Quantification of air quality impacts of London Heathrow Airport (UK) from 2005 to 2012

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DOI:
10.1016/j.atmosenv.2015.06.048

QUANTIFICATION OF SOME AIR QUALITY IMPACTS OF LONDON HEATHROW AIRPORT (UK) FROM 2005 TO 2012

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HIGHLIGHTS

- Eight years of hourly air pollution data from 8 sites around Heathrow are analysed
- Temporal analysis reveals diurnal, weekly and seasonal patterns and annual trends
- Statistical tools are applied to depict the inter-site relationships
- The relationships with weather parameters and atmospheric circulation are studied
- The contributions of airport and motorway traffic are quantified

ABSTRACT

Among other emission sources in the Greater London area, the international airport of Heathrow is recognised to be a major source of air pollution and is one of the UK locations where European air quality Limit Values are currently breached. However it is very difficult to differentiate between pollutants arising from airport operations and those from the large volumes of road traffic generated by the airport, as well as the nearby M4 and M25 motorways, A4 and A30 major roads, the conurbation of London and other external sources. In this study, eight years (January 2005–December 2012) of measurements of various air pollutants (NO, NO_2, NO_x, O_3, CO, PM_{10} and $PM_{2.5}$) were investigated from 10 sites: eight sites are located within a distance of 2.5 km from the airport, while two sites representative of the regional background and of background air quality in London (Harwell (60 km WNW) and North Kensington (17 km ENE), respectively) were included. A series of statistical tools was thus applied to: (1) investigate the time series by analysing hourly data as diurnal, weekly, seasonal and annual patterns; (2) reveal the effects of the atmospheric circulation upon air pollution by analysing background-corrected polar plots and (3) quantify the impact of the airport upon air quality in the local area using the inter-site differences of measured concentrations. The results show different diurnal patterns in emissions of NO_x from the airport and from the motorways. The concentration increment arising from passage of air across the airport during airport activity (6am-10pm) and with wind speed > 3 m s^{-1} is ca. 1-9 μg m^{-3} of NO_2 and 2-20 μg m^{-3} of NO_x at background stations. Such results are slightly lower than in a previous study analysing the 2001-2004 period. Air quality impacts of the M25 and M4 motorways are substantial only at the Hillingdon site (30 m from M4). Concentration increments of particulate matter can take either small positive or negative values.

Keywords: Airport; aircraft; road traffic; emissions; nitrogen oxides; particulate matter

1. INTRODUCTION

During the last decades, an increasing number of epidemiological studies have established a direct association between the exposure to some ambient air pollutants and adverse effects on human health due to respiratory and cardiovascular diseases (e.g., Dockery, 2009; Katsouyanni et al., 2009; Raaschou-Nielsen et al., 2013). Recently, outdoor air pollution has been classified as known carcinogenic to humans (Group 1) by the IARC. However, in the last decades, most European countries have experienced a general drop of ambient levels for many air pollutants. Generally, this air quality improvement has followed the implementation of legislation, technological advances, the application of successful abatement technologies and other mitigation measures. However, air pollution in Europe remains an actual and serious concern. Under this scenario, the identification, characterisation and quantification of the most relevant sources is amongst the main objectives addressed in research by policy-makers and stakeholders.

In Europe, air quality is monitored by local and national authorities through an extended monitoring network and data are managed to meet EC Directive requirements. In case of the exceeding of Limit Values or even lower assessment thresholds, such data can be used to inform the population about air quality and potential impacts upon health. Moreover, such data represent a valuable resource to develop and implement possible mitigation measures.

Among the EU-27 countries, UK has fewer critical issues in relation to air pollution than some other regions, such as Benelux, Northern Italy and some Eastern European countries (EEA, 2014). However, high levels of air pollutants exceeding the European air quality Limit Values are still recorded in the Greater London urban area (GL), where an extensive and densely populated conurbation hosts more than 9 million inhabitants, with the related high traffic and energy demand for domestic heating. In particular, those pollutants which currently do not fulfil the EU and UK air

quality standards and objectives (DEFRA, 2013a) are nitrogen dioxide (> Limit Value) and ozone (> target value).

Among other emission sources in the Greater London area, the airport of Heathrow (LHR) is recognised to be a major source of nitrogen oxides (e.g., Carslaw et al., 2006; 2008; Stettler et al., 2011; Yim et al., 2013) and NO_2 concentrations have breached the EU and UK annual mean Limit Value (40 µg m^{-3}) at some locations around the terminals in the last decade (UK Department of Transport, 2006; HAL, 2011). The Airports Council International (ACI, 2014) reported that LHR is amongst the busiest airports for arriving and departing passengers (~72 million passengers y^{-1} in 2013), and consequently has congested flight traffic with near capacity utilisation during many hours of the day (e.g., Gelhausen et al., 2011; Bernhart et al., 2012). In the past decade some studies have attempted to estimate the contribution of LHR to local air quality, especially for nitrogen oxides ($NO+NO_2=NO_x$). For example, Carslaw et al. (2006) estimated that airport operations accounted for ~27% of the annual mean NO_x and NO_2 at the airfield boundary and less than 15% (<10 µg m^{-3}) at background locations 2–3 km downwind of the airport. Carslaw et al. (2008) investigated the nitrogen oxides levels in individual plumes from aircraft departing on the LHR northern runway and found that aircraft operational factors such as take-off weight and aircraft thrust setting have effects on concentrations of NO_x. Results of a model evaluation for the 2008/9 period by AEA (2010) indicated that the source attribution from airport operations at surrounding monitoring sites was similar to that calculated by Carslaw et al. (2006). Stettler et al. (2011) estimated that emissions due to the landing and take-off (LTO) cycles accounted for ~8.19×10^6 kg NO_x in 2005, of which more than 80% are in form of NO. HAL (2011) reported that 46% of the total ground level NO_x from aircraft in 2010 was emitted during take-off roll, 21% in taxi-in and taxi-out phases, 19% by the auxiliary power units (APUs), while the remaining 14% is attributed to hold, landing roll and engine testing. Carslaw et al. (2012) quantified the impact of the flight-ban due to the eruption of the Icelandic volcano Eyjafjallajökull on concentrations of NO_x in April 2010

and stated that airport closure resulted in an unambiguous effect on NO_x and NO_2 concentrations. Yim et al. (2013) applied a multi-scale air quality modelling approach to assess the air quality impacts of UK airports and calculated that 24% of UK-wide aviation-attributable early deaths could be avoided in 2030 if Heathrow were replaced by a new airport the in Thames Estuary, because the location is generally downwind of London, and at greater distance.

This study analyses an eight year hourly time series (January 2005– December 2012) of air pollutants measured at 10 monitoring sites. Eight sites are located in the surroundings of LHR, while two stations were selected to be representative of regional background and GL pollution, respectively. The main aims are to investigate the time series for patterns and trends, and study the potential location and strength of the main sources and their impact upon air quality.

2. MATERIALS AND METHODS

Data were measured at 10 sites managed by the UK Department for Environment, Food and Rural Affairs (DEFRA; http://uk-air.defra.gov.uk/) and London Heathrow authorities (http://www.heathrowairwatch.org.uk/). A map of the sites is shown in Figure 1, with greater detail of the sites local to Heathrow in Figure SI1, while the site names, acronyms, some characteristics, the monitored pollutant and the periods of available data are summarized in Table 1. One site (LHR2) is situated 180 m north to the northern runway centreline and a few metres inside the airport boundary. Four sites (GRG, OAK, HAT, HOA) are positioned close (<330 m) to the outer perimeter of the airport, while three sites (HRL, HIL, SLC) are located farther from the airport (> 1 km). The maximum distance between any pair of sites is 6 km (SLC-HOA). A very similar set of monitoring stations was used in a previous study (Carslaw et al., 2006) which investigated data up to 2004. Because of their relative proximity, the eight sites are affected to differing degrees by the same set of sources, which include airport activities (aircraft, ground support equipment, auxiliary

power units), road traffic (mainly due to the M4 and M25 motorways, A4, A30 and minor local roads) and urban emissions (domestic heating). However, due to the high density of potential emission sources in the study area, sites are categorized differently (Table 1). Two supplementary sites were selected to provide comparative data for regional (HAR) and urban London (LNK) background pollution. Despite being classified as "urban background" the Hillingdon site is only 30 metres from the busy M4 motorway, and hence heavily influenced by it.

Analysed pollutants were measured hourly using automatic instruments according to European protocols. Quality assurance and quality control procedures follow the standards for the Automatic Urban and Rural Network (AURN) and the London Air Quality Network (LAQN): all instruments are routinely calibrated, and every six months are fully serviced and undergo an intercalibration audit. Weather data measured at Met Office Heathrow (station ID no. 708) including wind direction and speed, atmospheric pressure, air temperature and relative humidity (RH) were provided by the Met Office (http://www.metoffice.gov.uk) and BADC (http://badc.nerc.ac.uk/data/).

Data were analysed using R version 3.0.1 (R Core Team, 2013) and a series of supplementary packages, including 'Openair' (Carslaw and Ropkins, 2012; Carslaw, 2013). Preliminary data handling and clean-up were carried out to check the datasets for outliers and anomalous records. Particulate matter (PM_{10} and $PM_{2.5}$) was measured automatically using TEOM or TEOM-FDMS (Table 1). However, the main concern with the use of the TEOM technique is the loss of the more volatile component (principally some semi-volatile hydrocarbons and nitrates) because the inlet is held at a temperature of about 50 °C. A simple adjustment applied to the UK data is to apply a factor of 1.3 to TEOM-measured concentrations to give approximate comparability with the European gravimetric reference method. Recently, the use of more sophisticated techniques (TEOM-FDMS and the Volatile Correction Method (VCM)) has allowed robust estimations of PM mass. To harmonise the datasets and obtain comparable data, PM_{10} were reported as gravimetric

equivalent (TEOM x 1.3), VCM corrected and TEOM-FDMS, depending on the technique used. Unfortunately, no suitable correction method yet exists for $PM_{2.5}$ and the sampling stations are equipped with differing instruments, which were sometimes changed during the study period (Table 1). The best compromise is thus to use TEOM for LHR2, GRG, OAK (full period, if available) and TEOM-FDMS for HRL, HAR, LNK (starting about in 2009). Due to this, a cross-comparison between the two groups is not possible.

