Measurement and analysis of local urban CO$_2$ emissions

by

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Declaration of Originality

The contents of this thesis are my own work except where otherwise acknowledged.
Abstract

High frequency CO\textsubscript{2} and wind speed measurements were used to examine the urban baseline eddy covariance CO\textsubscript{2} flux and analyse the CO\textsubscript{2} rich plume from a local power station. A reliable relationship between high frequency CO\textsubscript{2} maxima and the rate of CO\textsubscript{2} emission at the power station was established. This relationship was shown to be highly dependant on wind speed. The ensemble mean plume was found to be approximately Gaussian in horizontal profile with a width dependant on wind speed. The relationship between peak CO\textsubscript{2} mixing ratio and averaging time was shown to be a simple power law with a time exponent of approximately 0.5. The large, short pulses in CO\textsubscript{2} mixing ratio in the power plant plume were found to have an approximately Lorentzian shape. These pulses generated negative vertical eddy flux measurements so data from the plume sector were necessarily excluded from the flux baseline results. The plume-excluded flux had a similar magnitude and variability to those reported in other urban CO\textsubscript{2} flux studies despite this site not being ideal due to the proximity of roughness elements to the measurement point. A linear-eddy model was used to relate the mean concentration plume profile to plume profiles for different percentiles of concentration. It showed that for high concentration percentiles and short dispersion times the plume width can be several times greater than the standard mean concentration plume width.
Acknowledgements

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Chapter 1

Introduction

According to the Intergovernmental Panel on Climate Change, Carbon dioxide (CO$_2$) is the primary force behind global climate change (Intergovernmental Panel on Climate Change, 2007). Approximately half of the world’s population was living in an urban environment at the end of the twentieth century and this figure is expected to increase to two thirds by 2025 (cited by Grimmond et al., 2004). Urban emissions are recognised to be a significant contributor to global CO$_2$ emissions and attempts have been made to quantify these contributions using estimates derived from fossil fuel consumption (e.g. LAEI, 2006; NAEI, 2008) as part of CO$_2$ emission reduction schemes. Given these facts it is surprising that the majority of CO$_2$ monitoring occurs at rural sites. This is done primarily using the eddy covariance measurement technique. Only in the last few years has this method been applied to directly measure the amount of CO$_2$ being produced in urban areas to verify emissions inventories.

This introduction will state the objectives of this thesis then examine some of the existing studies on CO$_2$ flux from urban landscapes. Key findings and factors contributing to measured values will be discussed. An overview of their approach to data processing and analysis, which varies from study to study, will also be included here even though the basic methodology remains constant. The relevant results of the two CO$_2$ emissions inventories mentioned above will also be discussed. Finally, we will introduce the basic concepts and key results of pollutant plume dispersion from a continuous point source which we find to be
relevant to our CO$_2$ flux measurements.

1.1 Main objectives of this thesis

The aim of this study is to characterise CO$_2$ emissions measured at the Imperial College London site. Measured CO$_2$ fluxes are attributed to various sources and compared with existing measurements from urban sites. Analysis and processing techniques relevant to other existing or future urban flux studies are proposed.

1.2 Urban CO$_2$ flux studies

There are relatively few existing studies reporting on CO$_2$ flux measured in urban locations. The first direct measurements were reported by Grimmond et al. (2002) and Nemitz et al. (2002). A handful of studies followed these with results from cities in Europe, Asia, Australasia and North and Central America. They are generally short-term with data collection periods typically from days to weeks with a couple of notable exceptions discussed below. Recently Helfter et al. (2011) published a longer term study from the centre of London but at a large height from the ground. All the studies find urban areas to be CO$_2$ sources with fluxes constantly positive (A positive flux is defined as a flux away from the surface). The measured fluxes have a variety of magnitudes and display cycles on different timescales. A summary of the results from existing studies will be presented here along with a brief report on studies examining CO$_2$ mixing ratios in urban areas. Table 1.1 lists the existing urban CO$_2$ flux studies with the years and seasons during which the data were collected, fluxes reported and information about the site.
<table>
<thead>
<tr>
<th>Author</th>
<th>City</th>
<th>Year</th>
<th>Season</th>
<th>Site type</th>
<th>Normalised height ($z_m/z_H$)</th>
<th>Mean $F_c$ ($\mu$mol m$^{-2}$ s$^{-1}$)</th>
<th>$F_c$ range ($\mu$mol m$^{-2}$ s$^{-1}$)</th>
<th>$z_m$ (m)</th>
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<tbody>
<tr>
<td>Bergeron and Strachan</td>
<td>Montreal</td>
<td>2007-2009</td>
<td>All year</td>
<td>SR, CC</td>
<td>1.8, 1.9</td>
<td>3.74, 14.7</td>
<td>-8 – 11, 3 – 31</td>
<td>25, 25</td>
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<td>Crawford et al. (2011)</td>
<td>Baltimore</td>
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<td>All year</td>
<td>SR</td>
<td>3.2</td>
<td>0.95</td>
<td>4 – 10</td>
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<tr>
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<td>Chicago</td>
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<td>SR</td>
<td>4.3</td>
<td></td>
<td>0 – 11</td>
<td>27</td>
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<td>Helfter et al. (2011)</td>
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<td>190</td>
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<td>Kordowski and Kuttler</td>
<td>Essen</td>
<td>2006-2007</td>
<td>All year</td>
<td>CC, UP</td>
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<td>9.3, 0.8</td>
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<td>Autumn–Winter</td>
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<td>28.5</td>
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<td>Moriwaki and Kanda</td>
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<td>8.84</td>
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<td>Nemitz et al. (2002)</td>
<td>Edinburgh</td>
<td>2000</td>
<td>Autumn</td>
<td>CC</td>
<td>4.0</td>
<td>22</td>
<td>10 – 75</td>
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<tr>
<td>Pawlak et al. (2011)</td>
<td>Łódź</td>
<td>2006-2008</td>
<td>All year</td>
<td>CC</td>
<td>3.4</td>
<td>7.8</td>
<td>2 – 15</td>
<td>37</td>
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<tr>
<td>Soegaard and Møller-Jensen</td>
<td>Copenhagen</td>
<td>2001</td>
<td>All year</td>
<td>SR</td>
<td>2.0</td>
<td>5.3</td>
<td>6 – 32</td>
<td>40</td>
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<td>Basel</td>
<td>2002</td>
<td>All year</td>
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<td>1.0, 2.1</td>
<td>12.5, 9.9</td>
<td>3 – 12, 5 – 16</td>
<td>14, 31</td>
</tr>
</tbody>
</table>

Table 1.1: Existing measurements of urban CO$_2$ flux ($F_c$) at different site types (CC – city centre, SR – suburban/residential, UP – urban park). Height of measurement ($z_m$) normalised by height of surrounding roughness elements ($z_H$) is also shown.
1.2.1 Site locations

Measurements of CO$_2$ fluxes at a variety of urban sites around the world have been reported. The magnitude and variation in the reported fluxes is dependant on the nature of the site. Nemitz et al. (2002) find that the flux measured 65 m above a dense city centre location in Edinburgh in the autumn has a mean of 26 µmol m$^{-2}$ s$^{-1}$ with peaks from 50 to 75 µmol m$^{-2}$ s$^{-1}$. Grimmond et al. (2004) report early summer mean fluxes from a densely populated site in Marseille of 20 µmol m$^{-2}$ s$^{-1}$. Conversely, Coutts et al. (2007) report lower values of between 2 and 17 µmol m$^{-2}$ s$^{-1}$ throughout the year from a relatively sparsely populated suburban area of Melbourne, where the land type surrounding the measurement site is approximately 40% vegetation. From a site in Chicago, similar in terms of surrounding land use, Grimmond et al. (2002) observe typical summer fluxes from 0 to 10 µmol m$^{-2}$ s$^{-1}$. Crawford et al. (2011) measure a mean annual flux of 0.95 µmol m$^{-2}$ s$^{-1}$ from a suburban site with abundant vegetation. These differences suggest a dependence on the nature of the site but it is important to note that seasonal effects can affect comparisons between studies as discussed in §1.2.2.

An examination of Table 1.1 reveals the tendency of city centre sites to yield larger mean fluxes than suburban sites.

The height of the point of measurement has also been seen to affect the measured flux. Vogt et al. (2006) measure fluxes at the canopy height (the mean height of the surrounding buildings), $z_H$, and at $2.2z_H$ simultaneously. They find the daily mean flux at the lower height is around 25% greater than at the higher height. They attribute this to the three dimensional nature of CO$_2$ sources and sinks; they suggest that some sources such as emissions from residential heating and respiration of trees contribute less strongly to the $2.2z_H$ measurement as a result of increased blending with the background CO$_2$. Indeed Grimmond et al. (2002) propose that instruments must be mounted at a height at least twice the mean height of the roughness elements to ensure the measurements represent an integrated response at the local-scale ($10^2$–$10^4$ m).
1.2.2 Diurnal, weekly and annual cycles of CO$_2$ flux

Nearly all studies to date report a large diurnal cycle and those whose measurement period were long enough observe a seasonal cycle. Existing studies report mean diurnal ranges from around 10 $\mu$mol m$^{-2}$ s$^{-1}$ in Basel (Vogt et al., 2006) to 30 $\mu$mol m$^{-2}$ s$^{-1}$ in Marseille and Edinburgh. The urban CO$_2$ flux diurnal cycle is accepted to be a product of anthropogenic, biogenic and meteorological factors (Velasco et al., 2005). The diurnal pattern reported is usually similar with a minimum in the late evening or early morning and maximum during the day, often associated with peaks in rush-hour traffic activity (e.g. Moriwaki et al., 2006; Nemitz et al., 2002; Velasco et al., 2005). An example from Mexico City is shown in Fig. 1.1. In contrast to this, in rural studies the pattern is inverted with photosynthesis dominating during the day, acting as a CO$_2$ sink and generating a negative flux, then in the night the flux maximum occurs due to plant respiration (Schmid et al., 2000). This shows that, at least during the day, urban/rural differences in land use and anthropogenic activity must dominate the urban diurnal cycle. The effect of human activity has also been seen in weekly variations of CO$_2$ mixing ratio and flux. Gratano and Varone (2005) report differences between weekday and weekend CO$_2$ concentrations in Rome which correlate with traffic density. Velasco et al. (2005) find the weekday CO$_2$ flux to be greater than that at the weekend although it is uncertain if this difference is statistically significant (see Fig. 1.1).

A seasonal cycle of CO$_2$ flux has also been measured in some studies. Soegaard and Møller-Jensen (2003) present a large annual range from 2 to 8 $\mu$mol m$^{-2}$ s$^{-1}$ in the summer and winter respectively. Their results are shown in Fig. 1.2. This cycle is effectively modelled using fuel usage information and simulating CO$_2$ uptake by vegetation throughout the year. The broad maximum in the winter from December to March is explained by the combined effect of maximum residential fuel combustion for heating and minimum uptake of CO$_2$ by vegetation through photosynthesis during the coldest part of the year. In the summer the effects are reversed with maximum photosynthesis occurring in conjunction with little or no residential heating. A similar seasonal trend is reported by Coutts et al. (2007) in Melbourne and Pawlak et al. (2011) in Łódź with winter maximum
Figure 1.1: Average diurnal pattern of CO$_2$ fluxes for entire study and for weekdays and weekends in Mexico City in April 2003. The grey region represents ± 1 standard deviation from the total average (Velasco et al., 2005). Note the unit for flux used here: 1 mg m$^{-2}$ s$^{-1}$ = 22.7 µmol m$^{-2}$ s$^{-1}$.

Figure 1.2: Modelling and measurements of seasonal net CO$_2$ exchange for central Copenhagen, 2001 (Soegaard and Møller-Jensen, 2003). Note the unit for flux used here: 1 g CO$_2$ m$^{-2}$ d$^{-1}$ = 0.263 µmol m$^{-2}$ s$^{-1}$.
fluxes approximately double those measured in the summer.

1.2.3 The influence of traffic and source area type

Some of the studies mentioned above employ directional analysis to attribute features of the measured CO$_2$ flux to certain land types, activities or potential point sources of CO$_2$. Coutts et al. (2007) present the flux measurements as a function of wind direction and find that the flux is at a maximum when the wind is aligned with major roads and busy intersections but relatively small when coming from residential areas. Using the same technique, Nemitz et al. (2002) find that fluxes from the direction of the dense city centre are significantly larger than from areas with more park land and residential use. A single major building site is hypothesised to cause a narrow directional spike of 60 µmol m$^{-2}$ s$^{-1}$ against a low background of around 10 µmol m$^{-2}$ s$^{-1}$ in a direction away from the city centre. They also present results showing a direct connection between traffic density and CO$_2$ flux (see Fig. 1.3). The relationship is approximately linear as expected and from its intercept at 12 µmol m$^{-2}$ s$^{-1}$ the non-vehicle based contribution to emissions can be estimated. However, this does not consider a likely correlation between traffic density and industrial and commercial emission activity. Bergeron and Strachan (2011) find that the diurnal flux cycle at an urban site has a clear bimodal pattern corresponding to rush hour peaks. Kordowski and Kuttler (2010) segregate fluxes according to wind direction and find that mean fluxes from the direction of an urban park were only 0.8 µmol m$^{-2}$ s$^{-1}$ compared to 9.3 µmol m$^{-2}$ s$^{-1}$ from the city centre.

Velasco et al. (2005) use directional analysis for source attribution but also attempt to show how the contribution to the measured flux from a surface element varies with distance from the measurement point, hence calculating the source area, or ‘footprint’, of the measured flux (see §1.3.6). They report the upwind distance, or the ‘fetch’, over which surface elements are calculated to contribute 80% of the measured flux. This distance is, on average, seen to be a function of wind direction and ranges from around 500 m to 2 km. This analysis is used to explain why the expected relative reduction in flux in the direction of an urban park was not observed in the measurements; the majority of the park was beyond the
Figure 1.3: Dependence of the mean CO$_2$ flux on traffic counts for westerly wind directions (190°–330° clockwise from north; direction of Edinburgh city centre) (Nemitz et al., 2002).

calculated footprint for the flux measurement. There exist several models providing footprints for flux measurements including Hsieh et al. (2000) used by Matese et al. (2009) and Velasco et al. (2005) as described above and the FSAM model developed by Schmid (1994) and used by Soegaard and Møller-Jensen (2003) and Grimmond et al. (2004).

Soegaard and Møller-Jensen (2003) use texture-based classification of satellite images in an attempt to determine land use. Using a mobile equipment setup they measured the flux in several areas of Copenhagen with different image textures. They present results showing a correlation between a quality of the local image texture known as ‘variance’ with the CO$_2$ flux measured in that area. They propose that this texture ‘variance’ can be used as a proxy for CO$_2$ flux when determining areal CO$_2$ emission distributions.
1.2.4 CO₂ mixing ratio

While there are relatively few studies of CO₂ fluxes in urban environments there have been a numerous studies of the mixing ratio of CO₂ in urban atmospheres dating back to 1973 (see Grimmond et al., 2002, for a list of examples). Most urban CO₂ flux studies also report on the magnitude and variation of CO₂ mixing ratios. While this is not the primary focus of this review, it is certainly of interest as measured variations in this quantity are used to derive the flux and variations in the absolute mixing ratio will affect the calculation of flux measurements. Changes in CO₂ concentration over the averaging period are also responsible for the storage correction term discussed in §1.3.4.

1.2.4.1 Comparison with rural CO₂ concentration

Several comparisons of urban CO₂ concentrations with rural backgrounds have been made. Moriwaki et al. (2006) find that the urban site has consistently higher concentrations as expected, typically varying from 406 to 444 ppmv. However, under conditions of high wind speed the urban CO₂ concentration is reduced to the approximately constant rural level of 380 ppmv. In contrast to this, Rigby (2007) finds that during summer and autumn nights the rural concentration is often around 10 ppmv higher than in the city. This is attributed to a difference in heights of the two measurements and the urban heat island effect forming a deeper nocturnal boundary layer providing better mixing in the city. The effect is not observed in the winter when the diurnal cycle of turbulent intensity is reduced.

1.2.4.2 Diurnal variations

Most studies observe a similar pattern in the diurnal variation of CO₂ mixing ratio but the range can be significantly different. Diurnal cycles ranging 27 ppmv (Reid and Steyn, 1997) to 61 ppmv (Vogt et al., 2006) have been observed with largest ranges in the summertime. The predominant pattern is of an increase during the night as anthropogenic and biogenic source emit CO₂ into a stable, shallow boundary layer leading to an early morning maximum. Then as the sun rises, the boundary layer grows and increased mixing leads to a fast decrease in concentration with an early to mid-afternoon minimum. Variations in this pattern were
observed by Velasco et al. (2005) who attributed a significant mid-morning peak at around 06:30 h to vehicular emissions. While observing the pattern described above, Rigby (2007) noted that the range of the diurnal cycle increases with the diurnal temperature range which was used as an indicator of atmospheric stability.

### 1.3 Eddy covariance measurement and analysis techniques

The atmospheric boundary layer contains turbulent eddies with upwards and downwards components which transport CO$_2$ to and from the surface. The instantaneous vertical mass flux density is defined as:

$$ F_c = \rho_a w c, \quad (1.1) $$

where $F_c$ is the vertical CO$_2$ flux away from the surface in µmol m$^{-2}$ s$^{-1}$, $\rho_a$ is the molar density of air in mol m$^{-3}$, $w$ is the vertical wind speed in m s$^{-1}$, and $c$ is the mixing ratio of CO$_2$ to air in µmol mol$^{-1}$. Applying Reynolds’ decomposition to Equation 1.1, gives:

$$ F_c = (\bar{\rho}_a + \rho_a')(\bar{w} + w')(\bar{c} + c'), \quad (1.2) $$

where overbars signify averages over some time period and primes represent instantaneous fluctuations from the mean. Then with the assumption of negligible density fluctuations and zero mean vertical velocity, the above equation reduces to:

$$ F_c = \bar{\rho}_a \cdot \bar{w}'c'. \quad (1.3) $$

The technique has been used widely for measuring CO$_2$ fluxes from ecosystems with results dating back to 1969. Baldocchi (2003) provides a comprehensive review of the development of eddy covariance methods in rural settings. Its use in urban environments is relatively recent and brings new challenges. The method is traditionally applied to large, flat, homogeneous surfaces such as plant canopies and flux measurements are attributed to one type of surface cover. However, ur-
Ban environments are generally rougher and heterogeneous with different types of surface cover within the source area of the measurement point.

All the reported CO$_2$ flux measurements in this review were obtained using the eddy covariance technique. Experimental setups differ slightly between the groups and different analytical techniques have been applied. These will be discussed in the following sections.

### 1.3.1 Equipment

The equipment used by the various groups investigating urban CO$_2$ flux is similar. An accurate, high frequency, three-dimensional sonic anemometer (e.g. Campbell Scientific CSAT3) is used by all reported studies to obtain the required wind speed measurements. To measure the CO$_2$ fluctuations open- or closed-path infra-red gas analysers are used. Closed-path analysers (e.g. Licor LI-7000) require a sample of air to be drawn from the measurement point through a tube to the instrument with a pump. This introduces the need to correct for the lag between wind speed data and CO$_2$ data due to transit time in the tube (e.g. Grimmond et al., 2002; Nemitz et al., 2002). The transit in the tube can also have the effect of attenuating high frequency variations of CO$_2$ mixing ratio although this effect can be minimised by using a short tube and ensuring the flow is turbulent (Lenschow and Raupach, 1991). Closed-path analysers also typically require more frequent (approximately daily) calibration and a reference ‘zero’ gas to which the ambient sample is compared. Open-path analysers (e.g. Licor LI-7500) have the advantage of making in situ measurements without needing pumping equipment or frequent calibration but require corrections for density fluctuations (e.g. Moriwaki et al., 2006; Vogt et al., 2006) (see §1.3.4). Data are sampled at rates between 8 and 21 Hz and are stored either on a bespoke data logger (Campbell models are common) or on computer hard drives. Typically no processing is performed at the time of data acquisition although Nemitz et al. (2002) and Helfter et al. (2011) calculate online preliminary flux values.
1.3.2 Basic processing

Most studies report that before eddy covariance calculations were performed preliminary de-spiking of the acquired data was necessary. Hard spikes are instrument related, often non-physical (e.g. temperatures above 50°C) and can be filtered using simple rejection algorithms. Soft spikes are physical measurements which are short-lived departures from the mean and while dealt with explicitly by some groups at the pre-processing stage (e.g. Velasco et al., 2005), the processing of these features is more commonly subsumed into a later stage of validity checks (e.g. Grimmond et al., 2004).

The duration of averaging period for the covariance measurement is an important factor. It must be long enough to include the largest eddies contributing to the turbulent flux but short enough such that no significant trends (e.g. diurnal effects) are present. Baldocchi (2003) recommends periods between thirty minutes and one hour. Averaging periods reported in the studies examined here range from ten minutes (Coutts et al., 2007) to one hour (Grimmond et al., 2004; Moriwaki et al., 2006).

