground observations in several
22 urban environments have shown generally good agreement between benzene and toluene
23 mixing ratios obtained during PTR-MS and GC-FID intercomparisons (Rogers et al.,
24 2006; Warneke et al., 2001). However (Jobson et al., 2010) suggest a 16% overestimation of
25 benzene mixing ratios determined by PTR-MS compared to a GC method, attributed to the
26 fragmentation of higher alkyl-benzenes (eg ethyl-benzene). Inter-comparison of the two
27 sampling methods showed excellent agreement within uncertainty and in particular suggest
28 that the PTR-MS demonstrated minimal bias due to the fragmentation of higher alkyl
29 benzenes during this study, as shown figure S-2. Hence the PTR-MS signal obtained at m/z
30 79 is assumed to be due to benzene alone.

31 32 **3.2 Interpretation of temporal trace gas profiles**

33 Mixing ratios of VOCs, NO_x, O₃ and NO/NO₂ ratios from 27 individual flight-transects of
34 Greater London during RF 2 – 6 were averaged to assess how they changed with respect to

1 time over the 7 days of flights, table 2. As shown in figure 2, NO_x, benzene and toluene
2 mixing ratios followed the typical diurnal pattern previously observed in urban areas with
3 measured maxima during morning rush hours and a measured minimum at approximately
4 16:00 – 18:00 when O₃ reaches its maximum (Langford et al., 2010;Marr et al., 2013). The
5 highest NO_x and VOC mixing ratios were observed in the morning at 10:30 local time, ~ 40
6 ppbv NO_x, ~350 pptv toluene and ~200 pptv benzene at 360±10 m a.g.l., when emissions
7 from traffic related sources are highest and the mixing height relatively low. Mixing ratios
8 decreased throughout the morning, probably due to a combination of boundary layer
9 development leading to dilution and increasing OH oxidation leading to enhanced chemical
10 removal, with mixing ratios stabilising later in the day at 10 – 20 ppbv NO_x and between 90 –
11 150 pptv benzene and toluene. Variations in O₃ mixing ratio are generally attributed to
12 photochemical production in the mixing layer with some contribution from entrainment from
13 the free troposphere (Dueñas et al., 2002). In London, the low O₃ morning mixing ratios were
14 attributed to the destruction of O₃ by rapid titration with NO, which is emitted during the
15 morning rush hour and highest during the morning. As the day progresses, sunlight intensity
16 becomes higher increasing the radical concentration and hence NO to NO₂ oxidation rate
17 from the reaction of NO with peroxy radicals. Subsequent photolysis of NO₂ leads to
18 increased O₃ throughout the day (Pudasainee et al., 2010), with the rate of O₃ production
19 being a function of NO_x and VOC levels as well as sunlight intensity.

20
21 Recent studies of annually averaged daily VOC mixing ratios in London from the 191 m high
22 BT Tower have shown that benzene and toluene mixing ratios typically display two day-time
23 maxima, one occurring around 9:00 and a second larger peak occurring between 18:00 and
24 21:00 coinciding with morning and evening peak traffic periods (Langford et al., 2010;Lee et
25 al., 2015). NO_x mixing ratios are highest when traffic flow peaks, with higher O₃ mixing
26 ratios corresponding to lower NO_x mixing ratios and vice versa during a 24 hour period (Im
27 et al., 2013;Lu and Wang, 2004;Mazzeo et al., 2005). This indicates that patterns in VOC and
28 NO_x emission have a larger effect on observed mixing ratios in the boundary layer than does
29 boundary layer dynamics.

30

31 **3.3 Horizontal spatial distribution of VOCs and NO_x mixing ratios**

32 The predominant wind directions observed during the flights were north-westerly (RF 2-6),
33 perpendicular to the flight transects, (table 1). Research flights 2-6 were used to provide a

1 cross section of pollutant mixing ratios across London. The relative spatial distribution of
2 VOC and NO_x mixing ratios across greater London during these flights were superficially
3 consistent, with average mixing ratios for each flight leg only changing temporally (figure 2),
4 hence only RF 5 is shown here.