Data for traffic on the M4 and M25 motorways is provided by the UK Department for Transport, which commissions manual counts of traffic for a number of count points every year. The counts take place between 7 am and 7 pm; each road link is counted a maximum of one day in a year. Data for LHR air traffic is provided by Heathrow authorities.

3. RESULTS AND DISCUSSION

Data frequency distributions for each pollutant during the whole study period are given for all sites as boxplots in Figure SI2, while the time series of monthly averaged concentrations calculated from hourly data are shown in Figure 2. In this study NO_x mass concentrations are expressed as NO_2. The average concentrations of NO over the 8 years at eight sites at Heathrow varied from 18 μg m^{-3} (OAK) and 41 μg m^{-3} (LHR2), while NO_2 ranged from 31 μg m^{-3} (SLC) to 51 μg m^{-3} (at both LHR2 and HIL) and NO_x from 59 μg m^{-3} (SLC) to 114 μg m^{-3} (LHR2). Low levels of nitrogen oxides were recorded at the rural background site (HAR: 2, 11 and 14 μg m^{-3} for NO, NO_2 and NO_x, respectively). All Heathrow sites have NO levels significantly higher than LNK (14 μg m^{-3}), while NO_2 concentrations are comparable (37 μg m^{-3} at LNK). Since vehicular traffic is the major source of nitrogen oxides at LNK, this result gives a first indication that in the surroundings of Heathrow Airport there is an anomaly in NO levels. In recent years there has been growing attention towards NO_x emissions and the NO-NO_2 partitioning in Europe because of the evident discrepancy between achieving NO_x emission reductions and NO_2 ambient concentrations, which

182 do not meet the targets in many locations (e.g., Grice et al., 2009; Cyrys et al., 2012). In the UK,
183 electricity generation is recognized to be the main anthropogenic source of emissions (29.8%),
184 followed by road traffic (~27.5%, of which 14.5% is from passenger cars and 13% from heavy duty
185 vehicles), other stationary combustion sources (25%) and off-road transport (16.6%) (DEFRA,
186 2013b). However, it is evident that road traffic is the main contributor to ambient ground-level
187 concentrations of nitrogen oxides in urban environments, and the recent increase in NO_2 levels in
188 Europe has been related to the growing proportion of diesel-powered vehicles, which are known to
189 have higher primary (direct) emissions of NO_2 (Carslaw et al., 2007). Aircraft engines also emit
190 NO_x, and emissions increase monotonically with engine thrust, i.e. are higher during take-off and
191 lower in taxi and idle phases. The NO-NO_2 partitioning in the emissions of modern high by-pass
192 turbofan engines is also thrust-dependent: NO_2 is principally emitted at idle, while NO is dominant
193 at higher thrust regimes (Wormhoudt et al., 2007). Other in-airport sources of nitrogen oxides may
194 be attributed to: (i) the use of auxiliary power units (APUs), which are small on-board gas-turbine
195 engines; (ii) the ground power units (GPUs) directly provided by airports and (iii) the airport
196 ground service equipment (GSE), which refers to most of the equipment that an airport offers as a
197 service for flights and passengers and includes a large number of vehicles. In this study, the
198 NO_2/NO_x ratio was calculated and results show lowest ratios at LHR2, HIL and HOA.
199
200 Comparing results averaged over 8 years with the annual EC Limit Value for NO_2 (40 μg m^{-3}
201 averaged over 1 year), it is evident that the limit is exceeded at LHR2, HIL and HOA. However, the
202 HIL and HOA sites are strongly influenced by the M4 motorway (HIL) or A4 highway (HOA), and
203 LHR2 is within the airport boundary where the limit values do not apply. Moreover, it should be
204 remembered that NO_2 levels are much lower than those normally recorded in many hotspots in
205 Europe, such as Northern Italy and some areas of Benelux and Germany.
206

Data for ozone are available only for HAR, LNK, HRL and HIL (8 years), while at LHR2 and OAK measurements finished in 2007: highest concentrations were recorded at the rural site, followed by OAK (39 μg m^{-3}) and LNK (38 μg m^{-3}), whereas lower levels were recorded at HIL (27 μg m^{-3}). The information and alert thresholds were exceeded only on a limited number of days. Carbon monoxide and sulphur dioxide are emitted from both vehicular traffic (very little in recent years) and aircraft engines. However, data for CO and SO_2 are available only at 4 and 3 sites, respectively, and at no sites around Heathrow do such data cover the entire study period (generally measurements finished in 2007). The concentrations of CO and SO_2 are well below the limits set by EU Directives or recommended by the WHO (WHO, 2000). Because of the complex photochemistry of the NO-NO_2-O_3 system, the level of total oxidants ($OX=O_3+NO_2$ expressed in ppbv) is frequently reported in the literature (e.g. Anttila et al., 2011; Mavroidis and Chaloulakou, 2011; Notario et al., 2012) to give insights into the oxidative potential in the atmosphere (Kley et al., 1999). The highest OX levels are recorded at LHR2, however such data refer to measurements before April 2007, while the values were lower at HAR and HRL.

The concentrations of PM_{10} calculated over 8 years never exceeded the European annual Limit Value of 40 μg m^{-3} and varied from 28 μg m^{-3} (HIL) to 18 μg m^{-3} (HAR). $PM_{2.5}$ levels were recorded only at HAR and OAK (full period), GRG (missing data for about 20 months), LHR2 (from 2007), HRL and LNK (from 2009). Despite the sparse coverage of data for some sites, it is evident that the average concentrations are similar at all sites, varying from 15 μg m^{-3} (LNK) to 11 μg m^{-3} (HAR, LHR2, GRG, OAK), and the European target value of 25 μg m^{-3} averaged over a calendar year is far from being breached at any of the sites.

3.1 Seasonal and Weekly Variations

Figure SI3 and Figure 3 show the monthly time series and weekly cycles for all the monitored pollutants, calculated over eight years. For all the measured pollutants, similar seasonal trends and

weekly patterns are recorded at all the sites, except HAR. Generally, the cycles derive from the interaction of emissions, dispersion and atmospheric chemical processes. NO, NO_2 and NO_x show typical seasonality at all the road traffic-influenced sites, with maxima in the coldest seasons (Nov-Feb) and minima in the warmest months (May-Aug) and two daily peaks corresponding to the hours with higher traffic, i.e. morning 7-9 am and evening, as previously observed at London, North Kensington (Bigi and Harrison, 2010). Figure SI1 reports the average daily road traffic and aircraft movement profiles. Such patterns are the mirror image of the levels of ozone, which exhibit increased levels in the April-July period and two daily maxima at 2-4 am and 1-4 pm.

Particulate matter (PM_{10} and $PM_{2.5}$) exhibits two monthly peaks in spring and autumn, while minima are in August. This behaviour is evident at all the sites, except PM_{10} at HIL, which presents an additional increase of monthly-averaged concentrations in Jun-Jul, although data for this site only refer to two years of observations. The weekly cycles are similar to nitrogen oxides at all the sites: two peaks of concentration were generally recorded daily corresponding to the peaks of traffic. However, as for gaseous pollutants, particulate matter is also affected by the dispersion driven by the daily cycles of the mixing layer. Figure 3 also shows the weekday/weekend differences: nitrogen oxides, CO and PM_{10} clearly show lower concentrations during weekends, while $PM_{2.5}$ shows a much smaller effect. On the other hand, O_3 increases during the weekends, further underlining its interplay with nitrogen oxides.

3.3 Long-Term Trends

The long-term trends of the pollutants have been analysed by calculating the smooth trends of the monthly averages. This procedure is essentially determined using generalized additive modelling: further details of the adopted methods are provided in Carslaw (2013). Data were firstly deseasonalized using the seasonal-trend decomposition procedure of time series based

on ‘loess’ (STL). Results are provided in Figure 4 and Figure SI4: along with the fit smooth lines, which represent the long-term trends, the figure also shows the 95% confidence intervals of the fits as grey bands. Such intervals are calculated by bootstrapping the data (n=2000).

Generally, concentrations of nitrogen oxides show constant or slightly decreasing tendencies at all the sites, except in HIL, where a notable increase of NO_2 was recorded, i.e. annual means increased from 45 μg m^{-3} in 2005 to 57 μg m^{-3} in 2012. Decreases in nitrogen oxide emissions have been reported over all Western Europe in the last decades and were essentially attributed to the EU mitigation measures adopted since 1990 (Vestreng et al., 2009). However, the NO_2 levels have not decreased at the same rate as those of NO_x (e.g., Carslaw et al., 2007; Zamboni et al., 2009; Anttila et al., 2011). It is likely that the increase of NO_x levels at HIL is the result of an increased vehicular traffic on the adjacent M4 motorway. Despite trends for ozone having been computed for only 4 sites, it is evident that a slight increase of concentrations occurred in the rural background, while at remaining sites levels were almost constant. The increasing levels of ozone at HAR are not surprising as the same behaviour was predicted over recent decades for many rural regions in Europe, including the southern UK (e.g. Colette et al., 2011; Paoletti et al., 2014). Decreasing trends of PM_{10} were instead observed at all the sites, particularly for LHR2, while trends of $PM_{2.5}$ were almost constant at HAR, LNK, LHR, HRL and slightly decreasing at GRG and OAK. In summary, all the pollutants at almost all the sites underwent a decline of concentrations in the past eight years. In addition, the quantification and the assessment of the significance of the trends were evaluated by applying the Theil-Sen nonparametric estimator of slope (Sen, 1968; Theil, 1992) on the de-seasonalized monthly means (Carslaw, 2013). Since missing data can significantly affect this method, only months having at least 75% of available data were included in the computations and missing months were linearly interpolated. The trends are listed in Table SI1 along with the upper and lower 95th confidence intervals in the trends and the *p*-values, which indicate the statistical significance of the slope estimation.