Some groups (e.g. Nemitz et al., 2002; Velasco et al., 2005) detrend signals before calculating deviations from the mean although this is not recommended by Baldocchi (2003) who considers it a redundant historical artifact and affects the size of the flux.

An assumption made in the derivation of Equation 1.3, used to calculate covariance fluxes, is that the mean vertical velocity, $\bar{w}$, is zero. Over flat smooth terrain this assumption generally holds. In the urban environment, however, sloping terrain or more local effects (e.g. obstruction of wind flow by buildings) may give rise to non-zero $\bar{w}$ measurements. This is dealt with by rotating the coordinates of the wind speed measurements such that $\bar{w} = 0$ over the averaging period as recommended in Kaimal and Finnigan (1994). Most studies employ these rotations with the exception of Vogt et al. (2006) who do not state how or if they deal with non-zero mean vertical velocities. Nemitz et al. (2002) show that the mean elevation angle of the wind velocity is dependent on the wind direction and varies between -5° and 11° and attribute this to the effect of the site situation and measurement tower. It is noted that these ranges are within the working specifica-
tions of the sonic anemometer but their effect on measured covariance flux is not examined.

1.3.3 Validity checks

After the above considerations have been accounted for and fluxes for averaging periods have been calculated according to Equation 1.3, results are often checked against certain validity tests. Grimmond et al. (2002) state that all data are subjected to strict data limits to reject implausible values. Velasco et al. (2005) similarly affirm that their measured and derived variables are submitted to a plausibility test with statistically determined constraints. They also present the power cospectrum of $w'T'$ and $w'c'$ where $T$ is the temperature measured by the sonic anemometer. As $T$ and $c$ are measured by different instruments, the similarity in shape of the two spectra is apparently used as a validation criterion for their flux measurements although it is not clear how this is implemented. Nemitz et al. (2002) present example cospectral density functions of $w'c'$. The theoretical $-5/3$ slope is visible below a certain frequency and above this attenuation of the cospectrum is apparent. This is caused by limitations of the CO$_2$ sampling setup. The magnitude of the attenuation on the calculated flux was calculated to be negligible at less than 1%.

Another validity check used by several studies in different forms is the stationarity of the flux over the averaging period. Grimmond et al. (2004) notice that anomalies in fluxes over hourly averaging periods were often due to large, short-term excursions from the mean. Furthermore, these excursions were frequently found to coincide with sharp changes in mean CO$_2$ concentration. The apparent flux excursions in these cases were inadvertent products of the Reynolds’ averaging process rather than true variations in flux. In other cases flux excursions are assumed to be due to the variable nature of CO$_2$ sources and sinks in urban landscapes. To locate these excursions, 5-minute average period fluxes were calculated and those exceeding a threshold of 50 $\mu$mol m$^{-2}$ s$^{-1}$ were excluded from the hourly average. Nemitz et al. (2002) calculate a stationarity coefficient for
each averaging period using a time integrated covariance function, $f(t)$, given by:
\[
f(t) = \frac{1}{\tau} \int_{t_0}^{t} w'c'dt \quad 0 \leq t \leq \tau,
\]
(1.4)
where $\tau$ is the averaging time. As $f(t)$ is near linear for stationary flux conditions, the standard deviation, $\sigma_f$, of $f(t)$ from a fitted regression line gives a measure of the stationarity of the flux over the averaging period. A relative stationarity coefficient is defined by:
\[
\xi = \frac{2\sigma_f}{w'c'}
\]
(1.5)
Periods with stationarity coefficients above a background mean of 0.2 are rejected. It was found that periods with a high stationarity coefficient nearly always correspond to measured fluxes of around $0 \mu\text{mol m}^{-2} \text{s}^{-1}$. Coutts et al. (2007) found that non-stationarity was a significant problem when using a one hour averaging period and consequently reduced the period to ten minutes to overcome this.

1.3.4 Flux corrections

Flux measurements calculated with Equation 1.3 are commonly subjected to various corrections. Webb et al. (1980) report a necessary adjustment to fluxes calculated using measurements of CO$_2$ concentration rather than mixing ratio due to fluctuations in air density. All studies using open-path gas analysers apply this correction, known as the WPL density correction, which uses measurements of temperature and humidity as a proxy for density. Modern closed-path analysers are able to measure the mixing ratio directly and so are exempt from this correction.

An ideal eddy covariance experimental setup would measure the continuous wind speed and CO$_2$ mixing ratio simultaneously at a point in space. However, this is not technically possible and different types of averaging occur at a number of places. Averaging across lengths occurs when the mean wind speed is measured across the path of the sonic anemometer and the mean CO$_2$ mixing ratio or concentration is measured along the optical path of the analyser (both of these paths are typically 0.1 m). The distance between the measurement points of wind speed
and CO₂ (often around 0.3 m or larger) is another example of a length averaging effect. Time averaging may occur as a result the sampling time of the equipment. Measurements at 20 Hz are effectively block averaging over 0.05 s. Further to these, in systems involving aspirated tubes, mixing of the sample air in transit to the analyser adds another averaging effect. These are all examples of frequency response errors of the system. Horst (1997) proposes that all these effects act together as a high frequency filter to the cospectrum of $\overline{w'c'}$ and that their resultant attenuation of the measured flux can be estimated with a simple formula. The attenuation increases with the time constant associated with the overall response of the system and with the peak frequency of the $\overline{w'c'}$ cospectral maximum. Fortunately, urban measurements are typically made at greater heights than traditional eddy covariance measurements. At these heights, larger eddies with a lower frequency prevail over smaller, high frequency eddies. This relaxes the requirements on the response time of the equipment. Typically frequency response corrections are not applied by the urban CO₂ flux groups but $\overline{w'c'}$ cospectra are examined by two groups and are found to be satisfactory as described above in §1.3.3.

1.3.5 Storage term

Another adjustment to the measured flux discussed in the literature (Baldocchi, 2003; Nemitz et al., 2002; Leuning, 2007) is associated with the quantity of CO₂ stored between the surface and the measurement height, $z_m$, and is known as the storage correction. This term is different to the two described above as rather than correcting the flux measured at the point of measurement, the relationship between the actual flux at the surface due to emissions and the flux at $z_m$ is examined. For example, neglecting horizontal CO₂ gradients, if the concentration of CO₂ between the surface and $z_m$ increases over a given period then the flux at the surface must be greater than that at $z_m$ over the same period. Ideally, to measure this effect a profile of CO₂ concentration from the surface to $z_m$ is required. In practice, changes in stored CO₂ are often inferred from the mixing ratio at the point of flux measurement which leads to the equation:

$$\Delta F_c = \overline{p_a} \frac{\Delta c}{\tau} z_m,$$

(1.6)
where $\Delta F_c$ is the correction to the measured flux and $\Delta c$ is the change in CO$_2$ mixing ratio over the averaging period. This equation is adapted from Nemitz et al. (2002) who observe an average correction of 11% in either direction.

### 1.3.6 Source area calculations

Two of the previously mentioned studies (Soegaard and Møller-Jensen, 2003; Grimmond et al., 2004) use the parameterisation of the FSAM model (mini-FSAM) by Schmid (1994). This model uses a surface-layer dispersion model which includes thermal stratification and a realistic wind-profile to calculate the source weight function, $f$, over the upwind area. $f$ is the relative strength of contributions to a flux at $z_m$ from a surface element. This function is strongly dependant on $z_m$, and further affected by surface-layer scaling parameters: the Obhukov length, $L$; the surface roughness length, $z_0$; the friction velocity, $u_*$; and the standard deviation of lateral wind speed fluctuations, $\sigma_v$ (see §1.3.7 for descriptions of these quantities). From $f$, a source area of level $P$, $\Omega_P$, is calculated. The source area represents the smallest possible area responsible for a given contribution, $P$, to the flux measured at $z_m$. Its shape is roughly elliptical. This is illustrated schematically in Figure 1.4. A parameterisation for $P = 0.5$ (that is, source areas contributing to 50% of the total flux) is presented in terms of the scaling parameters mentioned above. At the heart of the FSAM model (and most other footprint models) is an, dispersion model, in this case analytic and based on solutions to equations generated using gradient transfer and K theory (see §1.5.1). These predict the concentration distribution of a scalar emitted by a point source as its plume reaches the horizontal plane of the measurement point. By calculating this distribution due to a large number of upwind surface source elements, the source area weighting is calculated. From this the footprint can be obtained as required.

The length of the footprint increases with measurement height and decreases with roughness length and atmospheric instability. When using this model in situations where the displacement height (see 1.3.7), $z_D$, is significantly large, such as in the urban environment, $z_m$ should be replaced with $z_m - z_D$.

It should be noted that this model assumes a flat surface with a two-dimensional emission distribution. Further to this, it was developed for use with measurements
over surfaces much smoother than typical urban landscapes. Therefore, the results from FSAM cannot be taken to be accurate over cities and plausibility analysis should be performed on any results obtained. Kljun et al. (2004) and Hsieh et al. (2000) present more recent footprint parameterisations which may be useful in the future. They will not be examined in detail here but are based on similar models to FSAM and rely on similar scaling parameters.

Figure 1.4: The source area and its relation to the source weight function. The total volume under the source weight function is $\phi_{tot}$. $P$ is the fraction of this volume bounded by the isopleth $f_P$ and the cylinder surface below it (hatched). The source area of level $P$, $\Omega_P$, is the area bounded by the normal projection of the isopleth $f_P$ on the $x$-$y$-plane. The mean wind direction is parallel but counter to the $x$-axis (Schmid, 1994).

1.3.7 Urban surface-layer scaling parameters

The following quantities are often used as scaling parameters in surface-layer models such as those mentioned above. Theoretically they can all be calculated using the measurement from a sonic anemometer (with the obvious exception of
The friction velocity is related to the wind stress on the ground and varies with the type of surface and the wind speed. It is defined by:

\[ u_* = \sqrt{\frac{\tau_0}{\rho}} = (u'w'^2 + v'w'^2)^{1/4} \]  

(1.7)

where \( \tau_0 \) is the Reynolds’ stress and \( u \) and \( v \) are the horizontal components of the wind velocity parallel to and perpendicular to the mean horizontal flow.

The Obukhov length is a measure of surface layer stability given by:

\[ L = \frac{T u_*^3}{k g (w'T')_0} \]

(1.8)

where \( k \) is the von Kármán constant, \( g \) is the acceleration due to gravity and \( (w'T')_0 \) is measured at the surface (see Grimmond et al., 1998, for formulae in this section). Positive values of \( L \) correspond to stable atmospheric stratification. Negative values signify unstable conditions with large values in either direction tending toward neutrality.

The surface roughness length, \( z_0 \), is a scaling parameter in the classical logarithmic wind profile:

\[ \bar{U}(z) = \frac{u_*}{k} \ln \left( \frac{z - z_D}{z_0} \right) \]

(1.9)

where \( \bar{U}(z) \) is the mean wind speed at height \( z \) and \( z_D \) is the zero-displacement height which is essentially where the logarithmic profile begins. It is necessary in tall, dense canopies as found in some urban areas where the logarithmic profile cannot be assumed to extend to the actual surface. Both \( z_D \) and \( z_0 \) are functions of the height, distribution and constitution of the surface roughness elements. In a review of aerodynamic roughness of urban areas, Grimmond et al. (1998) recommend using a morphometric method to calculate \( z_D \) using the formula:

\[ \frac{z_D}{z_H} = \left( \frac{\sum A_{rb} + \sum (1 - p)A_{rt}}{A_T} \right)^{0.6} \]

(1.10)

Here, \( z_H \) is the mean height of the roughness elements, \( A_{rb} \) is the area of buildings, \( A_{rt} \) is the area of trees, \( A_T \) is the total area and \( p \) is the porosity of the trees.
Equation 1.9 can then be rearranged to give $z_0$ using the calculated value of $z_D$.

In the urban CO$_2$ studies, $z_D$ is frequently obtained by using a rule of thumb estimate, $z_D = 0.7z_H$ (Grimmond et al., 2004; Velasco et al., 2005). Using the technique above, Grimmond et al. (2004) estimate $z_0$ at the Marseille site to be 2.5 m as well as presenting a detailed analysis of calculated values of $L$ over the study period which will not be discussed here. Soegaard and Møller-Jensen (2003) report a value of 1.7 m for $z_0$. In Edinburgh, however the average value is only 0.47 m after non-stationary contributions have been excluded. Velasco et al. (2005) simply assume the value to be 1 m for their source area calculations.

1.4 Emissions inventories

With public awareness of the potential problems associated with global warming and climate change increasing, governments are facing strong political pressure to take preventative action. In light of this, emissions inventories of CO$_2$ and other pollutants have been compiled using fossil fuel usage statistics. The hope is that the effects of various CO$_2$ reduction schemes will be apparent in these inventories over time.

Emissions inventories can be used in conjunction with flux measurements as a means of mutual validation. The estimates in these inventories are usually presented in terms of tonnes of CO$_2$ per year but can be readily converted to units of $\mu$mol m$^{-2}$ s$^{-1}$ for comparison with results found in scientific literature. It is important to note, however, that these estimates are annual means and significant seasonal and diurnal variation can be expected as discussed. Furthermore, the inventories reported here do not account for biogenic CO$_2$ exchange which also has seasonal and diurnal cycles.

1.4.1 National atmospheric emissions inventory

The National Atmospheric Emissions Inventory (NAEI, 2008) is the standard reference air emissions inventory for the UK. It is created using a largely ‘top down’ approach based on annual national emission estimates from various sectors. These sectors include domestic combustion (e.g. heating and cooking), industrial
and commercial combustion, road traffic emissions and point source contributors. Point sources are known sources at fixed locations such as power stations whereas the other contributors are known as area sources and apply to more general sources such as roads and residential land use areas. Based on these calculated annual national estimates and land use information (including point source locations which are incorporated ‘bottom up’), emission estimates are then attributed to 1 × 1 km squares covering the UK.

The NAEI results from 2005 for the grid square containing Imperial College (see Figure 2.1) are shown in Table 1.2 along with the results from the LAEI for 2003 as discussed below. The largest contributors are point sources and industrial and commercial combustion, combining to produce more than 70% of predicted CO₂ for the area. Traffic contributes only around 14% to the total. The mean annual flux is 47.9 µmol m⁻² s⁻¹.

1.4.2 London atmospheric emissions inventory

The London Atmospheric Emissions Inventory (LAEI, 2006) has been created by the Greater London Authority using a different methodology to the NAEI. A ‘bottom up’ approach for all sectors is used. This entails using local consumption and traffic data, hopefully giving a more accurate estimate at the local scale. Compared with the results from the NAEI in Table 1.2, the most obvious difference is due the point source contribution. Also notable is a reduction from the industrial and commercial sector compared with the NAEI estimate. The combined effect is that in the LAEI, traffic and domestic emission are the most significant contributions to a mean annual flux of 24.1 µmol m⁻² s⁻¹. The difference between the NAEI and LAEI estimates is presumably due the contrasting methodologies used in each inventory and raises issues about the accuracy of both.

The LAEI emissions estimates for the surrounding grid squares were also examined. The squares to the north and northeast, approximately 80% of which are occupied by Hyde Park, have significantly lower mean annual fluxes of 6.31 and 14.0 µmol m⁻² s⁻¹ respectively, nearly all of which is from traffic sources. The other surrounding squares have larger fluxes of between 29 and 36 µmol m⁻² s⁻¹ with the differences mainly due to greater traffic emissions in these areas.
<table>
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<th>LAEI 2003</th>
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<td></td>
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</tr>
<tr>
<td>Total</td>
<td>66,476</td>
<td>47.9</td>
</tr>
</tbody>
</table>

Table 1.2: CO₂ emission estimates in tonnes per year (t y⁻¹) and as a flux equivalent in µmol m⁻² s⁻¹ from the NAEI and the LAEI including percentage contributions by sector. Data shown are for 1 × 1 km grid square containing Imperial College shown in Figure 2.1.

1.5 Plume dispersion

The studies and techniques (eddy covariance) discussed previously are concerned with measuring fluxes from an areal source. However we find it important to consider the potential effect of large point sources on these measurements and hence review some of the relevant existing theory on plume dispersion. The plume source is assumed to be small, effectively a point, and we assume there are no boundary effects from the ground or any atmospheric inversions. Furthermore the theories here are based on the idealised conditions of isotropic, stationary, homogenous turbulence.

1.5.1 Gradient transfer theory

The most commonly used model by far for plume development in atmospheric dispersion applications is the Gaussian plume model which predicts a Gaussian concentration profile. This model can be derived from Fick’s Law, the basis of gradient transport theory, which is well tested for molecular diffusion and can be derived from statistical theory of gases. It states that the mass flux is proportional to and opposite in direction to the concentration gradient. It is given by:

\[ F = -D \Delta c \]  \hspace{1cm} (1.11)
where \( F \) is the mass flux, \( c \) is the concentration. \( D \) is named the molecular diffusivity and has a typical value of order \( 10^{-5} \) m\(^2\) s\(^{-1}\) for contaminants in the atmospheric boundary layer.

When substituted into the equation for conservation of mass in an elementary control volume a differential equation for the instantaneous concentration at any point \((x,y,z)\) is obtained (Arya, 2003a) where \( u \) is a constant wind speed along the \( x \) axis:

\[
\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)
\]  

(1.12)

This equation can be solved using the boundary conditions of vanishing concentration at very large distances and that source strength, \( Q \), must equal the mass flux through a plane normal to the plume axis to provide,

\[
c(x, y, z) = \frac{Q}{4\pi Dr} \exp \left[ -u \left( \frac{r - x}{2D} \right) \right]
\]  

(1.13)

where \( r \) is radial distance,

\[
r = \left( x^2 + y^2 + z^2 \right)^{1/2}
\]  

(1.14)

The equation behaves as a Gaussian in \( y \) and \( z \) when \( y^2 + z^2 \gg x^2 \) and when \( ux \gg D \). When these conditions apply the "slender plume approximation" is valid and reduces equation 1.13 to

\[
c \approx \frac{Q}{2\pi u \sigma^2} \exp \left( -\frac{y^2 + z^2}{2\sigma^2} \right)
\]  

(1.15)

where \( \sigma = (2Dt)^{1/2} \) is the plume diffusion parameter. Using the substitution \( t = x/u \) where \( t \) is the travel time of the plume the plume dispersion parameter becomes

\[
\sigma = (2Dx/u)^{1/2}
\]  

(1.16)

and is close to the half width at half maximum of the Gaussian concentration profile of the plume after time \( t \). It can be shown (Arya, 2003b) that equation 1.15 is an exact solution of the diffusion equation if diffusion in the direction of flow is neglected.
The above theory is often adapted from molecular diffusion to turbulent diffusion by replacing $D$ with $K$, which is then known as eddy diffusivity in what is known as K-theory. $K$ can be allowed to vary with direction such that, $K_x \neq K_y \neq K_z$, which produces variations on equation 1.15 which are not $y-z$ symmetric. Values of $K$ can be allowed to vary with position such that, for example, $K_z$ can be made to increase with height representing increasing turbulent intensity with altitude. In this study we focus on isotropic, homogenous turbulence so the relevant plume dispersion equations are the ones given with molecular diffusivity replaced with eddy diffusivity. Typical values of boundary layer $K$ are of order $1 \text{ m}^2 \text{ s}^{-1}$.

This analogy between Fickian diffusion and turbulent dispersion which leads to the popular use of the Gaussian plume model is questionable although partially supported by observational evidence of dispersing plumes.

### 1.5.2 Statistical theory of dispersion from a continuous source

Statistical theory provides a more fundamental technique to describe turbulent dispersion. This is used to characterise dispersion properties based on the statistics of the displacements of tracked particles. Taylor’s statistical theory of diffusion gives us the mean-square displacement of traced particles released from the same point in a stationary, homogenous turbulent flow. In the simple case of one-dimensional dispersion in the Y direction with the mean flow along the X direction, the result is

$$\overline{Y^2}(t) = 2v'^2 \int_0^t \int_0^{t'} R_L(\xi) \, d\xi \, dt'$$

(1.17)

where $v'$ is the instantaneous turbulent fluctuation in speed in the Y direction and $R_L(\xi)$ is the normalised Lagrangian autocorrelation function defined by

$$R_L(\xi) = \frac{v'(t)v'(t+\xi)}{v'^2}.$$  

(1.18)

where $\xi$ is a time-lag.