5
6 Figures 3 and 4 show 1 km averaged mixing ratios of VOCs and NO_x respectively during RF
7 5 against latitude across Greater London. Both VOCs and NO_x mixing ratios show
8 significantly higher mixing ratios in inner London. For all compounds the highest mixing
9 ratios were observed within inner London at 360±10 m a.g.l. particularly directly downwind
10 of the London CCZ. Average mixing ratios observed within inner London were 0.20±0.05,
11 0.28±0.07, 13.2±8.6, 21.0±7.3 and 34.3±15.2 ppbv for benzene, toluene, NO, NO₂ and NO_x
12 respectively. Mixing ratios for benzene, toluene, NO, NO₂ and NO_x for all flights are shown
13 in table 2.

14 Vehicular emissions are considered to be an important source for VOCs and NO_x in Greater
15 London (Langford et al., 2010; Lee et al., 2015). Toluene has a shorter atmospheric lifetime
16 than benzene due to faster photochemical removal by OH (rate constants of $1.45 \pm 0.06 \times 10^{12}$
17 k , cm³ molecule⁻¹ s⁻¹; $6.03 \pm 0.17 \times 10^{12}$ k , cm³ molecule⁻¹ s⁻¹ for benzene and toluene
18 respectively at 298 K; (Ohta and Ohya, 1985)), thus the T/B ratio can indicate the
19 photochemical age of the pollution carried by air masses (Warneke et al., 2001; Atkinson,
20 2000). Very close to the source of emissions (e.g. at the kerbside), the ratio of VOC mixing
21 ratios should be similar to those in the emissions themselves. As toluene is more rapidly
22 removed by oxidation, the T/B ratio progressively decreases as air is transported over longer
23 distances away from the source. Vehicular exhaust emission ratios from combustion during
24 transient engine operation is dependent on gasoline composition but within Europe typically
25 yield T/B ratios between 1.25 – 2.5 ppbv ppbv⁻¹ (Heeb et al., 2000). The introduction of
26 catalytic converters to vehicular exhausts significantly has been shown to decrease this T/B
27 ratio, attributed to the reduced catalytic conversion efficiency for benzene with respect to
28 alkylated benzenes (Heeb et al., 2000). Hence observed ambient T/B mixing ratios will be a
29 product of the photo-chemical age of the air mass since emission, vehicular fleet
30 composition, gasoline composition and the ratio of vehicles using catalytic converters.

31 Recent long-term VOC measurements made at two ground level sites in central London
32 dominated by traffic sources, Marylebone Road and North Kensington (Valach et al., 2014),
33 showed average T/B ratios of 1.6±0.3 ppbv ppbv⁻¹ and 1.8±0.3 ppbv ppbv⁻¹ respectively.

1 These T/B ratios are similar to the average T/B concentration ratio of 1.8 ± 0.5 ppbv ppbv⁻¹
2 observed within inner London in this study, where traffic sources are likely to be the highest
3 (figure 3). Average T/B concentration ratios in suburban (latitude 51.30 – 51.35°) and south-
4 western Greater London (latitude 51.35 – 51.42°) were 1.1 ± 0.3 ppbv ppbv⁻¹ and 1.3 ± 0.4
5 ppbv ppbv⁻¹ respectively. This could be interpreted as increasing air mass age from emission
6 and suggests that the sources of benzene and toluene in these regions are likely the product of
7 local emission and horizontal advection from inner London.

8

9 Linear regression analysis between NO, NO₂ NO_x, benzene and toluene mixing ratios yielded
10 correlation coefficients (R^2) ranging between 0.12 and 0.64. The weakest linear regressions
11 were observed between toluene and NO ($R^2 = 0.12$, $n = 7500$) and benzene and NO ($R^2 =$
12 0.14 , $n = 6500$), not shown. The strongest linear regressions were observed between toluene
13 and benzene ($R^2 = 0.51$, $n = 6500$) and toluene and NO₂ ($R^2 = 0.64$, $n = 7500$) (figure 5). A
14 strong covariance exists between benzene, toluene and NO₂ mixing ratios indicating that
15 these compounds potentially share the same or co-located sources within the Greater London
16 area, most likely vehicular emission. However the measured NO₂/NO concentration ratio at
17 360m a.g.l is likely to be dominated by photochemistry rather than emission sources
18 (Atkinson et al.2000).