3.4 Polar Plot Analysis

A preliminary investigation on potential sources of atmospheric pollutants at each site was assessed by mean of polar plot analysis. Polar plots essentially map the pollutant concentrations by wind speed and direction as a continuous surface (Carslaw and Ropkins, 2012). Simple polar plots computed for each site over the whole dataset are provided as Figures SI5 and SI6. Most polar plots show increasing average concentrations of nitrogen oxides and $PM_{2.5,}$ and decreasing levels of ozone when the wind comes from both the airport and motorway sectors, while PM_{10} appears to have major sources toward main roads and urban settlements. This is an environment with relatively high concentrations of NO_x and of VOCs. It is behaving as NO_x-saturated, whereby a reduction in NO_x will be accompanied by an increase in ozone, and vice versa. However, even if the sites are strategically located around the main sources, the concurrent effects of multiple emission sources makes it difficult to assess the contribution made by any specific sources.

According to Carslaw et al. (2006), the subtraction of "background" concentrations for certain wind sectors was further adopted in order to better investigate the effects of single sources. Pairs of sites were therefore selected on the basis of their locations with respect to the main sources and prevailing wind regimes: a reference site downwind of the investigated emission source and a background site located upwind, and hence not directly influenced. In this analysis, each background site is selected as representative of the general levels of air pollutants in the study area before the air masses pass over the investigated sources, i.e., the airfield and motorways. Since the study by Carslaw et al. (2006) only focused on the airport emissions, a larger number of site pairs were selected in this study to include a view on the motorway emissions. Table 2 lists the selected pairs. Resulting polar plots corrected for upwind sites are reported in Figure 5 and are computed over a wind sector spanning ca. 180° toward the background site to account all the potential sources. Generally, pairs of sites selected as indicative of airport emissions clearly indicate a rise of concentrations after passage of air over the airport sector. For example, the maximum average

increases of NO_x in the polar plots cells for some selected site pairs shown in Figure 5 were: LHR2-OAK (~30 μg m^{-3} for NO, ~60 μg m^{-3} for NO_2, ~90 μg m^{-3} for NO_x), HRL-OAK (~20 μg m^{-3} for NO, up to 20 μg m^{-3} for NO_2, ~35 μg m^{-3} for NO_x). In a similar way, pairs of sites affected by a motorway highlighted significant increases: HIL-HRL (~70 μg m^{-3} for NO, ~50 μg m^{-3} for NO_2, up to 150 μg m^{-3} for NO_x); SLC-GRG (~10 μg m^{-3} for NO, ~12 μg m^{-3} for NO_2, ~25 μg m^{-3} for NO_x). Despite few sites measuring ozone, an opposite behaviour was generally observed, with decreasing concentrations when air comes over the main sources, as a consequence of the NO-NO_2-O_3 reaction system. For example, a drop of up to 30 μg m^{-3} for ozone is observed for the HIL-HRL pair toward the M4 motorway, while a decrease of about 25 μg m^{-3} is seen for the LHR2-OAK pair toward the airfield. Despite the drop in O_3, OX (= NO_2 + O_3) is still increasing in such pairs toward the main sources. Results for PM_{10} reveal elevated concentrations when air masses moved over motorways, while a slight $PM_{2.5}$ increase seems to be mostly linked to airport emissions for the LHR2-OAK pair.

The polar plot analysis with background subtraction is a proven useful method to check the location of the main sources in the study area. However, as already reported by Carslaw et al. (2006), it gives only qualitative results and cannot be used to quantify the source emissions. A reliable quantification should include all wind sectors and not only those when the source contributions are highest.

3.5 Quantification of Airport Contributions

A further strategy aiming to quantify the source contributions was thus applied to site pairs which were proven as unambiguously representative of airport, M4 or M25 emissions by the polar plot analysis. Since the sites are located around the airport perimeter, the approach is based on the assumption that the difference in the levels of pollutants between pairs of sites located respectively upwind and downwind of a source may reflect the contribution of that source.

The first step of the approach was to follow the method employed by Carslaw et al. (2006) for estimating the upper limit of airport contributions. Briefly, it is performed by subtracting upwind background contributions from each site to give deltas, (ΔX) for appropriate wind direction sectors in the hours most affected by airport activities, i.e. between 06:00 and 22:00. These can be estimated separately for different wind speed classes. Since most of the sites can be affected by multiple sources (most sites are located near roads), wind speeds > 3 m s^{-1} were selected to remove periods with strong local contributions of pollutants. For example, this effect is evident in the polar plot for HRL-OAK (Figure 5) located close a secondary road whose effect cannot be disregarded, or in polar plots for LHR2, HOA and GRG, which are potentially affected by both airport and road traffic emissions (Figures SI5 and SI6).

Additional pairs were also selected to account the contributions of M4 and M25 motorways. Table 2 reports the selected site pairs and wind sectors. The final upper limit estimates of airport contribution were thus obtained by computing the average concentrations and frequencies of measurements in each wind speed/direction cell in the range as a proportion of the total number of hourly measurements (Carslaw et al., 2006).

Since the deltas may be affected by the strength of the sources and the subsequent dispersion of pollutants, the location of sampling sites and their closeness to the sources may play an important role that cannot be disregarded in the emission assessment. For example, the dilution effect is clearly evident from the polar plot of LHR2-OAK and HRL-OAK, which are computed over similar wind sectors, but return very differing results. In order to isolate the signal of the source under consideration, and thus reduce any interference due to other emission sources in the study area, a further strategy was adopted: deltas were calculated over both directions, i.e. using the two sites reciprocally as background or reference (both ΔX_{ji} and ΔX_{ij} are thus computed). This latter action may also give important indications about the differences amongst sites: it is plausible to expect that

362 pairs of sites having comparable deltas in both directions are similarly affected by sources, while
363 pairs having very different delta values over the two directions indicate that one site is affected by
364 the sources much more than the other.
365
366 Results are also listed in Table 2. Generally, most of the pairs selected for assessing the airport
367 emission show significant increases in levels of nitrogen oxides and particulate matter and
368 decreases of ozone over both directions. In general, the upper limit contributions of NO_2 and NO_x
369 from the airport are slightly lower than those calculated by Carslaw et al. (2006) for the period
370 2001-2004, which is consistent with the drop of pollutants recorded from 2005 to 2012 over the
371 study area (Figures 4 and SI4).
372
373 For LHR2-OAK, which was originally chosen by Carslaw et al. (2006) as the best estimate for
374 airport emissions, results of this study apportion ~27-29% of nitrogen oxides to airport operations,
375 i.e. 12 μg m^{-3} (29%) of NO, 13.3 μg m^{-3} (25.9 %) of NO_2, 31.5 μg m^{-3} (27.6%) of NO_x, but a
376 relatively low contribution of particulate matter, i.e. 1.5 μg m^{-3} (5.5%) of PM_{10} and 0.5 μg m^{-3}
377 (4.7%) of $PM_{2.5}$. Beside those results, it can be noted that the airport operations are responsible for a
378 reduction of 6.1 μg m^{-3} (-18.6%) of ozone, but the total amount of oxidants is slightly increased
379 (OX +3.5 ppbv; 7.9%). However, the LHR2-OAK pair is the only pair having an opposite trend
380 over the two directions, clearly indicating that the influence of the airport emissions on LHR2 is
381 extremely high and it is not possible to view it as a background site. Because of this, upper limit
382 estimates having LHR2 as reference site are strongly affected by the location of the site, which is
383 very close both to the runway and to the North Perimeter Road and therefore may give interesting
384 information about the direct airport emissions, but cannot be used as indicative for the assessment
385 of airport emissions over the entire study area.
386

Airport emissions in remaining pairs account for an average of 1-9 μg m^{-3} of NO_2, 2-20 μg m^{-3} of NO_x, an average decrease of -2 to -5 μg m^{-3} of O_3 (computed only for one pair), while particulate matter changes are quite low and variable. Generally, results also show that the levels of all the monitored pollutants decline rapidly with distance from the airport. On the other hand, upper limit estimates for non-LHR2 pairs selected to be representative of the airport emissions resulted in more comparable average levels over both directions. The increment in NO_x differs for a 180º change in wind sector: there will be a number of reasons for this. Specifically, the wind speed and stability may differ leading to differing dispersion characteristics on the two wind directions. Secondly, the distribution of emissions within the airport is not homogeneous and the proximity of emission sources to the airport boundaries closest to the sampling sites will have a major influence upon measured concentrations.

The effect of selecting wind speeds > 3 m s^{-1} for deltas was also investigated by separately computing ΔX for the pairs LHR-OAK (OAK-LHR) and GRG-OAK (OAK-GRG) over wind speeds in the range of 0.5 to 3 m s^{-1} and including a 1 h lag (time difference) between the two sites in a pair (Table SI2). Results indicate significantly lower airport contributions. The difference in results can be explained by: (i) the effect of strong local sources, i.e. LHR2, GRG and OAK are all located near busy roads and are strongly affected by non-airport sources of pollutants when wind speed are low; (ii) the fluctuations in wind direction at low wind speeds causing a disconnection between the sites. The results clearly indicate that the choice of selecting wind speeds > 3 m s^{-1} must be interpreted as the upper limit of airport contributions.