Without knowing the exact form of $R_L$, assuming only that at $\xi = 0$ it is 1 and decreases to zero by some value of $\xi$, it is possible to derive an important result describing the rate of growth of the width of a plume for short and long travel times. Using the plume diffusion parameter, $\sigma_y = \left(\overline{Y^2}\right)^{1/2}$, to describe the standard
deviation of particle displacement we get
\[
\sigma_y \approx \left( \frac{v' \Delta t}{2} \right)^{1/2}, \text{ for } t \ll T_L \tag{1.19}
\]
\[
\sigma_y \approx \left( \frac{2v'^2 T_L t}{2} \right)^{1/2}, \text{ for } t \gg T_L \tag{1.20}
\]
where \( T_L \) is the Lagrangian integral timescale which represents the timescale of the largest turbulent eddies contributing to the diffusion and is defined by
\[
T_L = \int_{0}^{\infty} R_L(\xi) d\xi. \tag{1.21}
\]
Equations 1.19 and 1.20 are significant as they show that turbulent diffusion begins with \( \sigma_y \propto t \) before slowing down to \( \sigma_y \propto t^{1/2} \). This shows that only when the diffusion time is much greater than the timescale of the largest eddies is the analogy with molecular diffusion appropriate. K-theory has been adapted such that the eddy diffusivity can vary with time to attempt to address the variable rate of dispersion.

### 1.5.3 Observation of plume concentration profile shapes

Measurements of short range plume concentration profiles are reviewed comprehensively in Pasquill (1975). Ensemble mean distributions are fitted to the form
\[
\frac{c}{c_0} = \exp \left( -ay' \right) \tag{1.22}
\]
where \( c_0 \) is the peak concentration and \( c \) is the concentration at crosswind distance \( y \) from the position of the peak. The exponent, \( r \), was found to have values from 1.5 to 2.5 rather than 2.0 as in the Gaussian form. However, both Arya (2003b) and Pasquill (1975) conclude that experimental inadequacies and the relatively small change in shape due to the changes in \( r \) question the significance of the departures from 2.0.

Analysis of plume width as a function of time is also covered in the above literature and is found to broadly agree with the results from Taylor’s statistical theory presented above. The lateral plume dispersion parameter was found to obey a power law, \( \sigma_y \propto x^p \), where \( x \) is the distance from the source. In relatively short
range experiments with distance from the source less than 1 km, \( p \) was found to be invariant with distance in this range but vary between 0.6 and 0.9 with atmospheric stability. Over longer distances the plume spread rate has been observed to reduce but not all the way to near square-root behaviour as predicted by the statistical theory.

1.6 Overview of chapters

Chapter 1 introduces the concept of urban CO\(_2\) flux measurements, analyses the existing studies and summarises the methodologies used. Relevant emissions inventories are discussed and the basic principles behind atmospheric plume dispersion are introduced.

Chapter 2 provides details of the measurement site and equipment used in this observational study.

The data processing methodologies used are dealt with in chapter 3 including a novel approach to coordinate rotations for eddy covariance calculations. A summary of the different subsets of data used in this and the following chapters is provided.

The main results of the CO\(_2\) flux analysis are presented and discussed in chapter 4. Stability and footprints are discussed before an in-depth characterisation of the CO\(_2\) flux and a comparison with inventory estimates.

Chapter 5 focuses on measurements of a CO\(_2\) rich plume from a local power station. Its affect on measured CO\(_2\) flux is examined and high frequency CO\(_2\) concentration measurements are linked to natural gas usage rates at the power station.

In chapter 6 an existing model is used in a novel way to characterise the dispersion of regions of high scalar concentration within a plume. The high concentration percentile plume is shown to be significantly wider than the tradition Gaussian plume.

Chapter 7 concludes the study, summarising the major results and discussing possible future work.
Chapter 2

Site and equipment

This thesis examines CO$_2$ measurements made at Imperial College. This chapter first describes the measurement site and details of the surrounding area pertinent to the analysis in chapters 4 and 5. Following this is a discussion of the equipment used along with some operational information.

2.1 Site

Measurements were made at the Imperial College South Kensington site, about 5 km west of the centre of London. The location is shown in Figures 2.1 and 2.2.

Eddy covariance equipment was mounted on a mast which was 2.5 m high and had a diameter of 0.06 cm. The mast was mounted vertically, on top of the western edge of a meteorological tower on top of the physics building such that the measurement height, $z_m$, was 50 m above ground level. The meteorological tower is an octagonal laboratory and has a diameter of approximately 6 m and rises above the immediately surrounding buildings by at least 5 m. The meteorological tower is shown in Figure 2.3. Most of the surrounding area in the direction of the south westerly prevailing wind is residential and commercial with buildings of a mean height of 25 m high. The view to the south west is shown in Figure 2.4. The measurement height was chosen as 50 m to be twice the height of the surrounding roughness elements such that the measurements should be representative of the local scale ($10^2$ - $10^4$ m) (Grimmond et al., 2002). However, as the mast only
Figure 2.1: Aerial photograph of surrounding area. 'X' shows the sampling location. The circles have 0.8 km and 1.6 km radii and correspond to the mean upwind distances containing 80% and 90% of the observed flux (see §4.2.2). The square designates the 1x1 km square referred to by the NAEI and LAEI estimates.
Figure 2.2: Map of the London area showing the location of measuring point. Built up area is shown in white.
elevates the measurement point 2.5 m above the nearest roughness element the site is not ideal for flux measurements. College offices lie in the immediate vicinity of the measurement site with some laboratories and the university power station emissions outlet to the east at a height of approximately 52 m. Hyde Park begins 300 m to the north of the measurement point with the Royal Albert Hall located to the northeast. A plan of the area immediately surrounding the measurement site and power station emission outlet is shown in Figure 2.5 with the approximate heights of the buildings.

On a bearing of 86° from the measurement site at a distance of 190 m is the emissions outlet stack for the Imperial College combined heat and power plant. The stack outlet is at approximately the same height as the measurement point. The power plant burns natural gas to produce heat and electricity for the college on demand and so has a highly variable output rate of CO₂ rich emission gas. Its estimated CO₂ emissions are 17,000 tonnes per year. A simple Gaussian plume model for typical urban dispersion conditions (e.g. Briggs, 1973) predicts a CO₂ concentration increase of around 10 ppmv in the centre of the plume as it travels over the measurement point when the power station is operating at full power.

### 2.1.1 Bluff body effects

Given the complex nature of the geometry of the buildings surrounding the measurement point it is worth considering the expected effect of a building or other obstacle on wind streamlines and how this may effect measurements made in the vicinity of such a building. Figure 2.6 shows the centre-line streamline pattern for flow passing over a cube. Even in this simple situation the flow is seen to be complex with recirculation patterns in front of, behind, and on top of the cube. Where the streamlines are continuous they can be seen to rise on the windward side of the object and fall on the leeward side. Flow over an irregular three-dimensional environment is expected to be far more complex and a thorough treatment is not attempted here although some attempt is made to explain measured wind disturbance patterns using the nature of the building geometry in §3.2.2.1. In the example of the centre-line streamline patterns over a cube the streamlines are not deflected horizontally, however, away from the centre-line we expect horizontal
Figure 2.3: The measurement site as seen from the south east near ground level with arrow marking the location of measurement point.

Figure 2.4: The view from the measurement point toward the south west.
Figure 2.5: A simplified plan of the area around the measuring point and power station emissions stack with numbers representing approximate heights of buildings in metres. North is indicated by the arrow. The horizontal scale is shown by the dotted line.

Figure 2.6: Centre-line streamlines of wind flowing over a cube. From Peterka et al. (1985)
deflections to be important. We therefore expect some deflection of the plume from the chimney stack as this is situated on the side of a building as shown in Figure 2.5. Again, a detailed analysis of expected effects is not attempted here, merely noted that they are likely to exist.

2.2 Equipment and operation

The experimental setup was required to satisfy the following main criteria:

1. Provide high frequency (≥ 10 Hz) CO$_2$ mixing ratio or concentration and three dimensional wind speed measurements.

2. Provide meteorological measurements, including pressure, humidity and temperature.

3. Require little or no in situ maintenance as access to the measurement point was limited by health & safety constraints.

For the wind speed measurements, the Campbell Scientific CSAT-3 sonic anemometer was chosen. This is capable of sampling at up to 60 Hz and has a low profile frame with minimal flow distortion. The manufacturers quote specifications for ±170° wind directions implying a 20° 'shadow' caused by the frame. This anemometer has been used in many prior eddy covariance measurement systems including the urban CO$_2$ flux measurements by Coutts et al. (2007) and Moriwaki et al. (2006).

The Licor Li-7000 gas analyser was chosen for the CO$_2$ measurements. It is a closed-path analyser and measures CO$_2$ mixing ratios at up to 20 Hz. Being closed-path is significant in two ways: the instrument can be kept in the office below the measurement point with the sample air drawn from above giving easy access for calibrations and maintenance; as the sample air is thermally stabilised within the machine the mixing ratio can be measured instead of concentration which means that the density correction to eddy covariance measurements suggested by Webb et al. (1980) is not necessary eliminating a possible source of error. The Li-7000 has been used previously by many eddy covariance study groups.
CSAT-3 Specifications

<table>
<thead>
<tr>
<th>Transducers</th>
<th>3 ultrasonic, non-orthogonal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Path length</td>
<td>10.0 cm vertical; 5.8 cm horizontal.</td>
</tr>
<tr>
<td>Path angle</td>
<td>60° from horizontal.</td>
</tr>
<tr>
<td>Outputs</td>
<td>3 orthogonal wind components, relative to transducer head, $u_x, u_y, u_z$; the speed of sound, $c$.</td>
</tr>
<tr>
<td>Frequency</td>
<td>1–60 Hz; oversampling modes from 60 Hz to 10 or 20 Hz.</td>
</tr>
<tr>
<td>RMS Noise</td>
<td>$u_x, u_y$: 1 mm s$^{-1}$; $u_z$: 0.5 mm s$^{-1}$; $c$: 15 mm s$^{-1}$.</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>-30°C to 50°C.</td>
</tr>
<tr>
<td>Max. Wind Speed</td>
<td>65.53 m s$^{-1}$.</td>
</tr>
<tr>
<td>Offset Error</td>
<td>$u_x, u_y$: &lt; ±4 cm s$^{-1}$; $u_z$: &lt; ±2 cm s$^{-1}$.</td>
</tr>
<tr>
<td>Gain Error</td>
<td>wind vector within ±5° of horizontal, &lt; ±2% of reading; within ±10°, &lt; ±3% of reading, within ±20°, &lt; ±6% of reading.</td>
</tr>
</tbody>
</table>

Table 2.1: Published specifications of the Campbell Scientific CSAT-3 sonic anemometer (Campbell Scientific, 2007).

including Moriwaki et al. (2006) while an earlier model of. Licor closed-path analyser was used by Nemitz et al. (2002) and Grimmond et al. (2002).

A Vaisala WXT 510 weather station provided the meteorological measurements required.

The published specifications of the anemometer (Campbell Scientific, 2007) and gas analyser (Licor Biosciences, 2005) are given in Tables 2.1 and 2.2.

2.2.1 Equipment overview

The Campbell Scientific CSAT-3 anemometer was mounted on a mast approximately 3 m above the western edge of the roof of the meteorological tower at Imperial College pointing towards the west. A Teflon tube with an internal diameter of 1/4 inch (6.35 mm) was also attached to the mast such that the inlet was level with and about 0.20 m away from the anemometer head. The tower and the anemometer are shown in Figure 2.7. A rotary vane pump (model no. GAST 3032-701-RM112) was used to draw the sample air through the tube (approximately 7 m) and through the sample cell of the Licor Li-7000 gas analyser operating in the room below. The flow in the tube was calculated to be fully turbu-
## Li-7000 Specifications

<table>
<thead>
<tr>
<th>General</th>
<th>Differential, non-dispersive gas analyser.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Differential, non-dispersive gas analyser.</td>
</tr>
<tr>
<td>Detectors</td>
<td>Two solid state detectors; one each for CO₂ and H₂O, filtered at 4.255 and 2.595 microns, respectively.</td>
</tr>
<tr>
<td>Chopping Frequency</td>
<td>600 hertz</td>
</tr>
<tr>
<td>Source</td>
<td>Single source, lifetime &gt; 20000 hours</td>
</tr>
<tr>
<td>Sample Cell Size</td>
<td>9.53 mm Dia. × 152.4 mm L.</td>
</tr>
<tr>
<td>Sample Cell Volume</td>
<td>10.86 cm³.</td>
</tr>
<tr>
<td>Cell Pressure Range</td>
<td>0–115 kPa absolute.</td>
</tr>
<tr>
<td>Max Flow through Cell</td>
<td>&gt;50 litres/min.</td>
</tr>
<tr>
<td>CO₂ Analyser</td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0–3000 μ mol mol⁻¹.</td>
</tr>
<tr>
<td>Accuracy</td>
<td>0.1% of full scale</td>
</tr>
<tr>
<td>Zero Drift (with temperature)</td>
<td>±0.3 μ mol mol⁻¹ °C⁻¹</td>
</tr>
<tr>
<td>Span Drift</td>
<td>±0.2% of reading/°C</td>
</tr>
<tr>
<td>Water Sensitivity</td>
<td>&lt;0.1 μ mol mol⁻¹ CO₂/mmol/mol H₂O (software algorithm corrects for band broadening effect).</td>
</tr>
<tr>
<td>RMS Noise</td>
<td>157 (ppb) @ 20Hz and 370 μ mol mol⁻¹</td>
</tr>
<tr>
<td>Peak-to-Peak Noise</td>
<td>1096 (ppb) @ 20Hz and 370 μ mol mol⁻¹</td>
</tr>
<tr>
<td>H₂O Analyser</td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0–60 mmol mol⁻¹</td>
</tr>
<tr>
<td>Accuracy</td>
<td>1%</td>
</tr>
<tr>
<td>Zero Drift</td>
<td>±0.02 mmol mol⁻¹ °C⁻¹</td>
</tr>
<tr>
<td>Span Drift</td>
<td>±0.4% of reading/°C</td>
</tr>
<tr>
<td>RMS Noise</td>
<td>11 (ppm) @ 20 Hz and 10 mmol mol⁻¹</td>
</tr>
<tr>
<td>Peak-to-peak Noise</td>
<td>75 (ppm) @ 20 Hz and 10 mmol mol⁻¹</td>
</tr>
</tbody>
</table>

Table 2.2: Published specifications of the Licor LI-7000 CO₂/H₂O analyser (Licor Biosciences, 2005).
lent ensuring minimum damping of mixing ratio fluctuations during transit caused by velocity profiles in the tube associated with lamina flow. The Vaisala WXT 510 weather station was mounted on the same mast as the anemometer and recorded meteorological data including temperature, pressure and relative humidity. Data acquisition from all three instruments was handled by a desktop PC running software written in visual basic by the author of this thesis. Digital outputs from all instruments were connected to the serial ports of the PC. Both the gas analyser and the anemometer were set to output data at 20 Hz and the weather station at 1 Hz. The anemometer was run in its oversampling mode where near instantaneous measurements at 60 Hz are block averaged to a 20 Hz signal. This is equivalent to the process used by the gas analyser which averages up measurements made at 300 Hz to a 20 Hz output and should reduce aliasing effects in frequency analysis.
2.2.2 Setup, calibration and maintenance

The anemometer requires no ongoing calibration after an initial test for zero offset. The gas analyser however requires careful setting up as well as zero and span calibrations approximately weekly. The Li-7000 is a differential analyser which means it works by comparing the gas in two cells, a sample cell and a reference cell. This creates an extra requirement: the analyser requires a constant supply of air with a zero CO\textsubscript{2} concentration as a reference. The setup of the gas analyser is shown in Figure 2.8.

Needle valves (1, 2 and 3 in the diagram, model no. Swagelok B-1RS8MM/B-1KS4) were used to control flow rates of different gases. Valve 1 could be closed to force air through the sample cell of the analyser if this was found necessary, however even when fully open the flow rate through the analyser was sufficient and opening the valve minimises strain on the pump.

To control the flow of the zero reference gas, needle valve 3 (in diagram) was used. This was set to produce the smallest possible positive flow from the zero gas.
cylinder. When this was finely tuned it was found that one BOC size ‘V’ cylinder of nitrogen gas would last for approximately one month. Valve 2 similarly controls the flow of the reference gas although this was less critical than the zero gas as it is only used for short periods during calibration.

Filtering any air entering the analyser cells is recommended to prevent dirt accumulating on the internal optical windows and affecting measurements. This was achieved using the recommended in-line filters which were replaced regularly.

Junction connectors (A, B, C and D in the diagram) were used to change the flow of gas during calibration periods. The junctions in the diagram all show gas flow as during routine operation, that is the sample air drawn from above passes through the sample cell, and the zero gas (nitrogen gas) flows through the reference cell.

Calibration consists of three main phases:

1. A zero calibration achieved by flowing the zero CO$_2$ gas through both cells of the analyser by changing the flow at junctions A, B and C (in that order to prevent unfiltered air being sucked into the analyser cells). When the measured mixing ratio has stabilised it can be set as the zero point for measurements on the analyser.

2. A span calibration is performed by flowing gas of a known mixing ratio through the sample cell by changing the flow at junctions A, B and D. Optimally the span reference gas mixing ratio should be similar to the sample mixing ratio (around 400 ppmv). Again, when the measured mixing ratio is stable it can be reset to the span gas mixing ratio.

3. The gas flow was returned to its routine operation setup and allowed to stabilise. The H$_2$O mixing ratio was calibrated at this stage using the relative humidity from the weather station before data collection resumed.

The span reference gas used here had a CO$_2$ mixing ratio of 432 ppmv in dry air. This was determined by comparison with a traceable reference gas provided by Royal Holloway University of London. We estimate the uncertainty in the span gas mixing ratio to be no more than 1 ppmv. Drifts in measured CO$_2$ mixing ratio
between calibrations were typically around 1 ppmv. The relative humidity measurement used to calibrate the water vapour concentration is stated to be accurate to within 5 percent (Vaisala, 2006). Given that the mean measured H$_2$O mixing ratio was 10.2 mmol mol$^{-1}$ this equates to an error of approximately 0.5 mmol mol$^{-1}$ in the calibration. This has a small follow-on effect on the CO$_2$ mixing ratio of approximately 0.05 ppmv, significantly smaller than other expected errors on this measurement.

The calibration procedure takes roughly 15 minutes in total and so typically one 30 minute period of measurement is lost for each calibration. As a consequence of this, calibrations were performed at different times of the day where possible to avoid biasing the available data.

2.2.2.1 Equipment failure

Two major equipment problems were encountered during the course of the observation period. First, in mid July 2008, after the equipment had been running for about 6 weeks the gas analyser failed and was sent for repair. The experiment was not running again until December 2008. Then in September 2009 the pump failed which again required repair and led to another two months of lost data. The equipment operated correctly after this until the end of the experiment at the end of February 2010.

2.2.3 Measurement accuracy

The results presented in this thesis focus on eddy covariance flux data calculated using instantaneous deviations from the mean, $c'$, therefore a very high accuracy of the absolute mean mixing ratio $\bar{c}$ is not necessary as long as its variation is captured accurately. However we still expect the absolute values to be accurate to within around 2 ppmv according to the uncertainty in the span gas mixing ratio and the observed drift between calibrations.

The error in $c'$ scales approximately proportionally to the error in $\bar{c}$. During the winter, when CO$_2$ fluxes are largest, the standard deviation of CO$_2$ mixing ratio, $\sigma_c$, measured at 20 Hz over 30 minutes was on average 4.9 ppmv and the mean mixing ratio was 422 ppmv. So the error in values of $c'$ passed on to the
flux measurement due to errors in the absolute measure mixing ratio are likely to be very small at around $4.9/422 = 1.2\%$. This error is lower in the summertime at 0.5\%. These errors while not strictly random are better treated as random as their sign and magnitude will change during operation as the analyser drifts and at calibration events.

The error in the vertical wind speed measurement is dependent on the angle of the wind vector from the horizontal. The mean wind elevation angle is often seen to be around between $8^\circ$–$15^\circ$ when the wind is from the prevailing south westerly direction and the error for wind in this range is quoted to be less than $\pm6\%$ of the reading. This is a systematic error.

Another potentially significant source of error is the noise in the gas analyser measurements. The instrument RMS noise at 20 Hz of a sample of air with an atmospheric CO$_2$ mixing ratio is reported to be 0.16 ppmv. During summer nights $\sigma_r$ is at its lowest value with a mean of 1.79 ppmv. This results in a signal to noise ratio of about 10:1 giving a possible 10\% error on contributions to flux values at 20 Hz. However we expect most of the flux to come from lower frequency variation below 1 Hz where the random noise would effectively be reduced by a factor of $1/\sqrt{20}$. For vertical wind speed measurements, the mean standard deviations is $0.55 \text{ m s}^{-1}$. The noise in the vertical wind speed measurement is quoted as $5\times10^{-4}$ m s$^{-1}$, less than 0.1 % of the ‘signal’.

Using the random shuffle method proposed by Billesbach (2010) the total instrumental random error on half hourly eddy covariance values from a sample of two weeks from the summer and the winter were calculated. The mean error was 2.5\% which is in good agreement with the above estimates.

Assuming all these errors are additive this gives us a maximum error on the measured flux of 9.7\%, at least 6\% of which is systematic.

Instrumental measurement accuracy is not discussed in any of the existing urban CO$_2$ studies but since the equipment is subject to similar limitations we can assume the error in their flux results is similar.
Chapter 3

Data processing

This chapter describes the various stages of processing performed on the data acquired using the experimental setup described in the previous chapter. This includes preliminary processing of the raw data from the anemometer and gas analyser and a detailed examination of subsequent eddy covariance flux calculations.