19

20 Figure 5 also suggests a secondary source contribution to toluene that is not shared with NO₂
21 or benzene and hence is not related to traffic emissions. This secondary source is localised to
22 a discrete peak in observed toluene in SE London within the borough of Lambeth (latitude
23 51.455°, longitude -0.141°). This was observed during three of the seven flight transects in
24 which toluene mixing ratios at 360 ± 10 m a.g.l. increased from 0.25 ppbv to 0.6 ppbv with a
25 T/B ratio of up to 3 ppbv ppbv⁻¹, as seen in figure 3. Toluene has numerous anthropogenic
26 sources including evaporative fuel losses, industrial solvents, paint thinners and the
27 manufacturing of ink and paints. Direct toluene emissions from industrialised areas in
28 Mexico city with T/B ratios of up to 8.5 - 12.5 ppbv ppbv⁻¹ have previously been reported
29 (Karl et al., 2009). In the absence of any identifiable industrialised areas upwind of the region
30 of high T/B ratios in Lambeth, this peak is possibly due to the horizontal advection of
31 industrial emissions from outside of London, or some unidentified localised source of
32 toluene.

33

1 The influence of NO_x and VOC emission from London Heathrow Airport (LHA) during this
2 study was investigated with plume dispersion modelling using the NOAA Hybrid Single-
3 Particle Lagrangian Integrated Trajectory (HYSPPLIT) model. The model isolates the region
4 of the flight track influenced by potential pollutant outflow from LHA during the flight. Four
5 hour averaged forward dispersion forecasting from LHA was modelled for RF1 and RF5
6 between 14:00 – 16:00 and 9:00 – 12:00 local time respectively. The lower and upper limits
7 of the averaged dispersion layer were 300 – 400m agl, similar to the measured average flight
8 altitudes during these flights. During RF1 and RF 5 the transport time from LHA to the flight
9 transect was approximately 25-50 minutes, calculated from the average observed horizontal
10 wind speed and the ~20 km downwind distance (figure 6).

11
12 Figure 6 shows the region of flight transects which were influenced by LHA outflow (51.39 –
13 51.45° latitude). On entering the LHA outflow plume, NO_x mixing ratios at 360±10 m a.g.l.
14 during both RF1 and RF5 were observed to double increasing from ~15 to 30 ppbv,
15 suggesting a strong NO_x source. As shown in figure 4 for RF5, the NO/NO₂ ratio also
16 gradually increased across the plume from 0.5 up to 0.8 ppbv ppbv⁻¹, which is consistent with
17 previous studies that have found higher NO mixing ratios in aircraft exhaust (Spicer et al.,
18 1994; Schäfer et al., 2000). Toluene and benzene mixing ratios showed a negligible increase
19 from ~0.20 – 0.26 and ~0.15 – 0.18 ppbv at 360±10 m a.g.l. across the plume respectively,
20 with T/B ratios of 1.5 - 1.7 ppbv ppbv⁻¹ indicative of vehicular exhaust emission as the
21 dominant VOC source. Previous ground observations (Carslaw et al., 2006) at LHA
22 suggested that approximately 27% of the annual mean NO_x and NO₂ were due to airport
23 operations at the airport boundary. At background locations 2–3 km downwind of the airport
24 they estimated that the upper limit of the airport contribution to be less than 15%. Our
25 measurements are in qualitative agreement with this study, suggesting that even though
26 Heathrow is an important emission source of NO_x, observed mixing ratios of NO_x close to the
27 airport are dominated by road traffic sources. As LHA was ~ 20 km upwind of the flight
28 transects, our observed mixing ratios are likely to be heavily influenced by emissions during
29 advection from LHA to the measurement locations and as such conclusions drawn from this
30 data is tentative.