The assessment of the M4 motorway emissions resulted in very high values for most pollutants when HIL was taken as reference (downwind) site. As with LHR2 for airport emissions, the results are strongly affected by the location of the site, which is very close to the motorway and cannot be used as indicative for the assessment of traffic emissions over the entire study area. However, upper

limit estimates are positive (except for ozone) in both directions, indicating that the traffic signal is high. Deltas for the SLC/GRG site pair indicative of the M25 motorway resulted in comparable distributions in both directions with the motorway emissions accounting for an average increase of 0.6-0.8 μg m^{-3} of NO, 0-2.6 μg m^{-3} of NO_2, 1-4 μg m^{-3} of NO_x and 0.2-0.4 μg m^{-3} of PM_{10}.

Despite the substantial variability of the data, the results expressed as ppbv indicate that upper limit delta values indicative of airport emissions for NO and NO_2 are quite similar, while estimates for vehicular traffic show higher values for NO than NO_2. Some of NO_2 is a product of the NO + O_3 reaction. Such results can give some insights into the NO_x partitioning of the two sources. Several studies have reported that the majority of the NO_x emitted from modern turbofan engines at idle is in the form of NO_2, while NO is dominant in high power regimes (Song and Shon, 2012; Masiol and Harrison, 2014 and references therein). In addition, HAL (2011) estimated that the emissions from take-offs at Heathrow account for 46% of total emissions, while other sources are APU (19%), taxi-out (13%), hold (10%), taxi-in (8%), landing roll (3%) and engine testing (1%). While data on APU emissions are sparse, most of the non-takeoff flight phases and aircraft operations involve engines at low thrusts and therefore NO_x partitioning can be expected toward NO_2 for those sources. The small differences between the deltas of NO and NO_2 suggest that the airport-related emissions of NO_x are the result of different processes: it can be speculated that the takeoff provides most of the NO, while the other operational phases emit mainly NO_2. However, external or unaccounted sources may also have a role in the NO_x partitioning, as well as NO atmospheric oxidation. More information on this point can be derived from the data for OX, available only for the HRL/OAK site pair (excluding the heavily source-influenced LHR2 and HIL sites). An increase in OX on the distance scale of the airport is indicative of primary nitrogen dioxide emissions, as emission of NO_x purely as NO would give an OX increment of zero. The substantial increment in OX for OAK-HRL is consistent with appreciable emissions of primary NO_2. Hence, although take-offs are the main

source of NO_x, an appreciable contribution from other aircraft operational phases and other sources seems likely.

Ozone concentrations in the study area appear to be determined by the upwind background and local NO emissions, which cause a suppression of ozone. Although the area of the airport is an appreciable source of NO_x and VOC emissions, any contribution to ozone formation is likely to occur only at large downwind distances.

Data for PM_{10} indicate that the motorways are a significant source of particulate matter (mainly for HIL-GRG). Road dust resuspension may play a role in enhancing the levels of particulate matter arising from the motorway source, as indicated by a large number of studies (e.g., Thorpe and Harrison, 2008). In a similar manner, the resuspension of particles due to the turbulence created by the aircraft movements may also be a significant source of particulate matter close to the airport, as for example is demonstrated by the Gatwick Airport emission inventory (British Airports Authority, 2006). In summary, even if subject to large variability, the results obtained applying this method demonstrate that both the LHR airport and the two motorways have a clear effect upon air quality but neither appears strongly dominant over the other. The data do however suggest that the influence of the airport is experienced over a greater geographic area.

3.6 Hourly Contributions of Motorway Traffic and Airport Emissions

Since all the air pollutants present characteristic diurnal and weekly patterns (Figure 3) which are strongly influenced by local sources, a further investigation was conducted to determine whether the contributions of traffic and airport emissions have different or covariant daily behaviours. The diurnally averaged cycles of the differences between pairs of sites were thus re-computed. Results are then investigated with airport and motorway traffic data (Figure SI1). As for the upper limit estimation, only hours between 06:00 and 22:00 were taken in account because: (i) the contributions

of both airport and motorways at other hours was minor; (ii) no data on airport and motorway traffic are available during nighttime, and there is no significant flight activity. Results are reported in Figure 6 and show that on average the contributions of motorway traffic and airport operations have different patterns. Generally, NO, NO_2 and NO_x estimated from site pairs indicative of airport emissions show an often dominant evening peak on both wind directions, while paired sites for vehicular traffic have higher morning peaks.

As similar mixing layer dynamics are expected over the entire study area due to the closeness of the sites, and aircraft traffic schedules are normally constant from 6am to 8pm (Figure SI1), this result indicates that the increased concentration of nitrogen oxides due to airport emissions are mainly driven by the variation in atmospheric turbulence/stability and wind speed. On the other hand, traffic mainly contributes to NO_x in the morning.

Ozone has the opposite behaviour relative to nitrogen oxides, further demonstrating the key role of nitrogen oxides in ozone behaviour. PM_{10} values generally show quite variable behaviour and some pairs have different patterns over the two directions (e.g., LHR2-OAK, HRL-OAK, SLC GRG). This result indicates that PM pollution is more sensitive to the local site characteristics than for the gaseous pollutants and no further information can be extracted.

CONCLUSIONS

This study gives some indication of the impact of Heathrow Airport activities upon air quality. However, the greatest difficulty in determining the contribution of the airport to local air pollution is the presence of other major sources in the study area, i.e. the two motorways and other main roads and the urban emissions of London. A series of tools has been therefore applied to analyse the levels of pollutants with respect to the spatial distribution of sites around the airport and the wind regimes. The main results for each monitored pollutant can be summarised as follows:

- nitrogen oxides deserve particular attention, mainly due to exceedence of the annual mean Limit Value for NO_2 at some sites around Heathrow. However, the only local monitoring sites that exceed the limit values for NO_2 are strongly influenced by busy roads (HOA from the A4 and HIL from the M4), or are on-airport (LHR2), where the limit values do not apply. Nitrogen oxides present their highest concentrations in colder periods, and two different daily peaks at all of the sites. Generally, LHR2 and HIL show the highest levels of nitrogen oxides during the whole study period, but while the levels at LHR2 are decreasing slowly, the concentrations of NO_x are increasing at HIL;
- Measurement of concentration differences (deltas) between a carefully selected downwind and upwind site is an effective means of expressing the impact of the airport upon ambient air quality;
- The results of the upper limit assessment study show that both road traffic and airport emissions are responsible for marked increments upon nitrogen oxide levels: in particular the peaks of concentration in the morning are the result of traffic, while the peaks in the late evening are mainly due to the airport emissions;
- The increments upon nitrogen oxide levels recorded for the period 2005-2012 are similar or slightly lower than those calculated for the period 2001-2004. The changes may reflect the reduction in emissions which some pollutants underwent from 2005 to 2012;
- There is evidence for emissions of primary nitrogen dioxide within the airport, consistent with jet engines operating at low thrust settings;
- ozone generally follows an opposite behaviour with respect to nitrogen oxides. This finding reflects the key role of the photostationary state, and the rapid consumption of ozone by the reaction with NO to form NO_2. Ozone levels are slowly increasing at most monitoring sites;
- particulate matter concentrations are always below the limit imposed by the EC, and the long-term analysis reveals that their concentrations are declining further. However, a moderate impact of road and flight traffic on PM_{10} concentrations can be seen, deriving from exhaust

and non-exhaust emissions including the resuspension of road dust from both motorways and airport runways. $PM_{2.5}$ seems not to be significantly affected by local sources.

ACKNOWLEDGEMENTS

We gratefully acknowledge: (i) the European Union for funding the Marie Curie Intra-European Fellowship for career development to M. Masiol through the project entitled 'Chemical and Physical Properties and Source Apportionment of Airport Emissions in the context of European Air Quality Directives (Project CHEERS, call: FP7-PEOPLE-2012-IEF, proposal no. 328542); (ii) the UK Department for Transport, Road Traffic and Road Freight Statistics, for providing traffic data; (iii) Heathrow and Ricardo-AEA for supplying aircraft movement data and for the valuable exchange of information and discussion, in particular David Wovles, Katherine Rolfe, Elizabeth Hegarty (Heathrow) and Brian Stacey (Ricardo-AEA); (iv) DEFRA Automatic Urban and Rural Network, London Air Quality Network, Heathrow airport and Airwatch website for providing pollutant data; (v) Met Office and BADC for weather data.

REFERENCES

ACI, 2014. ACI Releases its 2013 World Airport Traffic Report. Media Release, Airports Council International, Montreal. Available at: http://www.aci.aero/News/Releases/Most-Recent/2014/09/16.

AEA, 2010. Heathrow Airport Air Quality Modelling for 2008/9: Results and Model Evaluation. Report by AEA Energy & Environment on behalf of BAA, July 2010. AEAT/ENV/R/2948/Issue 1.

Anttila, P., Tuovinen J.P., Niemi J.V., 2011. Primary NO2 emissions and their role in the development of NO2 concentrations in a traffic environment. Atmospheric Environment 45, 986-992.

Barnhart, C., Fearing, D., Odoni, A., Vaze, V., 2012. Demand and capacity management in air transportation. EURO Journal on Transportation and Logistics 1, 135-155.

Bigi, A., Harrison, R.M., 2010. Analysis of the air pollution climate at a central urban background site. Atmospheric Environment, 44, 2004-2012.

British Airports Authority, 2006. Gatwick 2010 Baseline Emission Inventory. Available at: http://83.98.24.64/Documents/business_and_community/Publications/2006/2010_basline_emissions_inventory.pdf (last accessed September, 2013).

Carslaw, D.C., Beevers, S.D., Ropkins, K., Bell, M.C., 2006. Detecting and quantifying aircraft and other on-airport contributions to ambient nitrogen oxides in the vicinity of a large international airport. Atmos. Environ. 40, 5424–5434.