3.1 Preliminary processing

3.1.1 Wind speed

The wind speed and sonic temperature data from the anemometer required some simple but important treatment. Occasional instantaneous unphysical spikes in the data were easily removed with a simple threshold filter. The origin of these is uncertain. As the anemometer works on the principle of measuring the speed of sounds across the sensor path it is expected to be very sensitive to any obstacles in its path including rain. The anemometer has an in-built algorithm to detect problems of this nature which it flags in its diagnostics data stream (Campbell Scientific, 2007). This was found to be useful but not sufficient. In addition to excluding any periods flagged as problematic, data within one minute either side of any flagged event was also removed. This was found to be sufficient under all tested conditions.
3.1.2 CO₂ Mixing ratio

The raw CO₂ mixing ratio data had no obvious hard spikes to contend with and rain was not an issue as we used a closed-path sensor. We did however find that the signal was contaminated by physical, relatively short-lived, departures from the mean that were large compared to half-hourly standard deviations of the mixing ratio. They were thought to be caused by plumes of CO₂ from local sources which were poorly mixed. We initially used an algorithm based on that described in Schmid et al. (2000) to identify and reject contaminated sections of data. However the procedure of identifying a plume fluctuation from the background variation is somewhat arbitrary and requires setting a threshold. It was found that the thresholds which appeared successful in summer were not appropriate in winter due to changes in the background variability in CO₂ mixing ratio. Furthermore nearly all identified plume contamination events which had a significant effect on the measured flux were found to be when the wind direction was in the sector 30° – 120° and was later discovered to be due to the Imperial College power station emissions. For these reasons it was decided to simply exclude data from the contaminated sector from flux analysis (except directional analysis where the effect of the plume is highlighted) and to apply no further plume rejection algorithms.

3.2 Covariance calculations

This section describes the stages involved with the calculation of eddy fluxes used in this thesis. The order for this is as follows:

1. Divide data into non-overlapping blocks of a fixed time period.
2. Perform coordinate rotations on wind speed data.
3. Calculate the lag between analyser and anemometer data.
5. Calculate storage flux.
6. Apply data quality filters.
3.2.1 Block averaging

To perform eddy covariance calculations it is necessary to divide the data up into, usually non overlapping, blocks. For each of the blocks, means of the covariant quantities (e.g. CO\(_2\) mixing ratio and vertical wind speed) are calculated then instantaneous deviations from these are calculated. Some groups (e.g. Nemitz et al., 2002; Velasco et al., 2005) also apply linear detrending to the variables at this stage to remove meteorological effects however this is not recommended by Baldocchi (2003) as it is effectively a low pass filter removing lower frequency components of the flux. No linear detrending was performed here. The duration of the block is important: it needs to be large enough to capture the actions of the largest eddies contributing to the flux but small enough to avoid effects from changing meteorological conditions and also to provide a high enough time resolution to observe features in the flux time series. Averaging periods range from 10 minutes (Vogt et al., 2006) to one hour (Grimmond et al., 2004; Moriwaki et al., 2006) in existing urban CO\(_2\) flux experiments but the most common is 30 minutes (e.g. Nemitz et al., 2002; Velasco et al., 2005; Matese et al., 2009) and is what was used here. Figure 3.1 shows the effect of averaging period on the median CO\(_2\) flux, \(F_c\), measured over a sample period of around four months worth of data (data subset C in Table 3.2 when all other processing steps were kept as described in this chapter. Flux data considered to be unreliable due to the power station plume was excluded as described in §4.3. It shows that as the period increases from 5 minutes to 60 minutes the mean flux also increases as the effect of larger and larger eddies is included. Beyond this some decrease is seen, presumably as shifting meteorological conditions interfere with the flux values. Choosing 30 minutes gives us a higher time resolution data set and reduces stationarity problems but appears to lead to an underestimation of mean flux of 2.8%. 

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Figure 3.1: Median and interquartile range of CO$_2$ flux measurements against block averaging period. Analysis performed using data subset C (see Table 3.2) using 3,203 data points for the 30 minute period data.

### 3.2.2 Coordinate rotations

The next stage in processing is to rotate the coordinates of the wind speed data into a stream wise coordinate frame with some transform $A$ such that:

$$
\begin{pmatrix}
  u \\
  v \\
  w
\end{pmatrix}
= A
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix}
$$

(3.1)

where $x$, $y$ and $z$ are the original wind speed in a frame fixed according to the anemometer and $u$, $v$ and $w$ are the new coordinates in the rotated reference frame. In the transformed coordinates the mean wind direction points along the $u$-axis so the mean values of $v$ and $w$ are zero. This satisfies one of the assumptions made in deriving the eddy covariance equation (Equation 1.3) and is usually achieved using a series of two rotations. The first around the original $z$-axis by an angle $\alpha$ so that the new $y$ component is 0, followed by a rotation around the new $y$-axis by an angle $\beta$ such that the new $z$ component is zero. The transformation matrix
A (here composed of the product of two rotation matrices) is calculated for each half hour period. $\alpha$ is effectively the mean azimuthal wind direction and $\beta$ is the mean elevation angle. This is known as the double rotation method (DR). Note that third rotation around the new $x$-axis such that $\overline{v^2w^2} = 0$ used in some studies was not used here as it led to erratic results.

### 3.2.2.1 Wind field distortion

Figure 3.2 shows the relationship between angles $\alpha$ and $\beta$ in this observational study. The shape of the curve can be broadly understood as the effect of the building underneath the measurement point on the flow. From most directions $\beta$ is positive indicating the wind is being forced up by the building. From the east however the negative elevation implies the wind is being drawn back down after rising to flow over the building, this is consistent with the fact that the anemometer is mounted on the west face of the tower. The very large deviations from the curve usually coincide with low wind speed periods. To help understand the shape of Figure 3.2, the vertical angle from the point of measurement to the building beneath it has been plotted as a function of direction at horizontal radii of 3, 10 and 20 m in Figure 3.3. The plot reveals the complex nature of the local building geometry (see Figure 2.5) but the strong east to west asymmetry at the 3 m radius appears to correlate well with the measured wind elevation angles. Features in the 10 and 20 m radius graphs also seem to contribute to the shape of the measured wind profile.

### 3.2.2.2 Planar Fit method and extensions

One problem noted by researchers is that calculating the rotation for every period based on the mean wind direction is not always optimal and, especially at low wind speeds can lead to over rotation. One solution to this problem is known as the planar fit (PF) method (Wilczak et al., 2001). The method assumes that the local flow is flat and fits long term (i.e. many block period’s worth) wind speed data to a plane. The transform $A$ is then calculated for each period based on the wind direction and the fitted plane. This means that $\overline{v^2w^2}$ is not forced to equal zero which introduces vertical advective fluxes which are not discussed here. Yuan
Figure 3.2: Shows elevation angle, $\beta$, as a function of azimuthal angle, $\alpha$, with the fitted curve following the median of $10^\circ$ bins. Also shown are the sectors influenced by the plume (discussed in detail in Chapter 5) and the frame of the sensor. Analysis performed using data set A from Table 3.2.
Figure 3.3: Shows vertical angle from the point of measurement to the top of the building beneath it as a function of direction at a selection of horizontal radii indicated in the plot.
et al. (2011) developed the PF model so that a different plane is fitted for each 30° sector, effectively allowing for some curvature in the local wind flow.

### 3.2.2.3 ‘Fixed rotation’ and ‘Running rotation’ methods

Since the flow in the current observational study is expected to be highly curved the PF method is not appropriate and the DR method was used primarily. However a couple of experimental rotation methods were also developed and tested.

We have enough data that we can fit a curve to the median of 10° bins of half hourly data points as shown in Figure 3.2. This curve then gives us a good measure of the elevation angle due to the flow distortion as a function of azimuth, $\beta(\alpha)$. Then for any given period the required elevation angle for the transformation matrix $A$ can be determined from only the azimuth angle. We call this the Fixed Rotation (FR) technique.

Across all 30 minute periods during which the observational study was running, the mean standard deviation of wind azimuth directions was 22°. Given the steep gradients in $\beta(\alpha)$ with respect to $\alpha$, a change in the wind direction of 22° over the course of one measurement period could result in a change of elevation angle of 5°. All of the currently available methods ignore this because traditionally the rate of change of $\beta(\alpha)$ with respect to $\alpha$ is much smaller. If we calculate a running mean of the azimuth angle over some period smaller than the block averaging period we can calculate a running elevation angle and use this to generate a transformation matrix $A(t)$ which is a function of time. Note that the azimuthal rotation component of $A(t)$ is fixed, only the elevation angle changes. We call this the Running Rotation (RR) method. The period over which to calculate the running mean was chosen as 2 seconds as it is the approximate time taken for a parcel of air to travel 10 m which was estimated to be the range of the distortion caused by the tower on the wind field.

The DR, FR and RR methods were used to calculate CO$_2$ fluxes for a period using data from June 2008 to July 2009 (data set D, Table 3.2).

Figures 3.4 and 3.5 show the anomaly of fluxes calculated using the FR, RR compared to the standard DR method as a function of azimuthal angle for wind speeds less than and greater than 2 m s$^{-1}$ respectively. The anomaly was calculated
on mean values per direction bin using the formula \( \frac{(x - \overline{DR})}{\overline{DR}} \times 100\% \), where \( x \) is FF or RR appropriately. The fluxes measured in the 30°-120° are unreliable due to plume contamination and so excluded.

Under conditions of wind speeds of less than 2 m s\(^{-1}\) the FR flux is lower in most directions than the DR flux with a mean anomaly of -6.4%, however under conditions of wind speeds greater than 2 m s\(^{-1}\) we see that the anomaly is very small (-0.6%). We conclude that over-rotations cause the DR method to overestimate fluxes during low wind speeds.

The RR fluxes are similarly lower than DR during low wind conditions but with much larger anomalies of up to around 50% in the SE and NW directions. These directions are where the largest gradients are found in Figure 3.2 and so where the RR flux is expected to differ from the other methods. These large deviation are also observed under normal wind speed conditions but away from these sensitive areas the anomaly is small. The mean RR anomalies for low wind and regular wind conditions were 16.0% and 8.4% respectively.

Because the prevailing wind direction was SW and low wind speeds were relatively rare (< 10%), the mean anomalies of FR and RR fluxes are smaller at -1.5% and 3.7%. However these could become more important in other observation sites and setups.

In the rest of this thesis, the DR method was used as this is the prevalent method in the previous urban CO\(_2\) flux studies and the FR and RR are untested by any other studies.

### 3.2.3 Lag

As the sample has to flow though a tube before being analysed there is expected to be a delay between the analyser data and the wind speed data which is measured in situ. In order to correct for this lag, the standard technique in which the delay to the anemometer data required to achieve maximum covariance was calculated for each period over a range of lag times from 0 to 5 s (e.g. Nemitz et al., 2002). Figure 3.6 shows the covariance of rotated vertical wind speed and CO\(_2\) mixing ratio as a function of lag applied to the wind speed data for a consecutive sequence of half hour periods beginning at 12 h on 22/06/08. In most periods a peak is present
Figure 3.4: Difference between CO$_2$ fluxes calculated using the FR, RR and the standard DR methods as a function of azimuthal angle, $\alpha$, at wind speeds less than 2 m s$^{-1}$ for data period June 2008 – July 2009. Anomaly calculated as described in the text and $n$ is the number of data points for each directional bin. Bars show the standard error for each data point.

Figure 3.5: Difference between CO$_2$ fluxes calculated using the FR, RR and the standard DR methods as in Figure 3.4 but for wind speeds above 2 m s$^{-1}$. 

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at 0.65 seconds, assumed to be the approximate transit time of the sample in the
tube. Significant deviations from this usually only occur for periods with low flux
where no obvious peak is found on the covariance as a function of lag time. Cal-
culating the lag for every period rather than fixing it at 0.65 s allows for potential
variation on the flow rate over time as well as correcting for the longitudinal sep-
oration of the air inlet and the anemometer head. The lag corresponding to the
highest covariance was chosen for each period. The mean lag was 0.64 s and not
significantly dependent on atmospheric stability (see §4.2.1).

3.2.4 Covariance calculations

The CO\textsubscript{2} eddy flux, $F_c$, and sensible heat flux, $Q_H$ were calculated for each period
using the formulae (Kaimal and Finnigan, 1994),

$$F_c = \overline{\rho_a} \cdot \overline{w'c'}$$
$$Q_H = \overline{C_p \rho_a} \cdot \overline{w'T'}$$

Here, $w'$ is rotated vertical wind speed fluctuation, $w - \overline{w}$, and $c'$ is the CO\textsubscript{2} mixing
ratio fluctuation, $c - \overline{c}$. The molar density, $\rho_a$, is the density, $\rho$, divided by the molar
mass of air, taken to be 0.02897 kg mol\textsuperscript{-1}. $C_p$ is the heat capacity of air at constant
pressure. Both $\rho$ and $C_p$ were calculated using the mean temperature, pressure and
relative humidity data from the weather station for each half hour period.

The scaling parameters requiring covariance calculations (see §1.3.7, includ-
ing the friction velocity, $u_*$, the Obukhov length, $L$ and the aerodynamic roughness
length, $z_0$ were also calculated at this stage.

3.2.5 Frequency analysis

The covariant time series $w'T'$ (used to calculate sensible heat flux) uses only data
from the sonic anemometer, therefore it contains no high frequency attenuation
effects due to sensor separation or transit of sample air though a tube to the sen-
sor, the two most common mechanisms for high frequency fluctuation damping
in closed-path sampling systems. Assuming similarity between temperature and
CO\textsubscript{2} transport, by comparing the power spectrum $w'c'$ to $w'T'$ we can determine
Figure 3.6: A sequence of lag calculations with the red line showing the lag time giving maximum covariance. Sequence begins at 12 h on 22/06/08 and runs for 12 half-hourly periods. The numbers in the top left of the plots denote place in sequence.
any possible frequency damping effects caused by the CO$_2$ measurement setup. A Fast Fourier transform (FFT) was used to calculate the power spectrum of the two time series for each half hour period during the first six weeks of data collection (data set B from Table 3.2. The mean, normalised power spectra are shown in Figures 3.7 and 3.8 for unstable and neutral atmospheric conditions respectively (see §4.2.1 for definitions and discussion of stability conditions). The spectra for $w'c'$ and $w'T'$ are in good agreement in unstable and neutral conditions with only a very small shift to lower frequencies seen in the $w'c'$ spectrum. It was therefore decided to apply no frequency correction to $F_c$ following most other urban CO$_2$ flux studies.

3.2.5.1 Water vapour measurements

The water vapour measurements made by the gas analyser are not examined in this study. The data was found to have very little high frequency variation. The measurements were therefore assumed to have been subjected to substantial low pass filtering during transit in the tubing. Latent heat fluxes were therefore not included in this study.

3.2.6 Storage term

Ideally vertical profile CO$_2$ mixing ratio measurements would be used calculate the CO$_2$ storage beneath the measurement point. As these were not available the change in mixing ratio at the measurement point was taken to be representative of the change beneath the measurement point as in Nemitz et al. (2002). The CO$_2$ storage term was therefore calculated according to Equation 1.6 and added to the flux measurement for each period. This required finding the change in mixing ratio over the course of the half hour period and was accomplished by fitting a straight line to the mixing ratio time series and multiplying its gradient by the period length. Figure 3.9 shows how the mean storage term varies throughout the day and is a reflection of the mean diurnal CO$_2$ mixing ratio cycle. The mean absolute storage adjustment per period was 2.0 µmol m$^{-2}$ s$^{-1}$ which was roughly 10% of the mean measured flux value. This is similar to the value of 11% reported by Nemitz et al. (2002). However, overall the positive and negative storage ad-
Figure 3.7: Mean normalised power spectra of $c'w'$ and $T'w'$ calculated over six weeks beginning 05/06/08 in unstable conditions. Plot is a mean of spectra from 1,270 half hour periods.

Figure 3.8: Mean normalised power spectra of $c'w'$ and $T'w'$ calculated over six weeks beginning 05/06/08 in neutral conditions. Plot is a mean of spectra from 168 half hour periods.
justment terms balance out to a net effect of 0.01 μmol m$^{-2}$ s$^{-1}$, 0.5% of the mean total eddy flux.

3.2.7 Data quality filters

Periods with less than 50% of the c’w’ data available were rejected at the calculation stage. These events were mainly relating to analyser calibrations, rain affecting the anemometer, the hardware malfunctions described in §2.2.2.1, or occasional software problems.

Following the calculation of $F_c$, it was subjected to the following quality filters:

1. Very large (> 100 μmol m$^{-2}$ s$^{-1}$) positive or negative fluxes were removed affecting 0.13% of data points.

2. Following most eddy covariance groups (e.g. Coutts et al., 2007; Vesala et al., 2008; Matese et al., 2009), periods with low friction velocity ($u_* < 0.2$ m s$^{-1}$) were omitted and found to affect 4.3% of the data.
3. In 0.6% of periods the vertical wind coordinate rotation angle was calculated to be less than -10° or greater than 20°. These data were excluded as unphysical.

4. The stationarity coefficient of each flux period was calculated using the formulation described in §1.3.3 and used by Nemitz et al. (2002). This was used to exclude periods whose stationarity coefficient was significantly above the background level and mostly affected fluxes close to zero. This applied to 3.2% of data periods.

3.2.8 Data Availability

Altogether the above described filters removed 7.7% of flux periods. However including all possible periods from the beginning to the end of the observational study (05/06/08–27/02/10) only 47.4% were available which amounts to 12,904 data points. The low data availability is mainly due to the two large equipment failures. These broke the study up into three phases, the dates of and data availability in each of these is recorded in Table 3.1. The data was distributed reasonably equally across all hours of the day and days of the week as shown in Figures 3.10 and 3.11. Further to the three phases of observation discussed, various subsets of the data were used in different analyses presented in this study. These are listed in Table 3.2 with the number of available data points and some in each subset with some data on atmospheric conditions.
Figure 3.10: Distribution of data over hours of the day.

Figure 3.11: Distribution of data over days of the week.
### Table 3.1: Dates of and data availability during the three phases of measurement comprising the observation period. Also show are data figures for the total period.

<table>
<thead>
<tr>
<th>Observation phase</th>
<th>Dates</th>
<th>Potential data points</th>
<th>Points available</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>05/06/08 - 13/07/08</td>
<td>1,872</td>
<td>1,544</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>19/12/08 - 22/09/09</td>
<td>13,296</td>
<td>9,433</td>
<td>70.9</td>
</tr>
<tr>
<td>2</td>
<td>18/11/09 - 27/02/10</td>
<td>4,896</td>
<td>3,411</td>
<td>70.0</td>
</tr>
<tr>
<td>3</td>
<td>05/06/08 - 27/02/10</td>
<td>30,384</td>
<td>14,388</td>
<td>47.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.2: Date ranges of various subsets of data used in this study with number of available data points, N. 'Plume sector' is the number of data points with a mean wind direction between 30° and 120°, the sector identified as being affected by a power station plume (see §4.3). Number of data points in atmospheric stability classes as defined in §4.2.1 are also shown.

<table>
<thead>
<tr>
<th>Data subset</th>
<th>Date range</th>
<th>N</th>
<th>Plume sector</th>
<th>Unstable</th>
<th>Neutral</th>
<th>Stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>05/06/08 - 27/02/10</td>
<td>14,388</td>
<td>2,339</td>
<td>11,386</td>
<td>2,978</td>
<td>24</td>
</tr>
<tr>
<td>B</td>
<td>05/06/08 - 13/07/08</td>
<td>1,544</td>
<td>102</td>
<td>1,350</td>
<td>190</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>05/06/08 - 22/02/09</td>
<td>3,754</td>
<td>551</td>
<td>2,983</td>
<td>758</td>
<td>13</td>
</tr>
<tr>
<td>D</td>
<td>05/06/08 - 17/07/09</td>
<td>8,684</td>
<td>1,502</td>
<td>6,985</td>
<td>1680</td>
<td>19</td>
</tr>
<tr>
<td>E</td>
<td>05/06/08 - 21/09/09</td>
<td>10,977</td>
<td>1,742</td>
<td>8,787</td>
<td>2168</td>
<td>22</td>
</tr>
</tbody>
</table>
Chapter 4

CO₂ climatology

4.1 Introduction

Carbon dioxide has been identified as the primary factor causing global warming (Intergovernmental Panel on Climate Change, 2007) and urban CO₂ emissions are recognised as a significant contributor to global emissions with London alone estimated to contribute 9% to the UK’s total (AEA Energy and Environment, 2006). Attempts have been made to quantify these contributions using estimates derived from fuel consumption and traffic data by the London Atmospheric Emissions Inventory (LAEI) and the National Atmospheric Emissions Inventory (NAEI) as part of CO₂ emission reduction schemes. Direct measurement and characterisation of urban mean emissions and individual point source emissions of CO₂ is therefore important as a validation of these inventory estimates and emission reduction schemes.