31
32
33

3.4 Interpretation of vertical trace gas profiles

To date the influence of vertical transport on the distribution of trace gases in the urban boundary layer has primarily been studied with respect to vertical profiles of ozone, which are typically with in-situ instruments mounted on tethered balloons (Beyrich et al., 1996;Güsten et al., 1998;Newchurch et al., 2003). Vertical profiling of VOCs, NO, NO₂ and NO_x have also been studied using a combination of in-situ measurements from tethered balloons and ground based differential optical absorption spectroscopy (DOAS) over several American (Wang et al., 2003;Stutz et al., 2004;Velasco et al., 2008;Hu et al., 2012) and European cities (Glaser et al., 2003). To the author's knowledge, the work herein represents the first vertical boundary layer profiling of both VOCs and NO_x species using research aircraft over a European city.

Vertical profiling of VOCs, NO_x and O₃ above Greater London in this study was conducted during RF 1 on 24/6/13 between the hours of 17:00 -18:00 local time. Vertical profiling consisted of three sequentially stacked flights conducted at 350 m agl (17:00 – 17:20), 510 m agl (17:20 – 17:40) and 650 m agl (17:40 – 18:00). The trace gas mixing ratios observed at each altitude were then averaged along the ~35 km flight path over Greater London. These concentration profiles were then compared with hourly averaged upwind LAQN kerbside measurements made at 17:00 from the Marylebone Road air quality monitoring station to interpret how trace gas mixing ratios change vertically from the street canyon to above the urban canopy. At its closest point, flight legs were ~ 6 km downwind of the Marylebone Road measurement site. During RF 1, a predominantly north westerly wind direction was observed with a mean wind direction and wind speed of $285.9 \pm 17.1^\circ$ and 13.6 m/s respectively. Hence, the vertical concentration profiles observed represents a composite of local emission and horizontal advection of the Greater London region.

Figure 7 shows the comparison between the measured trace gas concentration profiles over Greater London and the Marylebone Road kerbside measurements. The measured concentration distributions of both benzene (0.15 ± 0.01 ppbv) and toluene (0.16 ± 0.01 ppbv) and their corresponding T/B ratio (1.1 ± 0.3 ppbv ppbv⁻¹) were vertically uniform with increasing altitude, suggesting rapid mixing between 350 – 650 metres. In this case VOC losses due to reaction with the OH radical are evidently too slow to produce observable concentration gradients in the vertical distribution. This suggests that turbulence mixes the species up to 650 m agl much faster than the OH radical depletes them. Over urban areas

1 turbulence is promoted throughout the day due to thermal forcing produced by the urban
2 energy balance (Velasco et al., 2008).

3

4 Both NO and NO₂ show a large decrease in mixing ratios between measurements at the
5 kerbside and at 360±10 m a.g.l. (43 and 4.4 ppbv for NO respectively and 28 and 17ppbv for
6 NO₂). In contrast to NO and NO₂, O₃ measurements were lowest at the kerbside site, 17 ppb,
7 increasing to 32 ppbv at 360±10 m a.g.l. The daytime vertical profiles of NO, NO₂ and O₃ are
8 caused due to a combination of turbulent mixing and three main simultaneous competing
9 effects. The chemical production of NO₂ by NO titration with O₃ and RO₂, causing higher
10 NO₂ and lower O₃ mixing ratios closer to the surface due to higher surface NO mixing ratios.
11 Photochemical production of NO and O₃ from NO₂ and subsequent O₃ destruction. NO₂ and
12 ozone dry deposition processes which dominate closer to the surface (Wesely and Hicks,
13 2000).