Carslaw, D.C., Beevers, S.D., Bell, M.C., 2007. Risks of exceeding the hourly EU limit value for nitrogen dioxide resulting from increased road transport emissions of primary nitrogen dioxide. Atmospheric Environment 41, 2073-2082.

Carslaw, D.C., Ropkins, K., Laxen, D., Moorcroft, S., Marner, B., Williams ,M. L., 2008. Near-field commercial aircraft contribution to nitrogen oxides by engine, aircraft type, and airline by individual plume sampling. Environmental Science & Technology 42, 1871-1876.

Carslaw, D.C., Williams, M.L, Barratt, B., 2012. A short-term intervention study – Impact of airport closure due to the eruption of Eyjafjallajökull on near-field air quality. Atmospheric Environment 54, 328-336.

Carslaw, D.C., Ropkins, K., 2012. openair - an R package for air quality data analysis. Environmental Modelling and Software 27-28, 52-61.

Carslaw, D.C., 2013. The openair manual — open-source tools for analysing air pollution data. Manual for version 0.8-0, King's College London.

Colette, A., Granier, C., Hodnebrog, Ø., Jakobs, H., Maurizi, A., Nyiri, A., Bessagnet, B., D'Angiola, A., D'Isidoro, M., Gauss, M., Meleux, F., Memmesheimer, M., Mieville, A., Rouïl, L., Russo, F., Solberg, S., Stordal, F., Tampieri, F., 2011. Air quality trends in Europe over the past decade: a first multi-model assessment. Atmospheric Chemistry & Physics 11, 11657-11678.

Cyrys, J., Eeftens, M., Heinrich, J., Ampe, C., Armengaud, A., Beelen, R., Bellander, T., Beregszaszi, T., Birk, M., Cesaroni, G., Cirach, M., de Hoogh, K., De Nazelle, A., de Vocht, F., Declercq C., Dedele, A., Dimakopoulou, K., Eriksen, K., Galassi, C., Grauleviciene, R., Grivas, G., Gruzieva, O., Hagenbjörk Gustafsson, A., Hoffmann, B., Iakovides, M., Ineichen, A., Krämer, U.,

Lanki, T., Lozano, P., Madsen, C., Meliefste, K., Modig, L., Mölterm, A., Mosler, G., Nieuwenhuijsen, M., Nonnemacher, M., Oldenwening, M., Peters, A., Pontet, S., Probst-Hensch, N., Quass, U., Raaschou-Nielsen, O., Ranzi, A., Sugiri, D., Stephanou, E.G., Taimisto, P., Tsai, M.-Y., Vaskövi, E., Villani, S., Wang, M., Brunekreef, B., Hoek, G., 2012. Variation of NO_2 and NO_x concentrations between and within 36 European study areas: Results from the ESCAPE study. Atmospheric Environment 62, 374–390.

DEFRA, 2013a. Air Pollution in the UK 2012. UK Department for Environment, Food and Rural Affairs. Issue of September 2013. Available at: http://uk-air.defra.gov.uk/library/annualreport/air_pollution_uk_2012_issue_1.pdf (last accessed: November 2013).

DEFRA, 2013b. Emissions of Air Quality Pollutants 1970 – 2011. UK Department for Environment, Food and Rural Affairs. AQPI Summary Report. Available at: http://uk-air.defra.gov.uk/reports/cat07/1305031312_EoAQP1970-2011_pq.pdf (last accessed: January 2014).

Dockery, D.W. (2009). Health effects of particulate air pollution. Annals of Epidemiology 19, 257-263.

EEA, 2014. AirBase—The European Air Quality Database. European Environment Agency. Available from: http://www.eea.europa.eu/themes/air/airbaseS (last access: July 28, 2014).

Gelhausen, M.C., Berster, P., Wilken D., 2011. Do airport capacity constraints have a serious impact on the future development of air traffic? Journal of Air Transport Management 28, 3-13.

Grice, S., Stedman, J., Kent, A., Hobson, M., Norris, J., Abbott, J., Cooke S., 2009. Recent trends and projections of primary NO2 emissions in Europe. Atmospheric Environment 43, 2154-2167.

HAL, 2011. Heathrow Air Quality Strategy 2011–2020. Heathrow Airport Ltd. Available at: http://www.heathrowairport.com/static/Heathrow/Downloads/PDF/air-quality-strategy_LHR.pdf (last accessed: August 2013).

Katsouyanni, K., Samet, J.M., Anderson, H.R., Atkinson, R., Le Tertre, A., Medina, S., Samoli, E., Touloumi, G., Burnett, R.T., Krewski, D., Ramsay, T., Dominici, F., Peng, R.D., Schwartz, J., Zanobetti A., 2009. Air pollution and health: a European and North American approach (APHENA). Research Report, Health Effects Institute 142, 5-90.

Kley, D., Kleinmann, M., Sanderman, H., Krupa, S., 1999. Photochemical oxidants: state of the science. Environmental Pollution 100, 19-42.

Masiol, M., Harrison, R.M., 2014. Aircraft engine exhaust emissions and other airport-related contributions to ambient air pollution: A review. Atmos. Environ. 95, 409-455.

Mavroidis, I., Chaloulakou, A., 2011. Long-term trends of primary and secondary NO2 production in the Athens area. Variation of the NO2/NOx ratio. Atmospheric Environment 45, 6872-6879.

Notario, A., Bravo, I., Adame, J. A., Díaz-de-Mera, Y., Aranda, A., Rodríguez, A., Rodríguez, D., 2012. Analysis of NO, NO2, NOx, O3 and oxidant (OX= O3+ NO2) levels measured in a metropolitan area in the southwest of Iberian Peninsula. Atmospheric Research 104, 217-226.

631 Paoletti, E., De Marco, A., Beddows, D.C.S., Harrison, R.M. and Manning, W.J., 2014.
632 Ozone levels in European and USA cities are increasing more than at rural sites, while peak values
633 are decreasing. Environmental Pollution 192, 295-299.
634
635 R Core Team, 2013. R: A language and environment for statistical computing. R Foundation for
636 Statistical Computing, Vienna, Austria. URL http://www.R-project.org/.
637
638 Raaschou-Nielsen, O., Andersen, Z.J., Beelen, R., Samoli, E., Stafoggia, M., Weinmayr, G.,
639 Hoffmann, B., Fischer, P., Nieuwenhuijsen, M.J., Brunekreef, B., Xun, W.W., Katsouyanni, K.,
640 Dimakopoulou, K., Sommar, J., Forsberg, B., Modig, L., Oudin, A., Oftedal, B., Schwarze, P.E.,
641 Nafstad, P., De Faire, U., Pedersen, N.L., Östenson, C.-G., Fratiglioni, L., Penell, J., Korek, M.,
642 Pershagen, G., Eriksen, K.T., Sørensen, M., Tjønneland, A., Ellermann, T., Eeftens, M., Peeters,
643 P.H., Meliefste, K., Wang, M., Bueno-de-Mesquita, B., Key, T.J., de Hoogh, K., Concin, H., Nagel,
644 G., Vilier, A., Grioni, S., Krogh, V., Tsai, M.-Y., Ricceri, F., Sacerdote, C., Galassi, C., Migliore,
645 E., Ranzi, A., Cesaroni, G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P., Dorronsoro, M.,
646 Trichopoulou, A., Bamia, C., Vineis, P., G. Hoek, 2013. Air pollution and lung cancer incidence in
647 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution
648 Effects (ESCAPE). The Lancet Oncology, doi:10.1016/S1470-2045(13)70279-1.

649 Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. The Journal of the
650 American Statistical Association 63, 1379-1389.
651
652 Song, S.-K., Shon, Z.-H., 2012. Emissions of greenhouse gases and air pollutants from commercial
653 aircraft at international airports in Korea. Atmospheric Environment 61, 148-158.
654
655 Stettler, M.E.J., Eastham, S., Barrett, S.R.H., 2011. Air quality and public health impacts of UK
656 airports. Part I: emissions. Atmospheric Environment 45, 5415–5424.
657

658 Theil, H., 1992. A rank-invariant method of linear and polynomial regression analysis. In Henri
659 Theil's Contributions to Economics and Econometrics. Springer, Netherlands, 345-381.
660
661 Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from
662 road traffic: A review. Science of the Total Environment 400, 270-282.
663
664 UK Department for Transport, 2006. Project for the Sustainable Development of Heathrow: Report
665 of the Airport Air Quality Technical Panels.
666
667 Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I.S.A., Tarrasón, L., 2009. Evolution of
668 NOx emissions in Europe with focus on road transport control measures. Atmospheric Chemistry &
669 Physics 9, 1503-1520.
670
671 WHO, 2000. Air Quality Guidelines for Europe. European Series No 91,World Health
672 Organization. WHO Regional Publications, Geneva.
673
674 Wormhoudt, J., Herndon, S.C., Yelvington, P.E., Lye-Miake, R.C., Wey, C., 2007. Nitrogen oxide
675 (NO/NO2/HONO) emissions measurements in aircraft exhausts. Journal of Propulsion & Power 23,
676 906-911.
677
678 Yim, S.H.L., Stettler, M.E.J., Barrett, S.R.H., 2013. Air quality and public health impacts of UK
679 airports. Part II: Impacts and policy assessment. Atmospheric Environment 67, 184-192.
680

Zamboni, G., Capobianco, M., Daminelli, E., 2009. Estimation of road vehicle exhaust emissions from 1992 to 2010 and comparison with air quality measurements in Genoa, Italy. Atmospheric Environment 43, 1086-1092.

TABLE LEGENDS

Table 1. Site characteristics: site name and acronym, geographic coordinates (decimal degrees, WGS 84 system), site categorization (if available) and analyzed gaseous pollutants. Periods of data availability are given in brackets.