CO₂ fluxes have been measured using the eddy covariance technique in a number of cities from around the world. All studies report cities to be net sources of CO₂ throughout the day. Mean reported values vary according to site location, height of measurement point, traffic activity and season. Nemitz et al. (2002) report a mean flux of 26 µmol m⁻² s⁻¹ measured at a city centre site in Edinburgh during the autumn. They also find an approximately linear relationship between local traffic counts and the measured CO₂ flux. In central Copenhagen, Soegaard and Møller-Jensen (2003) measured a large seasonal variation from 2 – 8 µmol
### Table 4.1: Summary of CO$_2$ flux, $F_c$, measurements presented in this chapter.

Analysis performed on data set A from Table 3.2 with data from the directional sector affected by emissions from the power station plume ($30 – 120^\circ$) excluded. Summer and winter are May to August and November to February respectively. Day and night are 11 h – 17 h and 23 h – 05 h.

<table>
<thead>
<tr>
<th>$F_c$ (µmol m$^{-2}$ s$^{-1}$)</th>
<th>Summer</th>
<th>Winter</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day</td>
<td>Night</td>
<td>Day</td>
</tr>
<tr>
<td>Mean</td>
<td>15.6</td>
<td>11.2</td>
<td>35.7</td>
</tr>
<tr>
<td>Median</td>
<td>14.9</td>
<td>9.46</td>
<td>34.4</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>11.1</td>
<td>6.20</td>
<td>24.4</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>19.3</td>
<td>15.0</td>
<td>44.5</td>
</tr>
</tbody>
</table>

m$^{-2}$ s$^{-1}$ in the summer and winter respectively. This is attributed largely to seasonal cycles in residential gas combustion for space heating and plant photosynthesis. Most studies report a significant diurnal cycle in CO$_2$ flux with an early morning minimum and a daytime maximum attributed mainly to traffic, residential and commercial activity.

Further to this a weekly cycle has been reported by some groups, Gratano and Varone (2005) observe large weekday to weekend differences in CO$_2$ mixing ratio measured at a height of 2 m which correlate well with traffic counts. In Melbourne, Coutts et al. (2007) report a difference between mean weekday and weekend CO$_2$ fluxes. In Mexico City Velasco et al. (2005) find fluxes at the weekend to be marginally smaller than during the week.

In this chapter we present a detailed analysis of CO$_2$ flux measurements made at the Imperial College London site from June 2008 to February 2010. An analysis of the atmospheric stability conditions during the observation period is first conducted before examining the footprint of the measurement. Following this the CO$_2$ flux behaviour is characterised, including examination of its directional behaviour and temporal cycles. Finally we compare $F_c$ to the estimates produced by emissions inventories. Table 4.1 is a summary of the CO$_2$ flux measurements discussed in the rest of this chapter.
4.2 Stability and scalar flux footprint

4.2.1 Stability

For each half hour period in data set A (Table 3.2) the stability, $\xi$, was calculated using $\xi = \frac{z'}{L}$ where $L$ is the Obukhov length as defined in Equation 1.8 and $z'$ is the measurement height. Figures 4.2 and 4.1 show the distribution of $\xi$ according to time of day and season respectively. Here, day is defined as 11 h - 17 h and night as 23 h - 05 h. Summer and winter are May to August and November to February respectively. These definitions are used hereon unless otherwise specified.

The atmosphere was found to be unstable for the majority of the time with the criterion for an unstable atmosphere, $\xi$ less than -0.1, satisfied for 80% of the time. Most of the remaining 20% are classified as neutral with $-0.1 < \xi < 0.1$. Only 1% of periods had a positive stability value. In another London study, Helfter et al. (2011) find the atmosphere to be stable more frequently but this is because of the height of the measurement leading to frequent decoupling from the surface. The unstable urban atmosphere observed here is similar to that observed in Grimmond et al. (2004). This is explained as part of the urban heat island effect resulting from the land use and surface types found in a city. Winter is typically more stable than summer with 24% of periods neutral compared to 16% in summer. A similar relationship exists between nighttime and daytime stabilities.

4.2.2 Footprint analysis

The scalar flux footprint was calculated for each half hour period using the model by Hsieh et al. (2000) as in Sparks and Toumi (2010). Required inputs to the model were the measurement height, $z = z_m - z_d$, the Obukhov length, $L$, as used in the above analysis and the aerodynamic roughness length, $z_0$. The mean aerodynamic roughness length over all wind directions, calculated from eddy covariance estimates of $u_*$ and $u$ in near neutral conditions and the logarithmic wind profile formula, as recommended by Grimmond et al. (1998), was 1.28 m. Near neutral conditions were determined using $|(z_m - z_d)/L| < 0.1$. The displacement height was taken to be $0.8z_h$ (as in Matese et al., 2009) with $z_h$ equal to 25 m. $z_H$ was treated as constant in all directions which is approximately true with the excep-
Figure 4.1: Stability $\xi = z'/L$ by season. Analysis performed on data set A from Table 3.2 with 5,156 and 5,861 data points for 'Summer' and 'Winter' categories respectively.
Figure 4.2: Stability $\xi = z'/L$ by time of day. Analysis performed on data set A from Table 3.2 with 3,372 and 3,797 data points for 'Night' and 'Day' categories respectively.
tion of some of the university buildings in the immediate vicinity to the East. \( z_0 \) was calculated for each period and not found to have any significant directional dependence. The measurement height is near the top of the roughness sublayer but proximity to roughness elements mean Monin-Obukhov similarity theory may not hold in this study (Grimmond and Oke, 1999; Rotach, 1999).

Using the above values the model then provides the footprint, \( f \), which is the cross-wind-integrated fractional contribution to the measured flux of the surface at a distance \( x \) upwind from the measurement point. Figure 4.3 shows the footprint as a function of distance for unstable, neutral and stable conditions using the mean roughness length over all periods, 1.28 m. For unstable conditions the upwind distance from the measurement point to the location of peak contribution to the measured flux, \( x_{\text{max}} \), is just under 100 m. The fetch, \( x_{80} \), which is the distance from the measurement point over which 80% of the measured flux is predicted to originate, is 9.0 times greater than \( x_{\text{max}} \). The footprint distances for neutral and stable conditions are much longer, but as discussed in the previous section these conditions are relatively rare. Table 4.2 shows the mean and standard deviation of \( x_{\text{max}} \) and \( x_{80} \) for summer, winter, daytime and nighttime as defined above. Footprints for summer and daytime are shorter than winter and nighttime due to the more unstable atmosphere during these periods. The differences aren’t large enough to suggest that a seasonal bias or time of day bias would affect the surface areas being sampled in this observational study. The footprint length was not found to have a strong directional dependence. The width of the footprint is not predicted by this model, however the width is expected to increase with atmospheric instability leading to shorter, wider footprints rather than long, thin footprints in the prevalent conditions.

The distances given here suggest that the flux results presented in this chapter characterise the area within around 700 m of the measuring point. This means that we can make a reasonable comparison between the \( \text{CO}_2 \) flux measured here with the \( \text{CO}_2 \) flux implied from inventory based emission estimates for the square kilometre containing the measurement point.

It should be noted however that the accuracy of footprint models detailed in Schmid (1994) and Hsieh et al. (2000) have not been tested over rougher urban terrain and are based on flat surfaces with two-dimensional emission distributions.
In particular, the model in Hsieh et al. (2000) was tested on surfaces with values of $z_0$ of 0.005 m and 0.05 m whereas urban surface roughness lengths tend to be close to 1.0 m. Further to this an ideal eddy covariance system would be mounted on a tower through which air can flow freely. In this observational study the tower is a solid building which has potentially complicated effects on the flux footprint. This could reduce the effective measuring height which would in turn reduce the predicted footprint size.

![Figure 4.3: Footprint as a function of stability.](image-url)

Table 4.2: Showing calculated footprint distances $x_{max}$ and $x_{80}$ in metres for different time categories. N is the number of data points in each category. Analysis performed using data set A from Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>$x_{max}$</th>
<th>$\sigma(x_{max})$</th>
<th>$x_{80}$</th>
<th>$\sigma(x_{80})$</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>85.2</td>
<td>46.2</td>
<td>764</td>
<td>414</td>
<td>5,156</td>
</tr>
<tr>
<td>Winter</td>
<td>91.2</td>
<td>59.2</td>
<td>817</td>
<td>534</td>
<td>5,861</td>
</tr>
<tr>
<td>Daytime</td>
<td>85.5</td>
<td>48.5</td>
<td>766</td>
<td>434</td>
<td>3,797</td>
</tr>
<tr>
<td>Nighttime</td>
<td>88.8</td>
<td>64.1</td>
<td>796</td>
<td>574</td>
<td>3,372</td>
</tr>
</tbody>
</table>

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4.3 CO\textsubscript{2} flux and mixing ratio data

Here we present a broad overview of the CO\textsubscript{2} data collected during the observation period between June 2008 and February 2010 before examining it in more detail in following sections. The CO\textsubscript{2} flux, $F_c$, data presented in this chapter were all calculated using data set A from Table 3.2 and corrected and subjected to the quality control filters described in chapter 3. Further to this, data from wind directions between 30–120° have been excluded from the analysis apart from the explicit directional analysis in §4.4. Data from this sector were found to be heavily influenced by emissions from the Imperial College power station and are examined in detail in chapter 5.

The mean, median and standard deviation of $F_c$ were 20.40, 17.19 and 13.86 µmol m\textsuperscript{-2} s\textsuperscript{-1} respectively. Figure 4.4 shows the total distribution of $F_c$. The flux was nearly always positive with less than 1% of periods giving a negative flux. This predominantly positive flux is consistent with most other urban CO\textsubscript{2} flux studies and is expected as there are no major CO\textsubscript{2} sinks within the expected footprint for most wind directions. The magnitude of the mean flux is similar to other studies at city centre locations (see Table 3.2). The distribution shape is very similar to that reported by Nemitz et al. (2002) measured in Edinburgh who fitted a shifted log-normal distribution to the data such that log($F_c + a$) was distributed as $N(\log(\mu + a), \sigma^2)$. The same distribution has been fitted here with parameters: $a = -2.7$ µmol m\textsuperscript{-2} s\textsuperscript{-1}, $\mu = 19.18$ µmol m\textsuperscript{-2} s\textsuperscript{-1} and $\sigma = 0.60$.

Daily mean fluxes were calculated for each day of data with at least 67% of data periods available. Each of these are shown along with maximum and minimum values from the day in Figure 4.6. From this plot we can see clear seasonal behaviour in the daily mean flux with larger means and diurnal ranges in the winter. Most days the flux remain positive throughout although there are relatively frequent exceptions to this. These negative events are not attributable directionally to a single cause but do tend to occur during the early morning when the $F_c$ diurnal cycle is at its lowest (see §4.5.2). The maxima occur in periods from all directional sectors but usually during the afternoon which is during the maximum in the diurnal cycle.

The mean, median and standard deviation of half hourly CO\textsubscript{2} mixing ratios,
\( \bar{c} \), were 408.5, 406.1 and 21.8 ppmv respectively. A histogram showing the distribution of \( \bar{c} \) is shown in Figure 4.5. The daily mean, minimum and maximum of half hourly CO\(_2\) concentrations, \( \bar{c} \), are shown in Figure 4.7. Similarly to the flux, a clear seasonal trend is visible in the mean and diurnal range \( \bar{c} \) with smaller values of both in the summer. The anomalously high maxima usually coincided with, early to mid morning periods with very low wind speeds when ventilation is poor.

Figure 4.8 shows half hourly \( \bar{c} \) and \( F_c \) against wind speed, \( U \), according to season. Extreme highs of \( \bar{c} \) can always be seen to coincide with low wind speeds. This effect was also observed in Tokyo by Moriwaki et al. (2006) amongst others. The \( F_c \) has no such clear trend although higher wind speeds seem to increase the minimum absolute observed flux. This maybe simply be coupling of the diurnal cycle of \( U \) and \( F_c \).

Figure 4.4: Histogram showing distribution of measured \( F_c \).
Figure 4.5: Histogram showing distribution of measured $\bar{c}$. 
Figure 4.6: Daily median $F_c$ with bars indicating 10th and 90th percentiles. Each point represents a day for which at least 67% of data points are available.
Figure 4.7: Daily median $\bar{c}$ with bars indicating 10th and 90th percentiles. Each point represents a day for which at least 67% of data points are available.
4.4 Directional patterns

In this section we perform directional analysis on the measured CO\textsubscript{2} data. To show how different direction sectors contribute to the measured CO\textsubscript{2} values the wind direction, $\theta$, frequency distribution is shown in Figure 4.9 for summer and winter periods. During the summer period the prevailing south westerly wind is dominant with 60\% of all periods coming from 180–270\degree. The wind direction is more evenly spread out during the winter with only 36\% from the south west quadrant.

In Figure 4.10 $F_c$ is plotted against wind direction in 15\degree bins. The flux is approximately uniformly distributed from 135\degree to 360\degree with a value of just over 20 \(\mu\text{mol m}^{-2} \text{s}^{-1}\). However between 30\degree and 120\degree there is a clear trough with a minimum at around 65\degree of just over -10 \(\mu\text{mol m}^{-2} \text{s}^{-1}\). Some wind distortion effects due to the anemometer orientation are expected in the 80–100\degree sector (see chapter 2), so special care is needed here. However, as the apparent trough is much larger than this 20\degree sector and not centred on it the effect is not thought to be caused by wind field distortions although these could have an effect on the measured magnitude of $F_c$. A negative CO\textsubscript{2} flux is usually attributed to CO\textsubscript{2} sinks such as large areas of vegetation below the measurement height. No such suitable sinks exist in the area ENE of the measurement site within the footprint. Instead we demonstrate in chapter 5 that this negative flux is the result of a CO\textsubscript{2} rich plume from the Imperial College power station emission stack at 86\degree passing above the measurement point and exclude the data from this contaminated sector in the rest of this chapter. We also see that fluxes from the northerly to north easterly direction are slightly lower than most values between from 135\degree to 360\degree. This is possible due to the presence of Hyde Park in this direction (see Figure 2.1). Other urban CO\textsubscript{2} flux studies have measured significant differences due to urban parks in their footprint. Notably, Vesala et al. (2008) find large differences between sectors containing roads and vegetation with the vegetation sectors producing mean negative fluxes in the summer. The effect in this study is more complicated because Hyde Park begins 300 m from the measurement point and the point of maximum contribution to the flux has already been seen to be at less than 100 m. Furthermore it is difficult to separate possible contributions of Hyde Park from the contamination
Figure 4.8: Half hourly $\bar{c}$ and $F_c$ against wind speed, $U$. 
from the power station in the NNE region.

Mean directional CO$_2$ mixing ratios are plotted in Figure 4.11. These are more uniform than the fluxes with directional variations of the mean within one standard deviation of its natural variability. There is no peak or trough centred on ENE as in the flux however there is a broad maximum in the easterly direction. The source areas of influence on concentrations tend to be an order of magnitude larger than for fluxes (Schmid, 1994) so we may expect to see contributions from sources within around 8 km. Therefore the maximum in $c$ in the easterly direction is probably from high CO$_2$ mixing ratios in the centre of London, approximately 5 km to the east.

### 4.5 Temporal CO$_2$ patterns

As well as the directional patterns in the previous section, CO$_2$ flux and mixing ratio display interesting variability on the seasonal, daily and weekly timescales.
Figure 4.10: CO$_2$ flux, $F_c$, against wind direction. Data collected into 15 degree bins. Bars show standard deviation of half hourly values.

Figure 4.11: CO$_2$ mixing ratio, $\bar{c}$, against wind direction. Data collected into 15 degree bins. Bars show standard deviation of half hourly values.
These will be examined in the following section.

4.5.1 Seasonality

First we examine how the CO$_2$ mixing ratio and flux change over the course of a year. Figure 4.12 shows the monthly values of $\bar{c}$, $F_c$ and temperature where data is present for at least 30% of the month.

4.5.1.1 CO$_2$ mixing ratio

The CO$_2$ mixing ratio shows a strong seasonal cycle with a maximum in January 2010 of 429 ppmv and a minimum in August 2009 of 385 ppmv. There is also larger variability within the months in winter compared to summer. We will see later that this is largely due to high nighttime variability in the winter. The seasonal cycle is explained primarily by the expected cycle in anthropogenic CO$_2$ emissions. In the winter, where the maximum $\bar{c}$ is observed, we expect maximum emissions from gas burning associated with central heating whereas in the summer little or no emissions due to heating are expected. However using a simple dispersion model Rigby et al. (2008) finds that the predicted seasonal cycle of London’s CO$_2$ emissions cannot alone be responsible for the seasonal cycle in mixing ratio and regional considerations must be made. On a regional scale we would also expect the cycle in biogenic uptake of CO$_2$ to reinforce the anthropogenic emission cycle.

The $\bar{c}$ cycle is similar to that reported by Rigby et al. (2008) measured at Imperial College during 2006 – 2007. A minimum was observed in both studies during August with similar maximum in winter. The mixing ratio was found to be higher in this study by about 3 ppmv at the summer minimum and 20 ppmv at the winter maximum. This can be partially explained by the lower measuring height of 50 m here compared to 87 m. Rigby (2007) measured the difference in mean CO$_2$ mixing ratio due to difference in measurement height to be only about 3 ppmv on average between February and April 2007. Meteorology may also play a strong role in the discrepancy and we have already seen that low wind speeds can produce very high mixing ratios. It is possible that more stable nights during
the winter affected the measured \( \bar{c} \) than in the earlier study, trapping in CO\(_2\) giving higher mixing ratios.

### 4.5.1.2 CO\(_2\) flux

The CO\(_2\) flux follows a similar seasonal pattern to the mixing ratio with lowest values in the summer and highest in the winter. The four lowest months, June – September, with fluxes around 12 \( \mu\)mol m\(^{-2}\) s\(^{-1}\) correspond with the four hottest months. The coldest months, December – February are the months with the largest fluxes of around 29 \( \mu\)mol m\(^{-2}\) s\(^{-1}\). A similar seasonal cycle has been found in other urban CO\(_2\) flux studies including Soegaard and Møller-Jensen (2003) who found a 4:1 winter to summer flux ratio in Copenhagen which was explained by the seasonal cycle of space heating gas use and biogenic CO\(_2\) uptake. Coutts et al. (2007) and Moriwaki and Kanda (2004b) found ratios closer to 2:1 and offered similar explanations of the origin of the seasonality.

The major contributors to \( F_c \) in this study are expected to be traffic and heating with a possible small effect from biogenic uptake although there is little green space in the footprint to the south west from which 60\% of the summertime wind comes. Since the amount of traffic stays relatively constant throughout the year, we attribute the seasonal change in flux to the seasonal pattern of space heating usage. We would expect the amount of space heating to increase as temperature decreases and in Figure 4.13 this relationship is confirmed where weekly mean \( F_c \) is plotted against weekly mean temperature. Below about 15\(^\circ\)C the relationship is approximately linear as found in Florence by Matese et al. (2009). Above this temperature the fluxes are clustered at around 12 \( \mu\)mol m\(^{-2}\) s\(^{-1}\). Soegaard and Møller-Jensen (2003) used 15.5\(^\circ\)C the threshold daily mean temperature below which people were predicted to begin using heating, this values agrees with the observations in this study. Intermittent emissions from heating related CO\(_2\) sources could also explain the increased variance in winter \( F_c \) values.

Where there are data from more than one year for a given month (Jan, Feb, Jun, Jul) the \( F_c \) values are in agreement to within about 10\%. What is perhaps surprising is that the fluxes for Jan and Feb 2010 were lower than 2009 even though the months were colder.
Figure 4.12: Monthly means of $\bar{c}$, $F_c$ and temperature. Bars show standard deviation of half hourly values. Months shown have at least 30% worth of data.
4.5.2 Diurnal cycle

Diurnal cycles of urban CO₂ mixing ratio and flux have been reported by various groups (e.g. Grimmond et al., 2002; Coutts et al., 2007; Idso et al., 2002; Vogt et al., 2006; Sparks and Toumi, 2010) with a variety of shapes and ranges depending on a number of factors including measurement height, surrounding land use type and time of year. Mixing ratio cycles are generally attributed to meteorological factors and flux cycles to anthropogenic activity. Here we present diurnal cycles for both $\overline{c}$ and $F_c$ for each month with sufficient available data.