14

15 The vertical profiles of NO_x and O₃ are superficially anti-correlated with altitude. The
16 observed O₃ profiles, with lower values close to the ground and higher values aloft, agree in
17 their general behaviour with other observations (Beyrich et al., 1996;Glaser et al.,
18 2003;Güsten et al., 1998) The vertical profiles of O₃ and O_x (the sum of O₃ and NO₂) show
19 the importance of NO emission for O₃ depletion, with reduced surface O₃ mixing ratios closer
20 to the ground largely compensated by a corresponding increase in NO₂. As a result, O_x
21 exhibits a very uniform vertical concentration between 350 – 650 m agl. However, O_x mixing
22 ratios are reduced at ground level possibly due to enhanced deposition in proximity to the
23 surface.

24

25 **3.5 Comparison of airborne measurements with LAQN ground sites**

26 Data obtained from three LAQN air quality ground monitoring stations located in three
27 typical urban environments (urban kerbside: Marylebone Road; urban background:
28 Westminster-Horseferry Road; and suburban background: Greenwich-Eltham) were
29 compared against airborne mixing ratios at 360±10 m a.g.l. to assess how O₃ and its
30 precursors are distributed across the city. Dispersion modelling using the NOAA HYSPLIT
31 model was used to highlight regions of the flight track most influenced by pollutant outflow
32 from each of the ground monitoring stations. Briefly, four hour averaged forward and reverse
33 dispersion forecasting was modelled for Marylebone Road, Westminster and Eltham
34 respectively during flights with a prevailing north westerly wind direction (RF 1, RF4 - 6,

1 table 1). RF 2 and 3 were not used in the comparison due to low observed wind speeds, < 5 m
2 s⁻¹. The lower and upper limits of the averaged dispersion layer were 300 – 400 m agl, similar
3 to the measured average flight altitude of 360±10 m a.g.l during RF 1, RF4 - 6. Airborne
4 mixing ratios for comparison were given as the arithmetic average and 1 standard deviation
5 of the hourly measurements within the dispersion plume. The approximate transport times
6 from Marylebone Road, Westminster and Eltham to the flight transect ranged between 3 – 7,
7 7 – 15 and 14 – 28 minutes respectively, calculated from the observed horizontal wind speed
8 and the downwind/upwind distance for each ground station during each flight (figure S-1).
9 Figure 8 shows a linear regression analysis between airborne and ground mixing ratios of
10 benzene, toluene, NO, NO₂, NO_x and O₃. Strong positive correlations are observed for all
11 species at all three ground sites with R² values ranging from 0.54 – 0.97 (n = 7). Ground
12 mixing ratios of both VOCs and NO_x species were significantly higher at the Marylebone
13 Road kerbside site relative to the urban background (Westminster) and suburban background
14 (Eltham) sites. Average mixing ratios observed at ground level for benzene and toluene
15 respectively were 0.12±0.05; 0.21±0.08 ppbv at Marylebone Road and 0.07±0.01; 0.13±0.03
16 ppbv at Eltham, with T/B ratios of 1.7-1.8 ppbv ppbv⁻¹ indicative of vehicular emissions as
17 the dominant source at both sites. NO_x mixing ratios were also significantly higher at
18 Marylebone Road (121.96±45.28 ppbv) than Westminster (40±4.45 ppbv) and Eltham
19 (10.02±4.28). For O₃, the mean mixing ratios observed at Westminster (13.56±4.9 ppbv)
20 were lower than at Eltham (19.14 ± 3.2 ppbv) whilst the lowest mixing ratios were at the
21 Marylebone Road site (9.23±8.42 ppbv). The O₃ mixing ratios at these sites are anti-
22 correlated to that of NO (figure 8), through enhanced NO emission and subsequent titration
23 of O₃ in proximity to busy road networks.