Table 2. Site pairs used in bivariate polar plot analysis with background subtraction and quantification of upper limit for source contributions following the method proposed by Carslaw et al. (2006). Data were filtered for hour of day (6:00-22:00) and for wind speeds > 3 m s^{-1}.

FIGURE LEGENDS

Figure 1. Map of the study area showing the sampling sites.

Figure 2. Time series of monthly average concentrations of measured air pollutants. Only months with more than 75% of available data are included. Note that $PM_{2.5}$ data are measured with TEOM (LHR2, GRG, OAK) and TEOM-FDMS (HRL, HAR, LNK).

Figure 3. Weekly and hourly-resolved averages calculated over 8 years. Data are corrected for DST. Note that $PM_{2.5}$ data are measured with TEOM (LHR2, GRG, OAK) and TEOM-FDMS (HRL, HAR, LNK).

Figure 4. Long-term trends of analysed pollutants computed from the monthly averages.

Figure 5. Bivariate polar plots for selected sites with background concentrations subtracted. All values are expressed as μg m^{-3}, except OX (ppbv).

Figure 6. Daily patterns computed from the differences between pairs of sites (reference site - background site) shown in Table 2. Data were filtered for hour of day (6:00-22:00) and for wind speeds > 3 m s^{-1}.

715 **Table 1**. Site characteristics: site name and acronym, geographic coordinates (decimal degrees, WGS 84 system), site categorization (if available) and
716 analyzed gaseous pollutants. Periods of data availability are given in brackets.
717

Site	Lat.; Long.	Categorization	Analyzed compounds (periods)
Harwell (HAR)	51.571078, -1.325283	Rural background	NO, NO_2, NO_x, O_3, SO_2, PM_{10}, $PM_{2.5}$ (2005-2013)
London N. Kensington (LNK)	51.521050, -0.213492	Urban background	NO, NO_2, NO_x, CO, O_3, SO_2, PM_{10} (2005-2013); $PM_{2.5}$ (from Dec 2008)
Heathrow LHR2 (LHR2)	51.479268, -0.440556	Airport	NO, NO_2, NO_x, PM_{10}, (2005-2013); $PM_{2.5}$ (from Feb 2010); CO, O_3 (until Apr 2007)
London Harlington (HRL)	51.488790; -0.441614	Urban Industrial	NO, NO_2, NO_x, O_3, PM_{10} (2005-2013); $PM_{2.5}$; (from Apr 2008); CO (until Mar 2008)
London Hillingdon (HIL)	51.496330; -0.460861	Urban background	NO, NO_2, NO_x, O_3 (2005-2013); PM_{10} , SO_2, CO, (until Sep 2007)
Heathrow Green Gates (GRG)	51.481478, -0.486675	–	NO, NO_2, NO_x, PM_{10} (2005-2013); $PM_{2.5}$ (2005-Mar 2006 and Nov 2007-2013)
Slough Colnbrook (SLC)	51.480372, -0.508729	Urban background	NO, NO_2, NO_x, PM_{10} (2005-2013)
Heathrow Oaks Road (OAK)	51.459577, -0.479445	Urban background	NO, NO_2, NO_x, PM_{10}, $PM_{2.5}$ (2005-2013); O_3 (until Jul 2007)
Hounslow Hatton Cross (HAT)	51.463319, -0.427225	Roadside (10 m)	NO, NO_2, NO_x, PM_{10} (2005-2013)
London Hillingdon Oxford Avenue (HOA)	51.481130, -0.423760	Urban centre	NO, NO_2, NO_x, PM_{10} (2005-2013)

Table 2. Site pairs used in bivariate polar plot analysis with background subtraction and quantification of upper limit for source contributions following the method proposed by Carslaw et al. (2006). Data were filtered for hour of day (6:00-22:00) and for wind speeds > 3 m s^{-1}.

Source	Site pairs	Wind sector[a]	NO_2		NO_x		NO	O_3[b]	OX	PM_{10}[c]	$PM_{2.5}$[d]
			2001-2004[e]	2005-2012	2001-2004[e]	2005-2012	2005-2012	2005-2012	2005-2012	2005-2012	2005-2012
		degree	*μg m^{-3} (%)*	*μg m^{-3} [ppbv] (%)*	*μg m^{-3} (%)*	*μg m^{-3} [ppbv] (%)*	*μg m^{-3} [ppbv] (%)*	*μg m^{-3} [ppbv] (%)*	*ppbv (%)*	*μg m^{-3} (%)*	*μg m^{-3} (%)*
Airport	LHR-OAK	150-260	15 (27.3%)	13.3 [7] (25.9%)	33.9 (26.7%)	31.5 [16.5] (27.6%)	12 [9.6] (29%)	-6.1 [-3.1] (-18.6%)	3.5 (7.9%)	1.5 (5.5%)	0.5 (4.7%)
	OAK-LHR	340-80	—	-0.3 [-0.2] (-0.8%)	—	-5.8 [-3] (-9.5%)	-3.6 [-2.9] (-20.5%)	0.1 [0.1] (0.2%)	-0.1 (-0.2%)	-0.7 (-3.2%)	-0.1 (-0.7%)
	HRL-OAK[f]	160-260	6.6 (17.4%)	5.3 [2.8] (14.9%)	9.9 (14%)	8.2 [4.3] (12.6%)	1.9 [1.5] (9.8%)	-4.7 [-2.4] (-13.7%)	0.4 (1%)	-1.2 (-5.7%)	—[h]
	OAK-HRL	340-80	—	3.6 [1.9] (10.4%)	—	6.8 [3.6] (11.1%)	2.1 [1.7] (11.9%)	-1.9 [-1] (-4.8%)	0.8 (2.1%)	0.5 (2.1%)	—[h]
	HOA-OAK[g]	200-260	6.5 (18.1%)	9.2 [4.8] (21.5%)	9.5 (12%)	19.7 [10.3] (23.4%)	6.9 [5.5] (25%)	—	—	0.7 (3.3%)	—
	OAK-HOA[g]	340-80	2 (5.9%)	3.8 [2] (11.1%)	5.9 (8.9%)	7.4 [3.9] (12%)	2.3 [1.8] (12.9%)	—	—	0.6 (2.6%)	—
	GRG-OAK	100-170	1.5 (3.9%)	1.2 [0.6] (3.3%)	3 (4%)	1.9 [1] (2.8%)	0.5 [0.4] (2.3%)	—	—	-0.1 (-0.4%)	0 (0%)
	OAK-GRG	340-80	—	3.2 [1.7] (9.2%)	—	6.4 [3.3] (10.4%)	2.1 [1.7] (12%)	—	—	0.7 (3%)	0.2 (2%)
	SLC-OAK[i]	100-170	1.5 (4.2%)	1.2 [0.6] (3.9%)	1.8 (2.6%)	2.6 [1.4] (4.4%)	0.9 [0.7] (5%)	—	—	0.1 (0.4%)	—
	OAK-SLC	350-80	—	2.9 [1.5] (8.3%)	—	5.7 [3] (9.3%)	1.9 [1.5] (10.6%)	—	—	0.5 (2.1%)	—
	GRG-HAT	100-200	—	2.8 [1.5] (7.4%)	—	4.5 [2.4] (6.6%)	0.8 [0.6] (4%)	—	—	0.5 (2.4%)	—
	HAT-GRG	260-30	—	3.5 [1.8] (9.4%)	—	9 [4.7] (13.6%)	4.1 [3.3] (18.4%)	—	—	0.5 (2.3%)	—
M4	HIL-HRL	100-260	—	16.4 [8.6] (32%)	—	47 [24.6] (42%)	20.1 [16.1] (50.4%)	-8.3 [-4.2] (-30.4%)	4.4 (11%)	4.1 (14.7%)	—
	HRL-HIL	280-80	—	1.2 [0.6] (3.4%)	—	2.6 [1.4] (4%)	0.9 [0.7] (4.6%)	-1.1 [-0.6] (-3.2%)	0.1 (0.4%)	1.2 (5.6%)	—
	HIL-GRG	100-260	—	16.9 [8.8] (32.9%)	—	46.5 [24.3] (41.5%)	19.3 [15.5] (48.7%)	—	—	3.3 (12%)	—
	GRG-HIL	340-70	—	1.1 [0.6] (3%)	—	1.7 [0.9] (2.5%)	0.4 [0.3] (2%)	—	—	0.4 (1.9%)	—
M25	SLC-GRG	30-180	—	0 [0] (0%)	—	1 [0.5] (1.7%)	0.6 [0.5] (3.5%)	—	—	0.4 (1.9%)	—
	GRG-SLC	240-340	—	2.6 [1.4] (7.1%)	—	3.9 [2] (5.7%)	0.8 [0.6] (3.9%)	—	—	0.2 (0.9%)	—

a) Selected wind sectors were keep identical to those used in Carslaw et al. (2006), whereas wind sectors for new pairs of sites were selected on the basis of polar plot analysis. b) O_3 was measured until ca. mid-2007 in LHR2 and OAK; c) PM_{10} was measured until mid-2007 in HIL. d) $PM_{2.5}$ measurements in LHR started in 2010. e) Data from Carslaw et al. (2006); f) HRL-OAK in Carslaw et al. referred to 2001 only. g) Hounslow was used in Carslaw et al. whereas Hillingdon Oxford Avenue (HOA) was used in this study. h) Stations are equipped with differing instruments and a cross-comparison is not possible. i) SLC-OAK was used in Carslaw et al. for quantifying the airport emission, but is also potentially affected by M25 motorway emissions.

Note: The percentage values in parentheses express the source contribution as a percentage of the average concentration at the reference (upwind) site.

Figure 1. Map of the study area showing the sampling sites.