4.5.2.1 CO₂ mixing ratio

Figure 4.14 shows the monthly diurnal cycle of CO₂ mixing ratio. Each point represents the median of at least 10 hours worth of data and the bars show the range from the 10th to the 90th percentile of half hourly $\overline{c}$ for a given hour in a month. The cycles are very similar to those reported by Rigby et al. (2008) in an earlier study at Imperial College. The summertime diurnal cycle is similar to that reported in Vancouver in July by Reid and Steyn (1997) with an early morning maximum collapsing into a broad afternoon minimum. This is explained by
the growth of the boundary layer through entrainment of clean air after sunrise followed by a gradual accumulation of CO$_2$ in the night into a more stable nocturnal boundary layer. The morning collapse can be seen to shift forward from winter to summer as sun rise begins earlier. Behaviour is more complex in winter months when the cycle of solar radiation reaching the surface and hence mixing induced by surface heating is reduced. This leads to two minima in mixing ratio throughout the day, clearly visible in December here. The first is the afternoon minimum due to enhanced mixing and the second is an early morning which is hypothesised to be related to low nocturnal emissions. Diurnal ranges are largest from March to August with a mean range of 21.8 ppmv compared to a mean of 12.6 ppmv for September to February (not including October where there are no data). This supports the theory that meteorological diurnal cycles are mostly responsible for the mixing ratio diurnal cycle. Also visible in January – April is the source of the large variance observed in the winter values of CO$_2$ mixing ratio in Figure 4.12. These seem to be due largely to relatively infrequent (judging from the skew) morning events with a very large mixing ratio. These may be caused when emission rates increase before sunrise such that turbulent mixing is low and mixing ratios build up quickly.

4.5.2.2 CO$_2$ flux

Figure 4.15 shows the monthly diurnal cycle of CO$_2$ flux. Each point represents the median of at least 10 hours worth of data and the bars show the range from the 10th to the 90th percentile of half hourly $F_c$ for a given hour in a month. Here, because we expect the cycle to be driven by anthropogenic activity, the times have been converted to local times. British Summer Time (BST) is GMT+1 and runs approximately from April to October inclusive.

The shape of the cycle is fairly consistent throughout the year. This supports the idea that the flux is a measurement of anthropogenic CO$_2$ emissions and not strongly affected by meteorology or biogenic activity. While London sleeps, there is a minimum between midnight and 04 h. Then as London wakes up emissions from traffic and heating (in the winter) create a fairly gentle increase of the flux from around 05 h to 09 h. Then we see a broad maximum which continues through
Figure 4.14: Diurnal $\bar{z}$ cycles by month. Each point represents a median of at least 10 hours worth of data with bars showing the 10th to 90th percentile range.
the working day until around 20 h when the flux decreases back to the minimum at midnight. This is similar to the diurnal cycle measured elsewhere in London by Helfter et al. (2011) and those measured in cities such as Basel (Vogt et al., 2006) and Mexico City (Velasco et al., 2005). The magnitude of the cycle is greater in winter with a mean range of $25.3 \mu\text{mol m}^{-2} \text{s}^{-1}$ from November to March compared with $10.0 \mu\text{mol m}^{-2} \text{s}^{-1}$ from June to September. The cycle in the summertime is expected to be dominated by traffic as little or no heating use is predicted. No significant peak due to rush hours are seen as in Coutts et al. (2007) but this is not a surprise. Figure 4.16 shows traffic counts at Marylebone Road which is approximately 3 km to the north east of Imperial College. Helfter et al. (2011) report that traffic counts at Marylebone Road correlate well with other central London counts and it may be used as a good proxy for central London traffic. The London rush hour lasts all day long from 07 h until 20 h, which agrees with the measured $F_c$ cycle here. Since the traffic density is not strongly seasonal (about 10% difference between maximum and minimum monthly mean counts) we assume that gas burning for heating or otherwise accounts for the seasonal change in the diurnal $F_c$ cycle range as well as the seasonal change in the mean $F_c$.

4.5.3 Weekend effect

Since the CO$_2$ flux is driven by anthropogenic activity and humans follow a weekly routine, it is reasonable to look for a weekly pattern in the CO$_2$ flux. As we also believe the mixing ratio is affected by the local emission to an extent it is possible there will be an effect here too. Further to this some studies have measured an anthropogenic heat flux in cities so there could potentially be a ’weekend effect’ in the sensible heat flux, $Q_H$, measured here.

Figure 4.17 compares the annual, daytime (10 – 17 h) means and standard deviations of $F_c$, $\bar{\epsilon}$ and $Q_H$ for each day of the week. The clearest pattern is in the CO$_2$ flux with highest values in the middle of the working week and lowest values at the weekend, approximately 20% lower than weekday values. The mixing ratio displays less clear behaviour with variation of only a few percent and a surprisingly low Friday mean. However, Sunday has the lowest mixing ratio although it
Figure 4.15: Diurnal $F_\alpha$ cycles by month. Each point represents a median of at least 10 hours worth of data with bars showing the 10th to 90th percentile range. Time has been converted to local time.
Figure 4.16: Diurnal cycle of traffic activity at Marylebone Road (www.airquality.co.uk).
is uncertain whether this is significant at this stage. The $Q_H$ doesn’t not display a clear weekly pattern at all although Sunday has the lowest mean $Q_H$.

4.5.3.1 CO$_2$ flux

We analyse the weekend effect on $F_e$ in more detail in Figure 4.18 which compares the weekday and weekend mean diurnal cycles in winter and summer. It is clear that there is a week to weekend difference in both the summer and winter that is significant during the day between around 5 h to 19 h. Outside of these hours there is no weekend effect. On average, in the winter the week day flux is 29% greater than the weekend flux, equivalent to a mean difference of 6.6 µmol m$^{-2}$ s$^{-1}$. This compares to the summer when the week day flux is 39% bigger than the winter flux, a difference of 3.9 µmol m$^{-2}$ s$^{-1}$. The weekend effect ratios observed here are larger than that reported in Mexico City by Velasco et al. (2005), presumably because of differences in the surrounding land use types. Coutts et al. (2007) find a similar weekend effect ratio but do not report any variation of this with season.

The week to weekend difference in traffic counts on the Marylebone road is only about 5% so this can only explain part of the effect. It is possible that the weekly cycle of traffic density is larger in the area immediately surround the college. Another signal which could have a strong diurnal and weekly cycle is human exhalation of CO$_2$ which Moriwaki and Kanda (2004b) predict to contribute 38% and 17% to summer and winter CO$_2$ fluxes respectively in a residential area of Tokyo with a similar population density to the area surrounding Imperial College. In winter the larger weekly cycle is assumed to be mainly due to more space heating being used during the week in local buildings.

4.5.3.2 CO$_2$ mixing ratio

The weekend effect is much smaller in the mixing ratio compared to the flux. With a mean week to weekend difference of 0.5 and 2.6 ppmv in the summer and winter respectively. This effect is much smaller than that measured in Rome by Gratano and Varone (2005) when a weekend effect of 30 – 90 ppmv was observed depending on proximity to the city centre but at a height of 2 m. At that height, much closer to most sources of CO$_2$, a more direct effect between mixing ratio and
emissions is expected. The larger effect in winter can be explained by two factors: The weekend effect on emissions is larger in the winter according to the measured fluxes. Less mixing in the winter due to reduced boundary layer depths would amplify this effect. These explanations are borne out by the diurnal cycles (Figure 4.19) which show that the biggest weekend effects occur in the morning between the time when the week day flux begins to increase above its base level after 04 h and before the mixing ratio collapses after sunrise as the boundary layer depth increases. This time interval is largest in winter so we see the biggest weekend effect here.

4.5.3.3 Sensible heat flux

Finally we can look at the sensible heat flux. Offerle et al. (2005) determine the anthropogenic heat flux, that is the heat energy generated by human activity, using energy balance closure methods in a downtown area of a Polish city. They find that in the winter this value is 32 W m\(^{-2}\) but in the summer it is close to 0 with the difference due to building heating used in during the winter. Although we do not have the data required for energy balance closure methods, we believe that heating usage has a weekly cycle which may therefore also be apparent in the sensible heat flux. Figure 4.20 shows the week day and Sunday diurnal cycles of \(Q_H\) for winter and summer. In summer when no heating use is expected the weekend effect is almost non-existent but in the winter the Sunday heat flux is clearly lower than the weekday for the whole day with largest differences during the working day. The mean winter difference between weekdays and Sunday was 15.6 W m\(^{-2}\), approximately half of the total measured by Offerle et al. (2005).

4.6 Comparison with inventory estimates

We can compare our measured CO\(_2\) flux data with the inventory based emission predictions discussed in §1.4 after making a few important considerations.

1. The emission predictions given by the inventories are based on annual figures. Care must be taken that the measured flux value used for comparison is representative of an annual mean with no seasonal, weekly or diurnal bias.
Figure 4.17: Daytime (10 - 17 h) $F_c$, $\overline{c}$ and $Q_H$ and traffic count against day of the week. Bars show plus and minus one standard deviation of half hourly values (hourly for traffic count).
Figure 4.18: Diurnal $F_c$ by day of week for winter and summer. Bars show the 10th - 90th percentile range.
Figure 4.19: Diurnal $\bar{e}$ by day of week for winter and summer. Bars show the 10th - 90th percentile range.
Figure 4.20: Diurnal $Q_H$ by day of week for winter and summer. Bars show the 10th - 90th percentile range.
2. The calculated footprint of the flux values measured in this study indicates that 80% of contributions to the measured flux come from within around 800 m with the maximum contribution from a distance of just under 100 m. Hence, the area sampled here does not match up exactly with the 1 km × 1 km square used by the NAEI and LAEI (which is fortunately almost centred on Imperial College). Further to this the footprint is biased toward the south westerly prevailing wind, especially in the summer. This could further bias the measured flux from the true mean for the inventory square although the directional analysis in §4.4 revealed the flux was similar across all directions outside the sector containing plume effects.

3. The ‘point sources’ contribution to the inventories should be excluded from the comparison. These are likely to be large sources emitted from stacks at high elevation from the local museums and are hence not suited to measurement using eddy covariance techniques. This is particularly significant in the case of the NAEI in which point sources make up 34.1% of the total emission prediction compared to only 6.1% in the LAEI.

To address point 1. we note that there are a similar number of data points from each day of the week and from each hour of the day. However there is an uneven distribution of data across the months of the year with more data from winter months and no data from October. To even this out we simply take the mean of the individual monthly means where the value for October has been linearly interpolated from the months either side. This crude gap filling gives us an annual mean of 19.69 $\mu$mol m$^{-2}$ s$^{-1}$, slightly lower than the unfilled mean of 20.40 $\mu$mol m$^{-2}$ s$^{-1}$. This compares to values of 31.6 $\mu$mol m$^{-2}$ s$^{-1}$ and 22.6 $\mu$mol m$^{-2}$ s$^{-1}$ from the NAEI and LAEI with their point source contributions excluded. Our measurement is agrees well with the LAEI estimate to within 13% but is 38% smaller than the NAEI estimate.

4.7 Summary

This chapter examined the CO$_2$ climatology. The atmospheric stability, which is an important factor in calculating the flux footprint, was analysed and found
to be unstable for 80% of the half hour periods measure. It was almost never stable. This is compatible with other city centre observation. The flux footprint was relatively small with 80% of the contributions to the measured flux originating within 700 - 800 m. The mixing ratio at the site was similar to the previous study at this site by Rigby et al. (2008). The largest mixing ratios were observed at nights and during the winter, this was attributed to seasonal and diurnal patterns in mixing layer height and CO$_2$ emissions. The CO$_2$ flux was shown to have a strong seasonal cycle with winter fluxes about 2.5 greater than summer fluxes. This was attributed to increased space heating use in buildings in the winter. The flux also had a clear diurnal cycle which reflected traffic activity and heating usage and was therefore stronger in the winter. The measured CO$_2$ flux was 39% higher during the week than the weekend in the summer. This effect was 10% smaller in the winter. We also note a small but significant weekly cycle in the sensible heat flux attributed to space heating and human activity. The emission estimates for the square kilometre surrounding the measurement site from the NAEI and LAEI were compared to the measured flux and found to be 38% and 13% smaller respectively. Point source contributions to the emission estimates were excluded before comparison.
Chapter 5

Analysis of the Imperial College power station emission plume

5.1 Introduction

Large, near-field, elevated point sources of CO\textsubscript{2} and other pollutants (e.g. power plant emission stacks) are not suited to eddy covariance measurements. Signals from these sources are usually filtered out before eddy covariance processing takes place so there is little knowledge of the potential effect of these sources on an eddy covariance measurement. Furthermore, there are no detailed studies of CO\textsubscript{2} plumes that we can find in the literature. Harrison and McCartney (1980) test the performance of a simple Gaussian plume dispersion model against data collected from a NO\textsubscript{x} plume from a nitric acid works and Weil and Jepsen (1977) compare a similar model to data from a power plant stack emitting SO\textsubscript{2}. Fluctuations around the ensemble means predicted by Gaussian plume models have been the focus of work beginning with Gifford (1959) who derived a model for a meandering Gaussian plume. In Yee et al. (1994), fine-scale internal structure due to turbulent mixing is incorporated into a meandering plume model to predict concentration probability density functions. The effect of averaging time on pollutant concentration from an intermittent plume has been examined in Sykes (1984) and Venkatram (2002) where the variance in concentration is linked by a power law with exponent -0.5 to the averaging time indicating random white noise.
noise fluctuations. Garger et al. (1994) measured radionuclide concentration in the air near Chernobyl and found a similar power law with exponent -0.33 over longer time periods suggesting long-range correlations. Peak concentrations at very short time scales are traditionally important in the regulation of odours from industrial sources because a high concentration of pollutant for a short duration (one breath) causes complaints even if the mean concentration over, say, 1 hour is negligible. In this field, a simple power law is often used to convert from model ensemble means to short timescale peaks with a time exponent of 0.17 to 0.68 (Nicell, 2009). Studies of plumes from industrial sources usually focus on NOx or SO2 because these are high priority pollutants for regulation and because the background concentration is very small. The relatively high background levels of CO2 can mask emission plumes making traditional methods (long-range, low frequency, ground-based measurements) of emission detection and attribution unfeasible. Here we present a detailed study of a CO2 plume. We find that fast sampling can allow coherent plume structures to be attributed quantitatively to the local power station.

### 5.2 Directional analysis

To identify point sources it is useful to perform directional analysis. $F_c$ is shown as a function of wind direction in Figure 5.1. We see a trough in the CO2 flux between 0° and 135° which was previously discussed in §4.4. In this chapter we aim to demonstrate that the negative flux in this trough is the result of a CO2 rich plume from the power station emission stack passing above the measurement point. Also plotted in Figure 5.1 are the half-hourly maximum mixing ratios, $c_{\text{max}}$, calculated using the data sampled at 20 Hz. Coinciding with the flux trough is a peak in $c_{\text{max}}$ with a value of 550 ppmv against a background of just over 400 ppmv. The variance around the mean is also much larger in this peak compared to background levels from other wind directions suggesting a possible intermittency of sources or conditions from the ENE direction. The mean concentration displays no obvious peak at the ENE direction and remains within one standard deviation of its natural variability from all wind directions. This is consistent with the prediction from the basic Gaussian plume modelling of only a 10 ppmv increase due to the plume at
Figure 5.1: Mean directional plots of CO₂ flux, maximum CO₂ mixing ratio and mean CO₂ mixing ratio. The dotted lines represent ±1 standard deviation of half-hourly values. Analysis performed using data set A from Table 3.2.
Figure 5.2: Mean half-hourly CO₂ mixing ratio percentiles against direction. Data set A from Table 3.2 was used.
its centre. This large difference in behaviour between \( c_{\text{max}} \) and \( \bar{c} \) in the ENE wind direction suggests that the anomaly in this direction is caused by high-frequency variation in the CO\(_2\) mixing ratio.

To examine this further a range of percentiles of CO\(_2\) mixing ratio data sampled at 20 Hz for each half-hour data period are plotted against wind direction in Figure 5.2. The peak is visible in the maximum through to the 99th percentile. Below this the signal is lost in background variation. The top 1 percentile of data corresponds to just 18 seconds worth of data per half-hour period so a sampling rate in the order of seconds at the very least is required to observe this phenomenon.

We attribute the ENE anomalies in CO\(_2\) flux and peak mixing ratio to emissions from the local power plant. The direction of the observed peak signal in \( c_{\text{max}} \) and \( F_c \) is at 68°. This is offset from the geometric direction of the stack, 86°, by 18°. An offset of this magnitude could be explained by local wind field distortion due to structures around the measurement point or by building wake effects near the source of the emissions (see §2.1.1).

### 5.3 Spatial and temporal analysis of plume

Further spatial analysis of the plume from the power plant stack was performed on a set of plume events. A half-hour period was selected as a plume event if: (a) the mean wind direction was within 25 degrees of the centre of the observed directional peak in \( c_{\text{max}} \), and (b) \( c_{\text{max}} \) was above 600 ppmv. To remove the background CO\(_2\), \( \bar{c} \) was subtracted from the instantaneous CO\(_2\) mixing ratio time series for each event period giving a time series of anomalies, \( c_{\text{anom}} \), which was then binned according to instantaneous wind direction, \( \theta \). The 95th percentile \( c_{\text{anom}} \) from each direction bin was extracted to create a mean profile of the plume. This process was performed on three subsets of these plume event data divided according to mean wind speed, \( U \), as described in Figure 5.3. The wind speed classes were chosen such that there were an equal number of events in each subset. In total there were 314 half-hour plume events by the above definition. A Gaussian function with a quadratic background with the following formula was fitted to the data for each case:

\[
y = A_0 \exp(-((\theta - x_0)^2/2w^2)) + A_1 + A_2\theta + A_3\theta^2, \tag{5.1}
\]
where $A_0$ is the Gaussian amplitude, $x_0$ is the centre direction, $w$ is the width parameter and $A_1$, $A_2$ and $A_3$ are the background quadratic coefficients. The results of the above process are displayed in Figure 5.3 and the parameters for the Gaussian fit are recorded in Table 5.1. The 95th percentile was chosen as a compromise between signal strength and noise. All of the fit parameters are sensitive to this choice. The plots show that the ensemble mean plume has an approximately Gaussian horizontal profile indicating that some form of the Gaussian plume model may be applicable to plumes of this type at this range. The reduced $\chi^2$ fitting statistic suggests the plume is more Gaussian at lower wind speeds although this could be due to effects of background CO$_2$ on the fit. We also see that the plume is significantly wider at low wind speeds with a width parameter, $w$, of 20.7$^\circ$ compared to 14.1$^\circ$ and 14.7$^\circ$ at medium and high wind speeds respectively. At lower wind speeds the standard deviation of wind direction is typically higher enhancing horizontal spread of the plume. We also notice that the centre of the plume, $x_0$, shifts systematically closer to 86$^\circ$, the geometric direction of the stack, as wind speed increases. Hence, wake effects and other wind field distortions have a stronger effect on the measured centre direction of the plume at lower wind speeds.

Using the same plume event data sets as above, simple moving averaging with a range of periods, $\tau_{av}$ (corresponding to 20$\tau_{av}$ data points), was applied to the CO$_2$ mixing ratio time series. The maximum anomaly, $c_{max} - \bar{c}$ is defined as $c_{amax}$. Figure 5.4 plots $c_{amax}$ against $\tau_{av}$ for the low, medium and high U data sets. The data are fitted with a regression line with formula $y = Ax^\alpha$. The fit coefficient $\alpha$ along with uncertainty is included in Table 5.1. The plots show that a power law is a good approximation of the relationship and $\alpha$ is similar for the low and medium wind speed sets but significantly different for the high wind speed category. This could indicate a different level of mixing having occurred in the plume at the point of measurement for high wind speeds. The time exponent, $\alpha$, is similar to that of -0.5 in Venkatram (2002) relating averaging time to standard deviation of concentration which is generated using a simple model of plume intermittency. A power law is also used to estimate peak concentrations at short timescales from model mean predictions in odour impact regulation (see Nicell, 2009) with exponents ranging from -0.2 to -0.7. The value of around -0.5 from our observational study
Figure 5.3: Gaussian fits to 95th percentiles of plume events $c_{anom}$ data. Low, medium and high wind speeds, $U$, refer to three wind speed categories: $U < U_1$, $U_1 \leq U < U_2$ and, $U > U_2$, where $U_1 = 2.7$ m s$^{-1}$ and $U_2 = 4.2$ m s$^{-1}$. Fit parameters are recorded in Table 5.1.

is consistent with this. The data show that at high wind speed the dispersion generates an effectively uncorrelated random time series, but at lower wind speeds the exponent is slightly less than -0.5 suggesting some weak long-range correlations.