24

25 Also of interest, NO/NO₂ ratios were higher at the Marylebone Road site (0.62±0.25) than at
26 Westminster (0.50±0.15) and Eltham (0.25±0.09). Historically, vehicular diesel and petrol
27 emissions of NO_x were dominated by emissions of NO (NO/NO₂ ratios of 0.9 ≤). However,
28 recent developments in diesel emission technology, specifically diesel oxidation catalysts and
29 particulate filters, have caused significant increases in direct vehicular NO₂ emissions in the
30 UK and Europe. Current diesel emission control technology deliberately produces enhanced
31 NO₂ mixing ratios to oxidise and reduce black carbon particulates in the vehicular exhaust
32 gas (Carslaw and Rhys-Tyler, 2013). Increasing numbers of diesel vehicles in Central
33 London with this emission reduction technology could have contributed to the low NO/NO₂

1 ratios observed from all three ground air monitoring stations observed during this study. This
2 is in good agreement with the observed covariance of benzene, toluene and NO₂ mixing
3 ratios shown in figure 5, potentially indicating these species have common sources, most
4 likely from vehicular emission. However the measured NO/NO₂ concentration ratio at 360m
5 a.g.l is likely to be dominated by photochemistry rather than emission sources (Atkinson et
6 al.2000).

7
8 Airborne mixing ratios of O₃ were consistently higher than those at ground level, consistent
9 with the ground surface in London acting as a chemical sink for O₃, which is in good
10 agreement with the measured vertical profile of O₃ shown in figure 7. Mixing ratios of the
11 selective VOC and NO_x species observed at the roadside site at Marylebone Road were
12 significantly higher than those of the airborne measurements. Assuming this difference is due
13 entirely to mixing, this reduction in mixing ratio crudely indicates a dilution factor of 2 - 6
14 between the roadside site in the Marylebone Road and the 355 m sampling point. This agrees
15 well with comparisons made during REPARTEE I which concluded a dilution factor of ~5
16 for NO_x mixing ratios between Marylebone Road and the 190 m sampling point on the BT
17 tower (Harrison et al., 2012), well above the surrounding building height. Dilution factors for
18 VOC and NO_x species at Westminster and Eltham ranged between 0.46 – 2.34 which are
19 significantly lower than those observed at Marylebone Road. This difference in dilution
20 factors is largely due to firstly the Marylebone Road measurement site being in central
21 London, a very large source of VOCs and NO_x and being closest in proximity to the 6 lane
22 frequently congested road. Secondly Marylebone Road is within an urban street canyon
23 whose orientation serves to maximise mixing ratios of emissions therein. Street canyons are
24 not as well ventilated as with more open locations such as urban and suburban sites which
25 tends to result in increased surface mixing ratios (Pugh et al., 2012;Carlaw and Rhys-Tyler,
26 2013) .

27

28 **4 Conclusions**

29 Measurements of VOCs, NO_x and O₃ in the boundary layer were made in transects across
30 Greater London at 360±10 m a.g.l. during the summer of 2013, with a view to identifying the
31 dominant O₃ precursor sources within the region, and to better understanding the effects of
32 chemical interactions between these pollutants and meteorological variables on urban air
33 quality. Observed benzene, toluene and NO_x mixing ratios across Greater London were
34 mostly due to traffic emissions, with the highest mixing ratios observed over inner London,

1 where the density of traffic and other pollutant sources is higher than over outer London. The
2 highest T/B ratios (1.8 ± 0.5 ppbv ppbv⁻¹) observed within inner London is indicative of local
3 vehicular sources. Linear regression analysis of VOC and NO_x species which showed a
4 covariance between benzene, toluene and NO₂ mixing ratios, potentially indicating that their
5 dominant sources are the same or are co-located throughout London. Modern diesel vehicles
6 use emission control technology to reduce black carbon emissions but which also enhance the
7 NO₂/NO ratio in the vehicle exhaust (Carslaw and Rhys-Tyler, 2013). As the measured
8 NO/NO₂ concentration ratio at 360m .a.g.l. is likely to be dominated by photochemistry
9 rather than emission sources, VOCs correlate well with NO₂ but not NO due to its longer
10 atmospheric lifetime (Atkinson et al.2000).