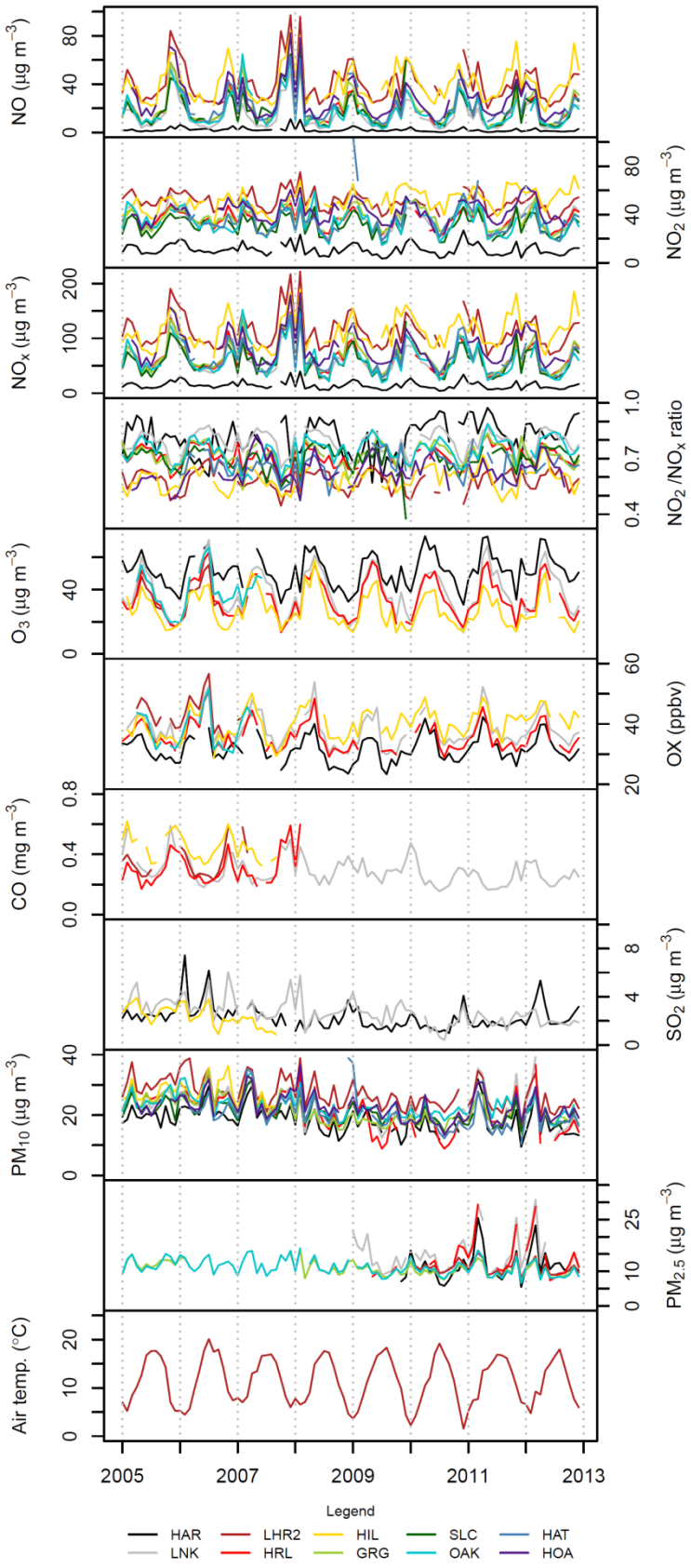

Figure 2. Time series of monthly average concentrations of measured air pollutants. Only months with more than 75% of available data are included. Note that $PM_{2.5}$ data are measured with TEOM (LHR2, GRG, OAK) and TEOM-FDMS (HRL, HAR, LNK).

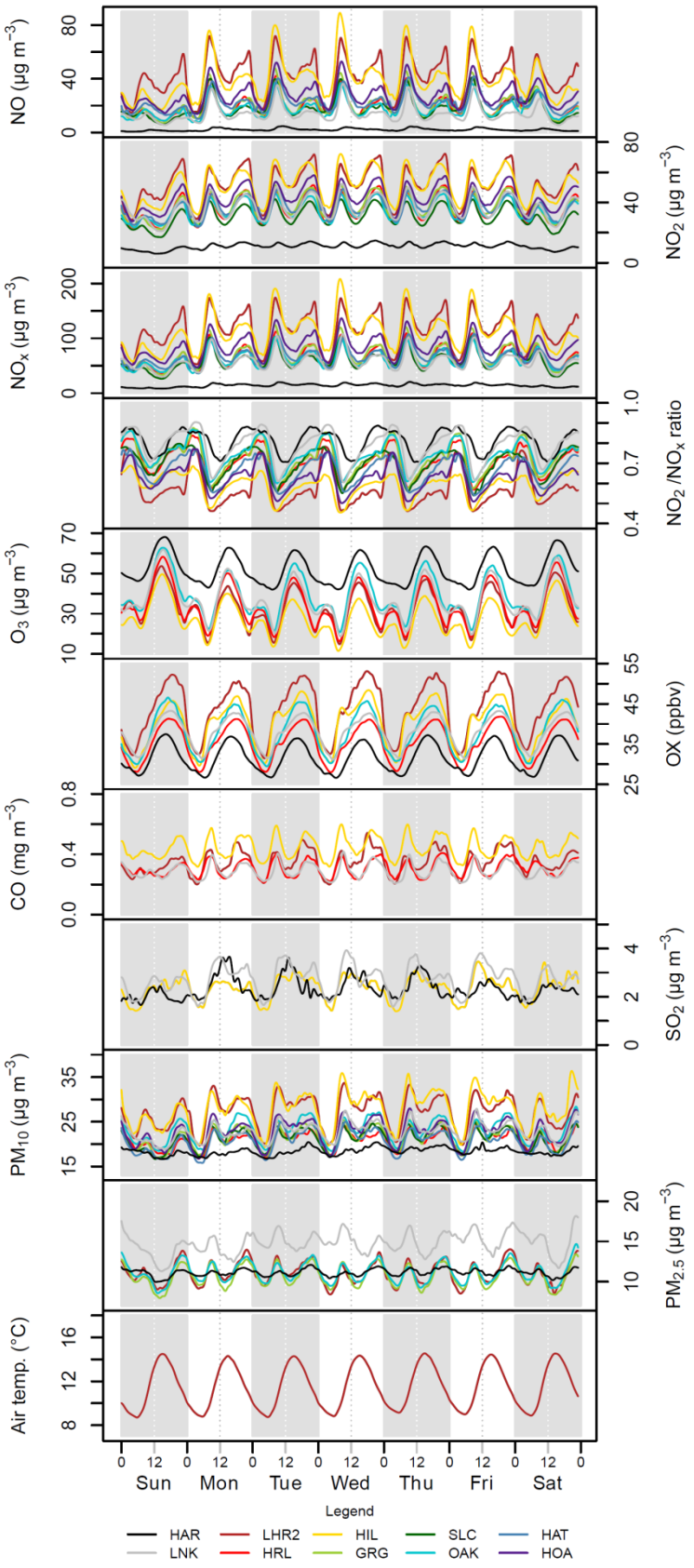

Figure 3. Weekly and hourly-resolved averages calculated over 8 years. Data are corrected for DST. Note that $PM_{2.5}$ data are measured with TEOM (LHR2, GRG, OAK) and TEOM-FDMS (HRL, HAR, LNK).