<table>
<thead>
<tr>
<th></th>
<th>Low U</th>
<th>Med U</th>
<th>High U</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2$</td>
<td>1.77</td>
<td>2.93</td>
<td>4.57</td>
</tr>
<tr>
<td>$A_0$</td>
<td>41.7±1.7</td>
<td>31.9±1.2</td>
<td>38.9±1.56</td>
</tr>
<tr>
<td>$x_0$</td>
<td>68.6±0.35</td>
<td>73.4±0.42</td>
<td>76.1±0.45</td>
</tr>
<tr>
<td>$w$</td>
<td>20.7±0.75</td>
<td>14.1±0.64</td>
<td>14.7±0.71</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>-0.452±0.018</td>
<td>-0.435±0.015</td>
<td>-0.515±0.018</td>
</tr>
<tr>
<td>$N$</td>
<td>104</td>
<td>104</td>
<td>106</td>
</tr>
</tbody>
</table>

Table 5.1: Fit parameters for Figures 5.3 and 5.4 where $A_0$ is the Gaussian amplitude (ppmv), $x_0$ is the centre direction ($^\circ$), $w$ is the width parameter ($^\circ$). $\alpha$ is the power index from fitted lines in Figure 5.4. $N$ is the number of plume events in each wind speed class.
Using the previously described sets of plume event data grouped according to wind speed we examine the nature of the individual pulses of CO$_2$ rich air contributing to the results so far presented. For each 30 minute event the time series of $c_{anom}$ was first normalised such that its maximum value is 1. Then by centreing each series in the set on the maximum value of normalised $c_{anom}$ and averaging across events we produced a mean ensemble pulse for each set. We also converted the time series to spatial information using Taylor's hypothesis and the wind speed data and plot the spatial pulses separately. These are shown in Figure 5.5. The time-based pulses show that at low wind speed the pulse has a longer duration, consistent with a parcel of high CO$_2$ air moving past the sensor slowly. Conversely at high wind speeds the pulse is narrower. When converted to spatial data the differences are eliminated showing that the parcels of air generating these pulses are of similar spatial size in all three wind conditions. The mean spatial pulse shape is well described by a Lorentzian function, $y = (a^2b)/(x^2 + a^2) + c$, where $a$ is the half-width half-height of the pulse, $b$ is a vertical scaling parameter.
Figure 5.5: Mean normalised half-hourly maximum pulses in three different wind speed categories. Dashed line - low U, dotted line, medium U, solid line - high U. The left plot shows time series data, the right plot shows the time series data converted to spatial data. The dash-dot line in the spatial plot is a fitted Lorentzian function as described in the text.

ter and $c$ provides a zero-offset. The fitted values of $a$ and $b$ were 2.83 and 0.77 respectively and $c$ was fixed at 0.1.

## 5.5 Measured CO$_2$ and local power station gas consumption

The Imperial College power plant provided a record of the volume of natural gas used by the plant per half hour, $V$, for the period from 5/6/2008 to 21/09/2009. This corresponds to data subset E in Table 3.2 which was used in this section’s analysis. Although the gas consumed by the power station is burnt in both boilers and engines with different combustion profiles, these data can be used as a proxy for the total rate of CO$_2$ emission from the plant stack. Figures 5.6 and 5.7 show the seasonal and diurnal pattern in the power station gas usage. On these plots each point represents a half hour gas usage reading. The precision of the measurement system was increased in May 2009 which explains the difference in the data from
this point in the seasonal plot. In the diurnal plot small random values were added to each point to help show the distribution of gas usage throughout the day. It can be seen that the operating baseline increases in the Winter responding to heating demands of the college. The biggest variability however is on the hourly scale as the plant responds to requests for power from different college departments throughout the day. From around 08 h until 22 h the power station is sometimes operating at approximately 3 times its base level while outside these hours this activity is rare. Figure 5.8 is a histogram of the gas usage and shows a relatively high number of 'low' cases between 0 and 500 m$^3$ per half hour and a smaller peak in high usage cases between 1000 and 1500 m$^3$ per half hour. There is however a lack of cases falling between these extremes.

Measured CO$_2$ data can now be compared to power plant gas usage data on a half-hourly basis to examine the link between plant CO$_2$ emissions and CO$_2$ at the measurement site. Figure 5.9 plots the measured CO$_2$ flux, $F_c$, against the
Figure 5.7: Power station gas usage, $V$, against time of day. Frequency relates to half hour periods.
volumetric rate of gas consumption at the plant, \( V \). The data shown are filtered such that only periods with mean wind directions within a 15° sector centred on the peak maximum from Figure 5.2 are used. A line of form \( y = bx + a \) was fitted with the fit parameters shown in the figure. There is a correlation between the two with higher gas usage giving larger absolute values of \( F_c \). This is especially clear when \( F_c \) is negative although also appears to hold when positive. This can be explained by the fact that eddy diffusion will tend to transport \( \text{CO}_2 \) away from the centre of the plume as it travels. If the centre of the plume is above the measurement point then the flux due to the plume will be downwards and negative. If the plume centre is below the measurement point the opposite will apply. We therefore expect the sign and magnitude of the flux contribution due to the plume to be dependant on the plume height as it reaches the measurement point. As the measurement point and plume emission point are at approximately the same height we would expect the plume usually to pass above the measurement point due to the plume buoyancy and momentum. However the complex terrain and subsequent flow distortions mean this may well not always be the case and could explain why
Figure 5.9: Half hourly $F_C$ against power station gas usage, $V$. Only periods with mean wind direction within 15° of measured plume centre are included. Data subset E from Table 3.2 was used.
Figure 5.10: Half hourly $c_{\text{amax}}$ against power station gas usage, $V$. Only periods with mean wind direction within 15° of measured plume centre are included. Data subset E from Table 3.2 was used.
Figure 5.11: Conceptual diagram showing how an expanding plume leads to negative flux at measurement point. The plume begins at the emission point on building A. By the time the plume reaches 1. it has stopped rising due to its buoyancy and initial momentum but is still has a relatively narrow concentration profile. As the plume passes from 1. to 2. its centre line is horizontal but there is a net flux away from the centre line as the plume expands and the concentration profile becomes wider. Hence, at the measurement point on building B, below the plume centre line, there is a downwards flux.

we see a correlations with positive fluxes as well as negative. No correlation was found between $V$ and the maximum or mean temperature measured by the sonic anemometer during plume events. As no thermal signal of the plume was detected we assume the plume has cooled to ambient temperatures by the time it reaches the measurement point and thus is no longer buoyant or rising. This is consistent with the plume generating negative fluxes below its centre line. Figure 5.11 is a conceptual diagram showing how a growing plume above the measurement point leads to negative fluxes.

Given that we have identified that the directional flux trough coincides with a peak in $c_{max}$ we can also look for a correlation here. In Figure 5.10 we plot $c_{amax}$ against $V$ for the same directional range as above. Here the clear positive correlation is more convincing than with the CO$_2$ flux. One reason for this is that the sign of the expected contribution from the plume to $c_{amax}$ is not dependant on the plume’s height relative to the measurement point as with the flux. However the magnitude of this component would still be related to the plume height. As we
have no reliable means of calculating this we try wind speed as a proxy for plume height.

Figure 5.12 plots $c_{amax}$ against $V$ for a sample range of wind speeds (4.8 – 5.3 m s$^{-1}$). Again we see the positive correlation. A lack of data at moderate levels of $V$ prevents confirmation of the full nature of this relationship. Here, we assume it to be linear and fit a straight line with gradient $S$.

We can then examine the wind speed dependence of the measured CO$_2$ gas consumption relationship. The above analysis was performed on the data divided into six different ranges of wind speed such that there was an approximately equal number of data points in each set. The gradients of the fit, $S$, which is the sensitivity of $c_{amax}$ to $V$, for each set are presented in Figure 5.13 with vertical bars showing the uncertainty in $S$ and the horizontal bars showing the range of wind speeds in each data set. At wind speeds below 2 m s$^{-1}$ $S$ is close to zero. Above this $S$ increases until it reaches a maximum at around 4.5 m s$^{-1}$ and then decreases to half maximum for wind speeds above 6.5 m s$^{-1}$. The increase from 0 to maximum can be explained by considering that the plume will tend to have risen less by the time it travels over the measurement point in stronger winds. At very low wind speeds, in the time taken for the plume to travel the 190 m horizontal distance to the measurement point, its centre will have risen, due to its buoyancy and momentum, to well above its starting height such that the plume is not observed in the measured data. However as the wind speed increases above 2 m s$^{-1}$, the plume has less time to rise so its centre is closer to the measurement height when it passes overhead and hence we begin to measure the plume. When the wind speed is above 5 m s$^{-1}$ another mechanism begins to decrease the observed sensitivity of $c_{amax}$ to $V$. This could be explained by increased mechanical mixing caused by higher wind speeds which enhances the dilution of the high CO$_2$ mixing ratio pulses measured as $c_{max}$. Similar relationships can be found between $F_c$ and $V$ although the scatter is significantly larger and the dependence of $S$ on wind speed is less clear.

Plume model dispersion parameters are usually highly dependent on atmospheric stability but in this case the relationship found between $S$ and atmospheric stability determined by $(z_m - z_d)/L$ was less clear than with wind speed (not shown). This is probably because only a limited range of stability conditions
Figure 5.12: Response of half hourly CO₂ mixing ratio maximum to power station gas use at wind speeds of 4.8 – 5.3 m s⁻¹. Wind direction within 15° of plume centre. S is the gradient of the best fit line. Data subset E from Table 3.2 was used.
were sampled. Almost all periods had a negative value of \( (z_m - z_d)/L \), so almost no examples of stable conditions were sampled.

5.6 Summary

The plume from the imperial college power station emission stack was analysed in detail in this chapter. The CO\(_2\) flux was found to be significantly reduced in data from the sector influenced by the plume. Data from this direction was therefore excluded from the CO\(_2\) climatology analysis. The negative signal in the flux was hypothesised to be due to short-lived puffs of CO\(_2\) from the stack passing above the measuring site. There was no significant deviation of the mean CO\(_2\) mixing ratio in the direction of the plume, only in high percentiles of the instantaneous CO\(_2\) mixing ratio measured high frequency. The plume concentration profile was approximately Gaussian when looking at the 95th percentile of instantaneous CO\(_2\) mixing ratio against wind direction. The maximum CO\(_2\) mixing ratio during a plume event was related to the averaging time by a simple power law whose exponent was dependent on the wind speed. The shape of the CO\(_2\) pulses measured during plume events was analysed and found to be approximately Lorentzian on average. Half-hourly power station gas usage data were obtained and correlated well with maximum CO\(_2\) mixing ratio when the wind direction was from the direction of the power station. The correlation was best at moderate wind speeds.
Figure 5.13: Relationship of $S$ to wind speed with vertical bars showing uncertainty in $S$ and horizontal bars showing range of $U$. Analysis performed using data subset E from Table 3.2.
Chapter 6
Plume modelling

6.1 Introduction

The previous chapter shows us that even when the mean concentration of pollutant due to a continuous point source is very small relative to background fluctuations, measured large deviations from this mean can be used to profile the plume. This was shown to be important to eddy covariance calculations which were strongly affected by the presence of the plume. It would therefore be useful to have some understanding of the spatial scale and distribution of the large concentration deviations and how these relate to the more frequently calculated mean concentration profile.

In this chapter the results of a simple one-dimensional, numerical model of a plume developing from a small source in heterogeneous turbulent conditions are analysed and compared to various predictions from plume dispersion theory. We also use this model to make predictions about the structure and shape of high concentration percentile plumes as measured in the previous chapter.
6.2 Method

6.2.1 Model overview

The Kerstein (1988) Linear Eddy Model (LEM) was used to examine the development of a plume from a near-field point source. It uses a combination of random, discreet eddy “events” and deterministic molecular diffusion to model turbulent transport and mixing. The ”linear” in the title refers the fact that the model is one-dimensional. The LEM has previously been used in a wide variety of applications with earlier work focusing on the turbulent mixing in a combustion chamber (Desjardin and Frankel, 1996) through to some later work on turbulent flames in a supernova (Woosley et al., 2009). This model was chosen because due to its simplicity it is much less computationally intensive than direct numerical simulation or large eddy simulation. This makes it relatively quick and easy to create a large enough ensemble of model runs from which to extract meaningful statistics as is required in the present case. It should be made clear that this model has some notable limitations. Being one dimensional, it cannot account for the effect of any roughness elements. Nor does it, in the form presented here, allow for any variability in diffusivity with height or stability as would be encountered in the atmosphere.

The basic operating principle of the model is as follows: a one-dimensional array, representing one dimension in space, is initialised with values which represent the concentration of a passive, scalar tracer at a point in space; Successive operations which represent eddies shuffle the array while an operation representing molecular diffusion smoothes the array; after a fixed number of operations, linked to a duration of time, the array reaches its final state.

6.2.2 Eddy event implementation

In this model eddies are represented by a discrete, instantaneous remapping of the concentration array onto itself. Three variables control each event. The duration of the event (technically the time until the next event as the remapping itself is instantaneous), the location of the eddy and the size of the section of the array affected by the eddy.
The location of the eddy, $x_0$, is simply chosen as a random position on the array modelling a homogenous turbulence field. The size of the eddy, $l$, is chosen according to a probability distribution $f(l)$ which is designed to replicate the Kolmogorov power spectrum across the inertial range from the Kolmogorov length scale, $L_K$, to the inertial length scale, $L_I$. The two lengths effectively provide lower and upper bounds respectively of the sizes of eddies represented in the model. The eddy size probability density function is given by,

$$f(l) = \frac{5}{3} \frac{l^{-8/3}}{L_K^{-5/3} - L_I^{-5/3}}.$$  \hspace{1cm} (6.1)

See Kerstein (1991) for more details and derivations of formulae used in this section. If we then introduce a diffusivity term, $D_E$, which is attributable to all eddy sizes in the modelled range the eddy event rate per length, $\lambda$, is:

$$\lambda = \frac{54}{5} \frac{D_E}{L_i^3} \frac{(L_i/L_K)^{5/3} - 1}{1 - (L_K/L_I)^{4/3}}.$$  \hspace{1cm} (6.2)

The ‘duration’ of each eddy is then determined by a Poisson process with rate $\lambda X$ where $X$ is the domain size. After the ‘duration’ of the eddy event has passed the next eddy event occurs. $\lambda X$ therefore controls the frequency of eddy events.

### 6.2.2.1 Eddy mapping

Each eddy event is a remapping of a portion of the domain onto itself. The mapping used here is the triplet map used in Kerstein (1991) amongst others. This
mapping is designed to reproduce the effect of an eddy on a concentration field as shown in Figure 6.1. Figure 6.2 shows the effect of the triplet map acting on a linear concentration profile schematically. It acts by compressing the scalar field of the chosen section by three. The compressed segment is then copied three times onto the original section with the middle section reversed. The concentration gradient is therefore tripled without introducing any discontinuities into the concentration field. Figure 6.3 shows how an eddy of size $l$ acts on a colour array.

This mapping can be expressed formally by the transform from $c(x)$ to $\hat{c}(x)$ which represents an eddy of size $l$ acting on the segment $[x_0, x_0 + l]$:

$$
\hat{c}(x) = \begin{cases} 
  c(3x - 2x_0) & x_0 \leq x \leq x_0 + \frac{1}{3}l \\
  c(-3x + 4x_0 + 2l) & x_0 + \frac{1}{3}l \leq x \leq x_0 + \frac{2}{3}l \\
  c(3x - 2x_0 - 2l) & x_0 + \frac{2}{3}l \leq x \leq x_0 + l \\
  c(x) & \text{otherwise.}
\end{cases}
$$

This map can be discretised as a simple reordering of $3k$ array elements where $k \geq 2$. One consequence of this is that the resolution of the model must be high.
enough such that the smallest eddy size to be represented must correspond to at least 6 array elements.

### 6.2.3 Molecular diffusion implementation

The equation governing changes in a one-dimensional concentration field due to diffusion, given by Fick’s second law is,

$$
\frac{\partial c}{\partial t} = D_M \frac{\partial^2 c}{\partial x^2},
$$

(6.3)

where \(c\) is concentration, \(t\) is time, \(x\) is distance, and \(D_M\) is the molecular diffusion coefficient or diffusivity.

This equation can be discretized using a second-order, central differencing scheme to give,

$$
c_{t+\delta t,x} = c_{t,x} + D_M \frac{\delta t}{(\delta x)^2} (c_{t,x-\delta x} - 2c_{t,x} + c_{t,x+\delta x}),
$$

(6.4)

where \(c_{t,x}\) is the concentration at time \(t\) at distance \(x\). This equation can be iterated to evolve the concentration field in time steps, \(\delta t\) on a fixed grid of separation \(\delta x\). The time step must be chosen such that the inequality,

$$
D_M \frac{\delta t}{(\delta x)^2} \leq \frac{1}{3} c_{\text{max}},
$$

(6.5)

where \(c_{\text{max}}\) is the current maximum concentration, is satisfied to ensure the iteration is convergent.

The diffusion algorithm could theoretically be applied after every eddy event but the typical eddy event frequency would make this very computationally inefficient. Molecular diffusion can therefore be applied after a fixed amount of time or number of eddy events.

### 6.2.4 Model operation

#### 6.2.4.1 Initial conditions

The model requires an initial concentration profile to act upon. In this study we used a top hat function of height 1 and half-width 1 m positioned at the centre...
of the space domain as shown in Figure 6.4. This approximates the normalised horizontal concentration profile of a scalar contaminant at the point of emission from an effective point source. The top hat is required to have a finite width rather than a dimensionless point in order to provide enough array elements with non-zero initial concentrations. 1 m is of the order of the typical initial plume width from the Imperial College power station stack and the diffusion times used in this study are such that the typical plume width becomes much greater than 1 m so the source can be effectively thought of as a point. The sensitivity to the top hat half-width was tested using a range of values from 0.5 m to 2 m and was found not to affect the mean concentration profiles generated once the width had grown beyond a few metres. Sensitivity to the shape of the initial concentration function was also tested. A Gaussian and a triangular starting profile were found once again not to affect mean concentration profiles once the width was bigger than a few metres with all acting similarly as an effective point source.

6.2.4.2 Boundary conditions

The boundary conditions used in this experiment were simple. Beyond the domain of the model all concentrations were fixed at zero. This meant that it was theo-
retically possible to 'lose' non-zero elements by a large enough eddy acting near the edge of the domain mixing scalar elements out of the domain. Therefore the domain was required to be large enough to keep this loss to a minimum. This loss was monitored and if it exceeded 1% the domain was extended. This approach was preferable to 'keeping in' all of the scalar, for example, by not letting eddies transfer out non-zero elements, as this could create artificial effects on the tails of the concentration profile.

Note that the initial and boundary conditions used here are very different from those used in previous work using this model (e.g. Kerstein, 1991, 1992). In those studies the initial concentration field was linear with distance and the boundary conditions were periodic. This difference is due to the proposed application in this study.

6.2.4.3 Model parameters

Since we were interested in modelling the evolution of an atmospheric boundary layer scalar plume the initial model parameters were chosen to reflect this. A typical boundary layer value for the smallest eddy scale, $L_K$, is around 0.001 m. $L_L$ can be taken as the approximate height of the boundary layer, say, 1 km. However the size and resolution required to capture the effect of eddies on all these scales made running the model prohibitively slow. Hence the initial results presented are for $L_L$ limited to 150 m and $L_K$ to 0.03 m. The spatial resolution of the array was therefore $6/0.3 \text{ m} = 200 \text{ m}^{-1}$ (see §6.2.2.1). The eddy diffusivity, $D_E$, was fixed at 1 m$^2$ s$^{-1}$, a typical atmospheric boundary layer value (Garratt, 1994). In the atmosphere the eddy diffusivity tends to increase with height and atmospheric instability. Different eddy diffusivity value are not examined in this study. Molecular diffusivity, when used, was set to $1.5 \times 10^{-5}$ m$^2$ s$^{-1}$.
6.3 Results

6.3.1 Individual model runs

We first present some examples of individual runs of the model with some qualitative analysis. Figure 6.5 shows the resultant concentration field after a simulation time $t = 1080$ s with the above described parameters and initial and boundary conditions and with the molecular diffusion algorithm enabled. The simulation time was chosen to allow the plume to grow well beyond the finite size of the initial top hat distribution so no effects observed are due to this. The plume width according to gradient transfer theory at this time is 46 m from Equation 1.16. The model run took approximately 40 minutes to complete. The profile is visibly irregular and asymmetrical. This is to be expected as instantaneous plume concentration profiles do not tend to be smooth regular functions, Gaussian or otherwise. The profile displays variability up to the scale of approximately $L_d = 150$ m representing the action of the largest eddies. Figure 6.6 shows a close-up detail of the same run. It reveals variations down to around the scale of $L_K = 0.03$ m.

It is clear that in order to examine mean profiles using this model a large ensemble is necessary. However, at 40 minutes per run this would be very time consuming, taking around 1 month to generate an ensemble of 1000. Figures 6.7 and 6.8 show sample results from a run where no molecular diffusion is implemented. Disabling molecular diffusion increased the model speed by a factor of around 20. The distribution is once again asymmetrical and irregular. Here we can see all the non-zero elements fixed at unit height as there is no mechanism for diluting concentrations. The width of the distribution is similar to the previous two examples. The detail shows discrete, non-zero concentration spikes. Here, the range and distribution of concentrations is identical to the initial condition, all values are 0 or 1. However, we can still analyse the spatial distribution of these discrete concentration spikes.
Figure 6.5: Example run for $t = 1080$ s with molecular diffusion implemented. The model parameters are: $L_I = 150$ m, $L_K = 0.03$ m, $D_E = 1$ m$^2$ s$^{-1}$ and $D_M = 1.5 \times 10^{-5}$ m$^2$ s$^{-1}$.