11

12 Airborne mixing ratios were compared to kerbside data from three LAQN air quality ground
13 monitoring stations within Greater London. Strong positive correlations were observed for
14 O₃, NO, NO₂, NO_x, benzene and toluene species at all three ground sites with R² values
15 ranging from 0.54 – 0.97 (n = 7) suggesting that airborne mixing ratios were characteristic of
16 surface mixing ratios during the analysis period. NO_x and VOC mixing ratios observed at the
17 Marylebone Road air quality monitoring site were 2 – 6 times higher than those observed at
18 360±10 m a.g.l due to a combination of its proximity to the emission sources, photochemical
19 aging and dilution of the air mass during vertical mixing.

20

21 An increase in NO_x mixing ratios from ~15 to 30 ppbv at 360±10 m a.g.l. during RF1 and
22 RF5 was observed ~20 km downwind of LHA. Our measurements tentatively support
23 previous studies that suggest that even though Heathrow is an important emission source of
24 NO_x, observed mixing ratios of NO_x even quite close to the airport are dominated by road
25 traffic sources. Since LHA was ~ 20 km upwind of the flight transects, these observed mixing
26 ratios are likely to be heavily influenced by vehicular emissions during advection from LHA
27 to the measurement location.

28

29 **Author contribution**

30 MD Shaw and JD Lee redesigned the PTR-MS and NO_x chemiluminescence instruments for
31 the aircraft. MD Shaw, JD Lee, A Harvey and B Davison designed the field experiment and
32 carried it out. MD Shaw, JD Lee, A Vaughan, RM Purvis, AC Lewis and CN Hewitt were
33 responsible for analysis/interpretation of the data.

1 **Acknowledgements**

2 We thank the UK Natural Environment Research Council (grant NE/J00779X/1) and the
3 Department of Environment, Food and Rural Affairs for funding We thank Captain Carl
4 Joseph, co-pilot James Johnson and instrumental engineer Thomas Millard (ARSF) for their
5 expert support during the flights and James Hopkins and Shallini Punjabi (National Centre
6 for Atmospheric Science, University of York, UK) for the WAS TD-GC-FID benzene and
7 toluene concentration data.

8

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3 Table.1. Summary of meteorological and flight conditions during campaign.

RF	Date	Time (local)	Mean Wind direction (°)	Mean Wind speed (m s ⁻¹)	Mean True airspeed (m s ⁻¹)	Mean Flight altitude a.g.l (m)
1	24/6/13	15:30 – 18:20	285.9±17.1	13.6±3.3	81.1±3.9	603±28.9
2	26/6/13	16:00 – 18:00	287.5±17.0	3.8±1.0	70.7±3.4	349.8±15.1
3	27/6/13	9:40 – 12:15	277.6±20.9	4.2±1.4	69.6±2.7	354.1±11.1
4	27/6/13	14:20 – 17:50	275.1±24.5	6.6±1.6	72.6±5.4	343.1±31.7
5	3/7/13	10:40 – 13:00	280.7±11.0	6.3±1.3	71.9±4.0	366.1±7.2
6	4/7/13	15:20 – 16:55	240.7±11.3	7.5±1.4	72.5±4.5	365.1±18.3