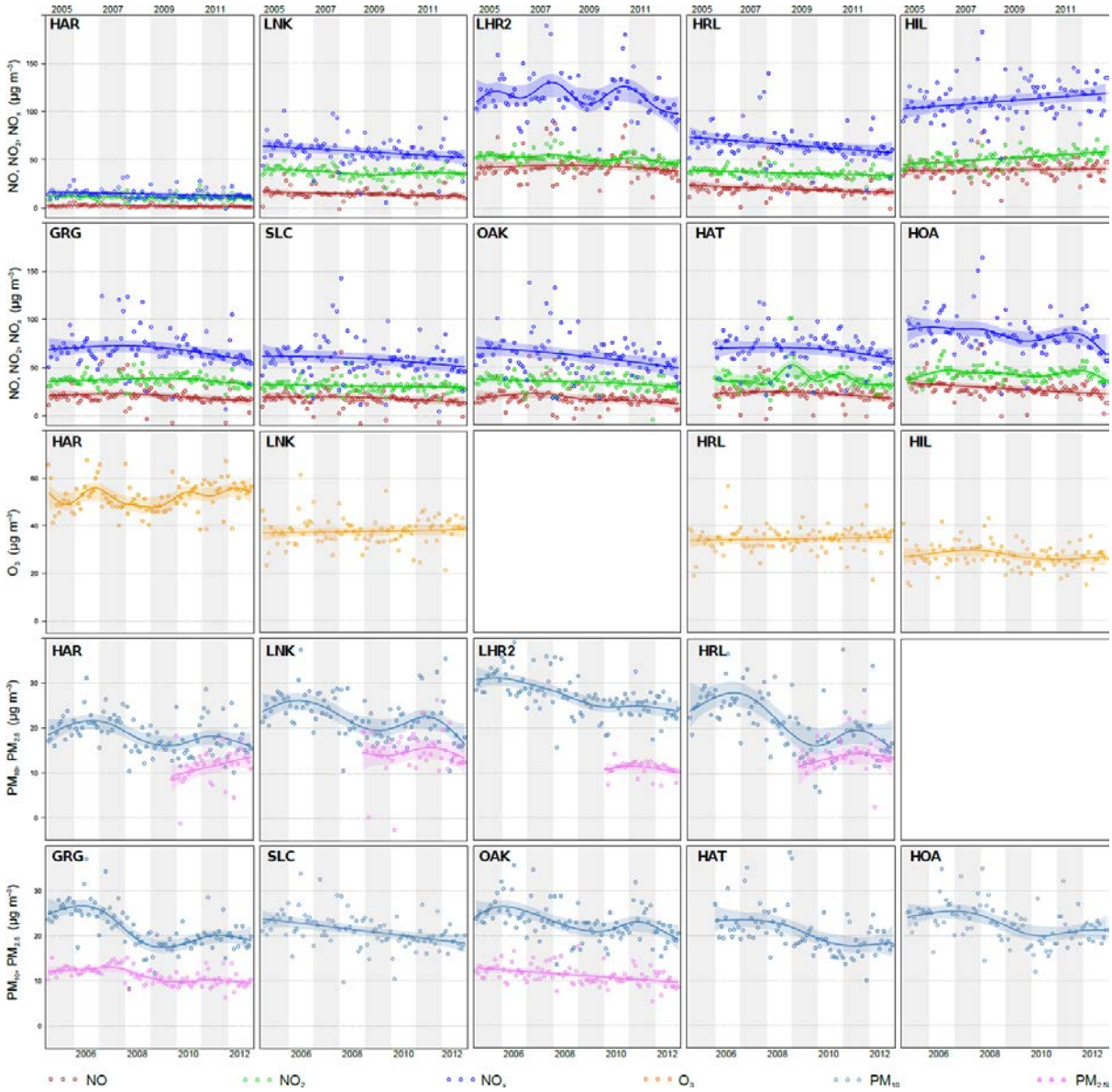

Figure 4. Long-term trends of analysed pollutants computed from the monthly averages.

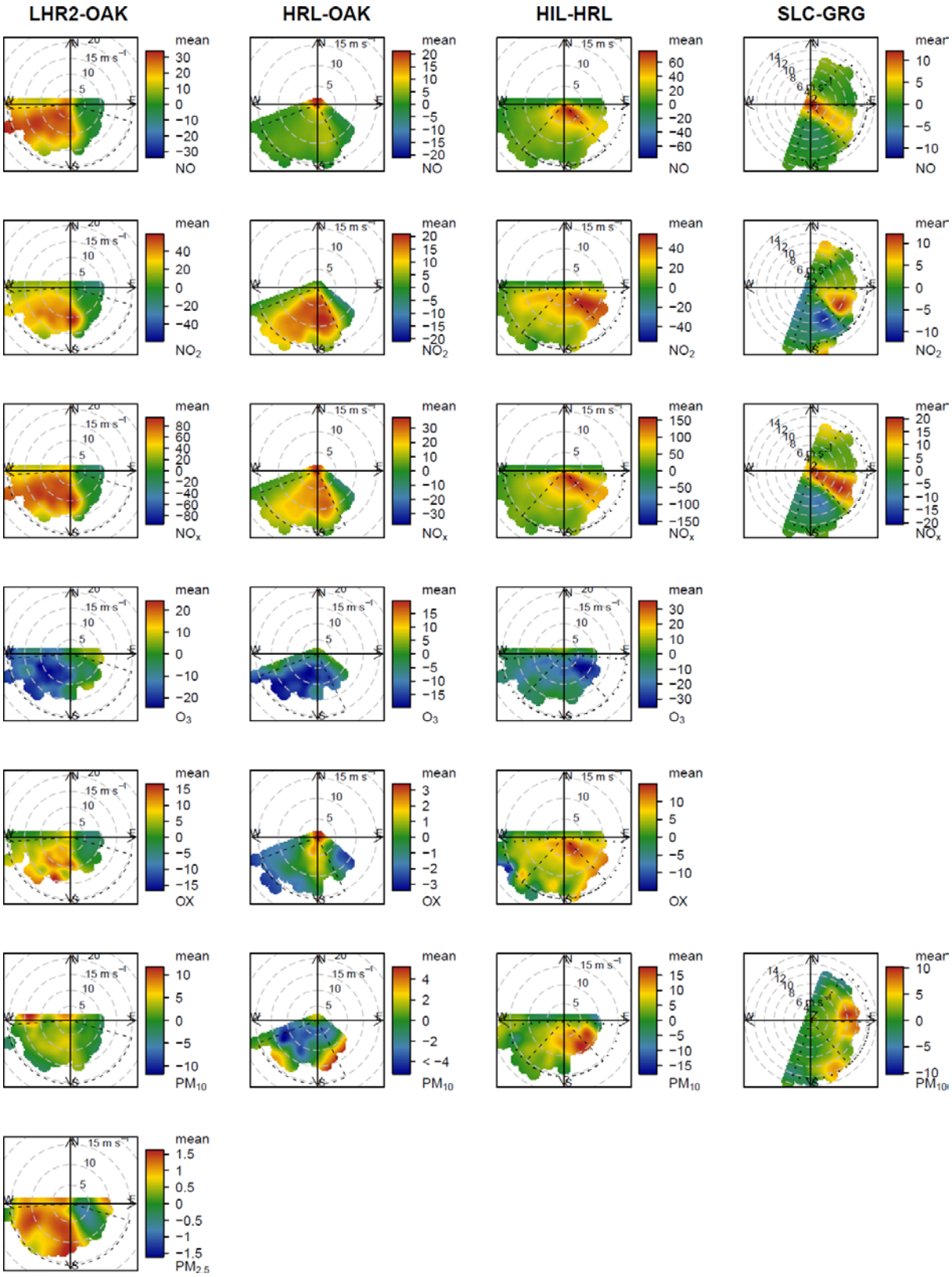

Figure 5. Bivariate polar plots for selected sites with background concentrations subtracted. All values are expressed as μg m^{-3}, except OX (ppbv). The location of the airfield is highlighted with dashed arcs, while the location of motorways with dotted arcs.

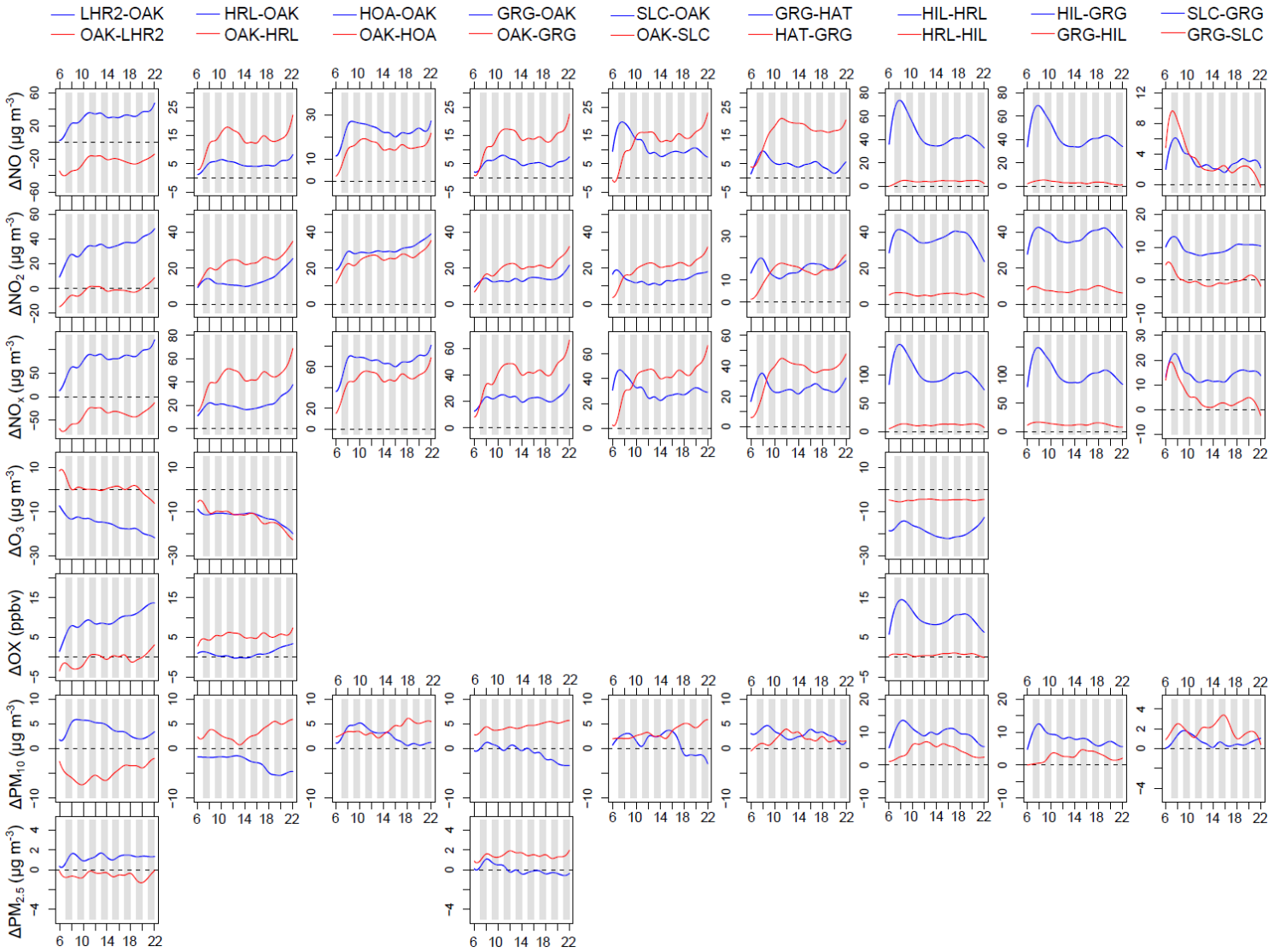

Figure 6. Daily patterns computed from the differences between pairs of sites (reference site - background site) shown in Table 2. Data were filtered for hour of day (6:00-22:00) and for wind speeds > 3 m s^{-1}.