Figure 6.6: Detail of the example run shown in Figure 6.5
Figure 6.7: Example run for $t = 1080$ s with no molecular diffusion. The model parameters are: $L_I = 150$ m, $L_K = 0.03$ m, $D_E = 1$ m$^2$ s$^{-1}$.

Figure 6.8: Detail of the example run with no molecular diffusion shown in Figure 6.7.
6.3.2 The effect of molecular diffusion on mean ensemble plume width

Having seen that the molecular diffusion implementation affects the range and distribution of concentrations produced by the model it is pertinent to test whether it has any significant effect on the mean ensemble plume profile. To do this we compare the mean concentration profile of two ensembles of 200 runs each; the first with the full implementation of molecular diffusion and the second with no molecular diffusion, both using the same model parameters as in the previous section. Ensembles were generated by using a different random number seed for each run keeping all other parameters the same. The results of these two are shown in Figures 6.9 and 6.10 respectively. The blue lines are running averages with a width of 5 m and the red lines are fitted Gaussian distributions of the form

\[ c = A \exp \left( \frac{(x - x_0)^2}{2w^2} \right). \] (6.6)

The fitting parameters for each ensemble are shown in their respective plots. The ensembles provide a reasonably smooth curve when averaged over 5 metres and the Gaussian distribution seems a reasonable place to begin although it can be seen to underestimate at the central peak and the tails in both ensembles. The \( x_0 \) values, which should tend to 0 with increasing ensemble size, of -1.96 m and 0.695 m provide some idea of how adequate the 200 runs in each ensemble are in terms of convergence. The width parameters agree to within 1 m which, given the level of convergence, is enough to suggest that molecular diffusion plays no significant role in the large scale plume concentration profile. This result is expected because the molecular diffusivity is several orders of magnitude smaller than the eddy diffusivity. However it was worth checking that there was no coupling effect between the phenomena in this model. We can now proceed with the examination of ensemble mean plume concentration profiles disregarding the effects of molecular diffusion.
Figure 6.9: Mean result of an ensemble of 200 model runs with molecular diffusion implementation. A 5 m mean is shown in blue and fitted Gaussian in red with fitting parameters as described in the text. Model parameters as in § 6.3.1.

Figure 6.10: Mean result of an ensemble of 200 model runs with no molecular diffusion. Fitted lines as in Figure 6.9.
6.3.3 Mean concentration profile

6.3.3.1 Long term mean concentration profile

Neglecting molecular diffusion allows us to use larger ensemble sizes and longer run times. In Figure 6.11 the mean concentration profile of an ensemble of 1000 model runs with a run time of 4320 s is presented. These data were generated using the same parameters as the preceding sections and fitted with a Gaussian function and a 5 m mean as before. The larger ensemble size provides a smoother, more symmetrical mean profile whose shape fits very closely with the Gaussian. The deviations from Gaussian in the tails and central peak observed in the previous section’s figures are no longer apparent. From this we conclude that in the long term the plume concentration profile converges to a Gaussian function as expected. However, the behaviour at shorter time scales needs further investigation and is examined in § 6.3.3.3. We also note that increasing the run time by a factor of 4 from 1080 s to 4320 s resulted in an increase of the width parameter by factor of approximately 2.25. Hence $w$ over this period was roughly proportional to $t^{0.56}$. This is between the short term and long term rates of $t$ and $t^{0.5}$ predicted by the statistical theory described in section § 1.5.2.

6.3.3.2 Plume width growth over time

As seen in section § 1.5.2, statistical theory predicts the initial growth of the plume to be linear with time slowing down to be proportional to the square root of time when the time is much bigger than the large eddy turnover time which can be defined as $T_L = L^2 / D_E$ (Kerstein, 1991). Figure 6.12 shows the plume width, $w$, plotted against model run time, $t$, normalised by $T_L$ on logarithmic axes. Each data point on the plot represents an independent ensemble of 1000 model runs. The dotted lines show the theoretical short and long term growth rate gradients of $w \propto t$ and $w \propto t^{1/2}$. The width value of the point representing the shortest dispersion time is approaching the initial top hat half width of 1 m and is consequently skewed by this. After that the plume can be seen to grow linearly with time until the rate slows down as predicted. The transition between the two limiting rates seems to occur mostly before $t/T_L = 1$, the reason for this is not obvious. It is
possibly due to the specific implementation of eddy events used here (see 6.2.2.1) overestimating the statistical value of $L_i$ and consequently $T_L$. However the model agrees with the basic principle predicted by the statistical theory of dispersion.

6.3.3.3 Plume shape development

It was noted earlier in the chapter that the Gaussian distribution may not be the ideal function to describe the modelled plume concentration profile at all timescales. Figure 6.13 shows an example ensemble mean concentration profile for when $t \ll T_L$. The blue line is a 5 m average of the model ensemble profile as used previously, the red line is a fitted Gaussian function and the green line shows a fitted sub-Gaussian exponential function (Pasquill, 1975) of the form,

$$c = A \exp \left( -\frac{x'}{2w^2} \right). \quad (6.7)$$

It is clear that the Gaussian does not fit the model distribution well, it underestimates at the centre and the tails. The sub-Gaussian exponential does a much better job and fits very well everywhere except the very centre of the peak.
Figure 6.12: Growth of plume width, $w$, beginning approximately linearly with normalised time, $t/T_L$, slowing to square root growth. Dotted lines show the theoretical gradients for short- and long-term plume growth.
Figure 6.13: Example ensemble result for $t \ll T_L$. Mean concentration profile in blue. Gaussian fit in red and sub-Gaussian exponential fit as described in the text in green.

Figure 6.14 displays the shape of the sub-Gaussian exponential for the range of $r$ values encountered in these results. There is a substantial difference in shape between the two extremes shown here. As $r$ decreases from 2.0 to 1.0 the tails of the distribution get fatter and the central peak gets thinner.

As we have previously seen in §6.3.3.1 that the long term profile is Gaussian in shape it is worth examining the transition the plume concentration profile makes from sub-Gaussian to its final Gaussian state.

It is expected that, $L_f$, the largest eddy size will have some effect on the large scale plume shape so the $r$ exponent fitting parameter was calculated for ensembles over a range of dispersion times and with $L_f$ values of 75 m, 150 m and 225 m shown as blue diamonds, black crosses and red stars in Figure 6.15 respectively. These value were chosen to represent a plausible range of maximum eddy sizes encountered an atmospheric plume. The dispersion time is shown without scaling here. Each group of ensembles can be seen to form a curve starting with $r$
Figure 6.14: Showing the variation in function shape of $y = \exp(-x^r/2)$ with $r = 1.0, 1.25, 1.5, 1.75, 2.0$. The curves with lower exponents have fatter tails and thinner peaks.

values of around 1.0 for short dispersion times which increase toward 2.0 as time increases. The shortest timescale data point for each group has again been skewed by the effect of the shape of the initial top hat concentration profile. The curves for the larger two $L_I$ values begin to reach $r = 2.0$ but do not reach convergence due to the long run times required to simulate the dispersion for the required time scales.

When $r$ is plotted against the width, $w$, of the fitted function, normalised by the large eddy length, $L_I$, the points all fall onto a single curve as shown in Figure 6.16 where the values skewed by short dispersion times have been excluded. As the width of the plume approaches the large eddy size the mean concentration profile becomes more Gaussian. Since atmospheric boundary layer values of $L_I$ are likely to be of the order of up to 1 km with correspondingly long large eddy turnover times, this model predicts that Gaussian concentration profile models may not be suitable for a considerable portion of a plume’s lifetime.

Interestingly, similar behaviour is predicted by Equation 1.13, the full solution to the gradient transport theory continuous source equation albeit on a different scale. Here the defining length scale is $D/u$, the diffusivity divided by the wind speed, typically of order unity in the atmosphere. When the plume width
Figure 6.15: Fitted $r$ exponent values plotted again dispersion time, $t$, for three different sets of ensembles with blue diamonds, black crosses and red stars representing ensembles with $L_i$ values of 75 m, 150 m and 225 m respectively.
Figure 6.16: The $r$ exponent of a sub-Gaussian exponential (equation 6.7) fitted to model concentration profiles plotted against width, $w$, scaled by $L_I$ with symbols as in Figure 6.15.
grows beyond this the slender plume approximation quickly becomes valid and the plume can be fairly said to be Gaussian. This effect is shown in Figure 6.17. While this model is purely based on gradient transfer theory, an equation of similar form could be scaled to describe the plume concentration profiles predicted by the model in this study.

6.3.4 Higher percentile concentration behaviour

Now we have examined the mean ensemble concentration profile predicted by the model we can examine the profile of higher percentiles of concentration. The results presented in this section are based on model runs with ensemble size 200 and with $L_I = 30$ m and $L_k = 0.03$ m and with molecular diffusion enabled. The spatial resolution, $d$, of the model for this $L_k$ value is $L_k/6 = 0.005$ m. The approximate timescale for molecular diffusion to act over this distance is $d/D_M = 1.7$ s so diffusion times much greater than this are used. The large eddy turnover time, $T_L$, in this case is 900 s. However it is assumed that the interaction of eddy based diffusion with molecular diffusion will introduce further timescales which depend on the spatial scale related to the concentration percentile under investigation. Dispersion times are therefore not normalised by $T_L$ in this section.

Concentration percentiles were calculated on data from all runs of an ensemble collected into 1 m bins. This method is similar to that used in chapter 5 in which mixing ratio percentiles were calculated on measured data collected into directional bins. Figure 6.18 shows example plume concentration profiles at a dispersion time of 50 s for a range of percentiles and the mean. The profiles have been fitted with a non-Gaussian exponential (see Equation 6.7) to aid comparison. The higher percentile profiles can be see to be greater in magnitude, wider and noisier than lower percentiles and the mean. Also observable is the tendency for the higher percentile profiles to have lower $r$ exponent values as earlier seen in the mean profiles for short dispersion times which is examined in the next section.

6.3.4.1 Upper percentile concentration profile shape

In Figure 6.19 the concentration profile shape exponent, $r$, is plotted against percentile for a range of dispersion times from 25 s to 200 s. The clear overall trend
Figure 6.17: The $r$ exponent values of a sub-Gaussian exponential (equation 6.7) fitted to concentration profiles given by the slender plume equation (equation 1.13) plotted against the plume width, $w$, scaled by $D/u$, the diffusivity divided by the wind speed.
Figure 6.18: Example of higher percentiles mixing ratio distributions for $t = 50$ s.
is for higher percentile distributions to tend towards the sub-Gaussian shape with lower $r$ values. This effect is more pronounced for the shorter dispersion times. Interestingly the mean profile shape parameter values, shown as asterisks on the y axis of the plot, are much closer to the extreme upper percentile shapes than the median. This demonstrates that at short timescales, the upper few percentiles of concentration strongly affect the mean profile. Then as the combined effect of small eddies and molecular diffusion smothers out the large spikes in concentration the effect is less important and the mean and upper percentile profile shapes become more Gaussian.

### 6.3.4.2 Upper percentile concentration profile width

The width of the plume for a given concentration percentile, $w$, relative to the width of the mean profile, $\bar{w}$, is shown in Figure 6.20. The errors in the fits are quite large due to the noise at higher percentiles but the overall trends are still clear. The relative plume width increases with percentile. For percentiles around the median the width is comparable with that of the mean at all timescales shown. However at higher percentiles the relative width increases, and the amount by which it increases is dependant on the dispersion time. The shortest dispersion time produces plume widths over three times the mean at high percentiles while at the longer timescales the equivalent multiple is only 1.7.

### 6.3.4.3 The effect of varying molecular diffusivity on plume width

It was shown in §6.3.2 that molecular diffusivity has a negligible effect on the mean ensemble plume width. It is expected however that the rate of molecular diffusion, $D_M$, would affect the upper percentile concentration profiles as an increase in $D_M$ would tend to dilute sharp peaks in concentration more quickly. We show the variation in upper percentile relative plume widths caused by factor of 10 variations in $D_M$ in Figure 6.21 for a dispersion time of 25 s. It shows that reducing $D_M$ to a tenth of its standard value increases the relative plume width at the 99.9th percentile from around 3 to 4. Increasing $D_M$ tenfold reduced the relative plume width from 3 to 2.5 at the same percentile.

In the boundary layer, $D_M$ maybe be expected to vary by around 10% through-
Figure 6.19: Plume concentration profile shape exponent $r$ against concentration percentile. Values for the mean profile shown as stars on the y-axis.
Figure 6.20: Width of concentration percentile plume normalised by width of mean plume against percentile.
out the course of a year due to fluctuations in temperature and pressure (Arya, 2003b). While the level of variation tested here is unrealistic in the atmosphere, it serves a useful purpose in the model as doubling $D_M$ is equivalent to doubling the dispersion time and halving $D_E$ the eddy diffusivity. So this serves as a way of examining the relationship between $t$, $D_E$ and $D_M$. This then tells us that under very turbulent conditions when $D_E$ is very high the 99.9th percentile plume maybe significantly larger relative to the mean than under standard conditions. An examination of the full extent of this effect including how it evolves over time is beyond the scope of this work.

6.4 Summary

In this chapter a linear-eddy model was used to model plume dispersion from a point source in homogeneous turbulence. The ensemble mean concentration plume profile agreed with existing statistical theory and converged to a Gaussian profile, growing initially with $t$ but slowing to growth with $t^\frac{1}{2}$ as the plume size approached that of the largest eddy. At short timescales the plume shape was found to be non-Gaussian with a sub-Gaussian exponential providing a good fit. The ensemble plume profiles of higher concentration percentiles were also studied. It was shown that for very high percentiles at short timescales, the plume width could be several times that of the mean plume width. The shape of the higher percentile plume profiles tended away from Gaussian to sub-Gaussian exponential with increasing percentile. These results could be useful when calculating the possible contaminating effect of a point source on eddy covariance measurements. As the previous chapter showed, high percentile concentrations from a plume measured at high frequency can interfere with eddy covariance flux measurements. This chapter then shows that the plumes from point sources should not, in this case, be treated as mean concentration plumes, as the high percentile plumes could be significantly larger and of a different profile shape.

This model could be improved by incorporating a variable eddy diffusivity which could be controlled by factors such as the plume height and atmospheric stability. This would make the model more useful for predicting real atmospheric plumes.
Figure 6.21: Width of upper percentile plume profiles against concentration percentile. Plot for a factor of ten increase and reduction of molecular diffusivity are shown.
Chapter 7

Conclusions

The continuing focus on CO₂ emissions as a primary driver of climate change has resulted in a number of emission reduction targets being set in various countries around the world. Direct measurements of CO₂ fluxes due to these emissions are therefore very desirable as a means of verifying actual reductions currently calculated through inventory-based methods. While using the eddy covariance method to measure scalar fluxes has a relatively long history in rural environments, measurements in urban spaces are a more recent development. Since a considerable fraction of emission reductions are expected to take place in cities it is important that the challenges of making measurements in the urban environment are better explored and understood as we characterise urban emissions. With a view to contributing to this developing field an eddy covariance CO₂ flux measuring system was built at a tower site in central London mounted 50 m above the ground and operated from June 2008 to February 2010.

One key difficulty with instruments sited in urban environments is that buildings may disturb the local wind field so that the mean vertical wind speed is a strong function of wind direction. This effect was demonstrated in Chapter 3 and was shown to significantly affect the CO₂ flux measured from directions where the mean vertical wind speed was very sensitive to direction. A data processing method using a running coordinate rotation angle was suggested to correct for this effect.

The CO₂ climatology was examined in Chapter 4. The atmosphere was found
to be unstable for most of the time as seen in other urban studies. This leads to a relatively small footprint for flux measurements with 80% of contributions to the measured flux calculated to come from within 700 m of the measurement point according to one model. The CO₂ mixing ratio displayed variability similar to that presented in a previous study at this site. Seasonal and diurnal changes in mixing layer heights and emissions were used to explain this behaviour. The CO₂ flux was shown to be strongly seasonal with winter fluxes about 2.5 times greater than summer fluxes. This difference was largely attributed to increased space heating during the colder months. A diurnal cycle was also observed and caused by similar patterns in traffic density and heating usage and was therefore weaker in the summer. A weekend effect in CO₂ flux was measured with summer weekday fluxes 39% higher than the weekend values. A smaller effect was observed in winter. A small but potentially significant weekly cycle in sensible heat flux was noted.

The measured CO₂ flux was compared to two inventory-based estimates for the square kilometre surrounding the measurement site and was 13% smaller than the LAEI and 38% smaller than the NAEI. It was noted that the present measurement technique is not suited to measuring large point sources and contributions from these were excluded from the inventory estimates before comparison.

Approximately 180 m to the east of the measurement point, at roughly the same height, is the Imperial College power station emissions stack. The plume from the emission stack was analysed in detail in Chapter 5. The CO₂ flux was found to be significantly lower, even negative, when the wind was coming from the direction of the Imperial College power station emissions stack. Data from this direction was excluded from the CO₂ climatology analysis. It was deduced that the negative signal in the flux was due to short-lived puffs of CO₂ from the stack passing above the measuring site as although there was no significant deviation of the mean CO₂ mixing ratio in the direction of the plume there was a peak in the maximum instantaneous CO₂ mixing ratio measured at 20 Hz. The plume was found to be approximately Gaussian in profile when looking at the 95th percentile of instantaneous CO₂ mixing ratio against wind direction. The plume was wider at lower wind speeds as the standard deviation of lateral wind speed is greater. The maximum CO₂ mixing ratio during a plume event was related by a simple power law to the averaging time. The exponent was dependant on the wind speed with
a higher number at higher wind speeds indicating a less structured, more random plume at the measurement point. The mean shape of the pulses of CO\textsubscript{2} measured during plume events was analysed and found to be approximately Lorentzian and of a similar spatial size in low and high wind speeds. Half-hourly power station gas usage data were obtained. The gas usage was found to correlate well with maximum CO\textsubscript{2} mixing ratio when the wind direction was from the direction of the power station. Wind speed was found to be an important factor in this relationship with moderate winds bringing the biggest response of mixing ratio to gas usage.

In Chapter 6, plume dispersion was modelled using a linear eddy model. Eddies are represented by discrete remappings of the concentration field while molecular diffusion acts effectively as a continuous smoothing on the field. It is useful in this case as it can make predictions of the spatial distribution of higher percentiles of scalar concentrations in a plume which were previously shown to be important to eddy covariance measurements. Plume width growth in the model agrees with statistical theory of dispersion in that it begins as linear with time but slows down to grow with the square root of time. When the plume width is smaller that the size of the largest eddies the model predicts the mean concentration to fit a sub-Gaussian exponential profile shape rather than the traditional Gaussian. The profile tends towards Gaussian as the plume width approaches that of the largest eddies. The concentration profile shape was shown to deviate from Gaussian for higher percentile concentration profiles at short timescales. The width of the high percentile concentration plume was shown to vary with time and with percentile, with short dispersion times and high percentiles giving the largest plume widths. These widths can be several times greater than the mean concentration plume width for short time scales. Turbulent intensity was also shown to be a factor controlling the width of the high percentile concentration plume relative to the mean plume width.

### 7.1 Future work

In Chapter 3 we showed that local wind field distortion can have an effect on eddy covariance measurements and suggested one method of reducing this. It would be informative and relatively straight forward to install identical eddy covariance
systems on opposite sides of a tower such as that used here to compare the effects of the very different distortions they experience for a given wind direction. A different approach would be to apply a technique similar to that used by Griessbaum and Schmidt (2009) who model the flow distortion at the measurement point using a large eddy simulation. Wind tunnel modelling is another possible approach to the problem and suitable for complex urban geometries as demonstrated by Carpentieri et al. (2011).

Chapter 5 showed that measured peaks in high frequency CO\textsubscript{2} mixing ratio data can be linked to gas usage amounts at a local power station. This relationship could be explored further to allow predictions of actual quantities of emitted CO\textsubscript{2} or pollutants to be made from measurements similar to these.

The model used in chapter 6 could be scaled and compared to measurements of a real plume for validation. One real difficulty is that this model makes no attempt to consider plume rise or the effects of vertical dispersion so methods to deal with this would be necessary.

7.2 Summary

This study involved the measurement and analysis CO\textsubscript{2} flux data measured at the Imperial College London site. The equipment was designed, set up and operated for over a year by the author providing a novel data set. A new coordinate rotation method was suggested and shown to have potentially significant effects on the calculated flux in certain situations. The CO\textsubscript{2} flux was found to exhibit strong diurnal, weekly and seasonal cycles which were attributed to anthropogenic factors. These effects were comparable with those observed at other city centre locations. The effect of an emissions plume from a local power station on the CO\textsubscript{2} flux was characterised. The spatial and temporal CO\textsubscript{2} signature of the plume at the measurement point was examined. A relationship between gas usage at the power station and measured CO\textsubscript{2} was established. An existing model was used to examine plume dispersion, focusing on high concentration percentile statistics. The model was shown to reproduce existing plume theory results, as well as making predictions about the relative width of the high concentration percentile plume profile.
References