4

5 Table.2. Summary of mixing ratios (ppbv) observed over inner London during campaign.

	RF1	RF2	RF3	RF4	RF5	RF6
Benzene						
Mean	0.08	0.09	0.22	0.10	0.20	0.10
Median	0.07	0.09	0.15	0.09	0.19	0.10
SD	0.06	0.05	0.06	0.05	0.05	0.05
5 th percentile	0.01	0.03	0.06	0.03	0.09	0.03
95 th percentile	0.178	0.20	0.27	0.17	0.22	0.19
N	16500	13900	14100	2560	7620	11260
Toluene						
Mean	0.17	0.12	0.28	0.15	0.28	0.12
Median	0.16	0.12	0.27	0.15	0.25	0.11
SD	0.07	0.08	0.11	0.07	0.07	0.09
5 th percentile	0.08	0.06	0.05	0.05	0.12	0.01
95 th percentile	4.34	0.26	0.39	0.32	0.38	0.28
N	16500	13900	14100	2560	7620	11260
NO						
Mean	3.83	2.06	17.46	8.81	13.20	4.80
Median	3.46	2.44	16.19	7.76	12.43	3.41
SD	2.16	2.50	7.42	1.88	8.60	3.61
5 th percentile	1.06	0.70	3.49	1.91	1.98	1.23
95 th percentile	7.82	7.94	25.71	7.44	21.33	12.17
N	82500	69500	70500	12800	38100	56300
NO₂						
Mean	15.19	11.99	22.95	18.64	21.02	12.17
Median	13.59	11.44	26.54	22.13	20.23	10.65
SD	6.10	8.29	13.17	7.89	6.38	7.31
5 th percentile	7.56	7.91	11.45	10.21	6.03	3.65
95 th percentile	26.49	31.90	52.13	35.08	25.97	19.60
N	82500	69500	70500	12800	38100	56300
NO_x						
Mean	19.02	16.05	40.41	27.45	34.3	16.97
Median	17.49	17.91	36.02	26.78	32.40	15.95
SD	7.96	10.39	19.87	9.67	15.20	8.50
5 th percentile	8.71	9.00	15.53	12.16	9.35	5.20
95 th percentile	33.62	39.36	76.08	42.69	44.54	30.04
N	82500	69500	70500	12800	38100	56300

6

1 Figure 1a: top map showing all NERC Dornier-228 flights overlaid on UK transport map.
2 Figure 1b: bottom map showing total flight legs across Greater London. Grey area; Greater
3 London boundary, black area; inner London boundary, blue area; London CCZ.
4
5 Figure 2. Top: time series of averaged benzene and toluene concentrations observed at
6 360 ± 10 m a.g.l. during RF 2-6. Bottom: time series of averaged NO/NO₂ ratios and O₃, NO_x
7 concentrations during RF 2-6.
8
9 Figure 3. City cross section of 1km averaged benzene, toluene mixing ratios and T/B
10 instantaneous ratios (ppbv ppbv⁻¹) at 360 ± 10 m a.g.l. across Greater London during RF 5.
11 Figure 4. City cross section of 1km averaged NO NO₂ and NO_x mixing ratios across Greater
12 London at 360 ± 10 m a.g.l. during RF 5.
13
14 Figure 5. Top: linear regression analysis of benzene against toluene mixing ratios at 360 ± 10
15 m a.g.l. during RF 5. Bottom: linear regression analysis of NO₂ against toluene mixing ratios
16 at 360 ± 10 m a.g.l. during RF 5.
17
18 Figure 6. Top: NO_x concentration data (7 metre resolved at 360 ± 10 m a.g.l.) during RF1
19 (left) and RF5 (right) overlaid on UK transport map. Middle: Benzene concentration data (35
20 metre resolved at 360 ± 10 m a.g.l.) during RF 1 (left) and RF5 (right) overlaid on UK
21 transport map. Bottom: Toluene concentration data (35 metre resolved at 360 ± 10 m a.g.l.)
22 during RF1 (left) and RF5 (right) overlaid on UK transport map. Grey area; Greater London
23 boundary, black area; inner London boundary, dark blue area; London CCZ, light blue area; 4
24 hour averaged HYSPLIT dispersion trajectory.
25
26 Figure 7. Average vertical profiles of O₃, NO, NO₂, O_x, benzene and toluene across London
27 during RF1, 17:00 – 18:00 on the 24th of June 2013. X error bars represent standard deviation
28 (1σ) of mixing ratios observed during each flight leg. Mixing ratio at ground level is hourly
29 average from the LAQN Marylebone road air quality monitoring station.
30
31 Figure 8. Linear regression analysis between airborne (at 360 ± 10 m a.g.l.) and hourly ground
32 measurements at Greenwich-Eltham (empty), Westminster-Horseferry road (black) and
33 Marylebone Road (grey) from the LAQN monitoring network during RF1, 4, 5 and 6.