Can a Hemispherical Scanning Imaging Differential Optical Absorption Spectroscopy Technique be used to Improve Understanding of the Emissions, Dynamics and Chemistry of Nitrogen Dioxide in the Urban Boundary Layer?

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Abstract

Air quality is an international issue which has been the subject of several European directives on pollution levels as atmospheric pollutants can have significant effects on human health, ecosystems and climate change, especially at high levels. In the UK the largest sources of atmospheric pollutants are products of combustion from power generation and motor vehicles including NO\textsubscript{x} (NO and NO\textsubscript{2}), CO, VOCs and particulate matter. Hence it is becoming increasingly important to measure changes in these air pollutants especially in urban areas where these pollutants are at the highest levels.

Differential Optical Absorption Spectroscopy is now commonly used as an air quality tool; primarily through the measurements of nitrogen dioxide (NO\textsubscript{2}). CityScan is a Hemispherical Scanning Imaging Differential Optical Absorption Spectrometer (HSI-DOAS) which has been optimised to measure concentrations of NO\textsubscript{2}. This thesis will describe the development and subsequent deployment of three CityScan instruments and the first results from these deployments.

CityScan has a 95° field of view (FOV) between the zenith and 5° below the horizon. Across this FOV there are 128 resolved elements which are measured concurrently, the spectrometer is rotated azimuthally 1° per second providing full hemispherical coverage every 6 minutes.

Three CityScan instruments were built between 2009 and 2012 and deployed in various locations, including Leicester, London and Bologna. Data from one of these instruments has been validated with a MAX-DOAS instrument (TROPOGAS) and in situ monitors. The comparison with the TROPOGAS instrument produced gradient values between 0.7 and 1 with R\textsuperscript{2} values rarely lower than 0.7. An NO\textsubscript{2} detection limit of CityScan has been calculated to be 4 \times 10^{15} \text{ mol cm}^{-2}.

The extensive field of view of the CityScan instruments has allowed NO\textsubscript{2} concentrations to be mapped on city-wide scales allowing areas of high and low pollution to be identified with a spatial resolution which has never been possible before without
the use of models.
Executive Summary on the Performance of CityScan

A prototype instrument, CityScan has been developed, characterised and deployed during this thesis. The data analysis which has been subsequently performed is also relatively preliminary. This summary serves to explain what aspects of the following work can be considered to have met the traditional metrics of scientific rigour, and which should be read with caution.

The primary data products presented in Chapters 3 to 6 are CityScan differential slant column densities (DSCDs). These DSCDs require significant modelling before they can be used quantitatively to derive concentrations or mixing ratios owing to the nature of the radiative transfer effects. However, through preliminary modelling work, it has been shown that these results can be relied upon in the scenarios presented as the urban environments studied contain spatially resolved emissions. Therefore, it is possible to use this data to examine spatial effects where areas of high and low pollution have been observed. However, it should be understood that the measured column amounts are relative to the NO$_2$ amounts present when the CityScan instrument acquired its reference spectrum, and do not take account of how the light paths taken by photons through the atmosphere might have changed between the reference and the measurements due to, for example, path length enhancements from multiple aerosol scattering events.

Retrieval errors on the NO$_2$ SCDs have been calculated for several representative CityScan spectra from the PEGASOS measurements in Bologna, and vary between 3% on an NO$_2$ slant column of $1.62 \times 10^{17}$ mol cm$^{-2}$ and 25% on $1.29 \times 10^{16}$ mol cm$^{-2}$ for polluted and relatively clean days respectively. Data from clear sky days has been used to calculate an NO$_2$ detection limit for CityScan of approximately $4 \times 10^{15}$ mol cm$^{-2}$. The best performance scenario, where the fitting error of was 3%, is comparable with literature values. This value of error was calculated during a high pollution event demonstrating, that in situations with elevated concentrations of nitrogen dioxide the data produced by CityScan is at a level regularly used within this application area. A brief comparison with a well established MAX-DOAS instrument demonstrated that CityScan DSCDs can accurately capture the spatial variability and trends in NO$_2$ DSCDs over a day.

The performance of CityScan in general meets many of the design criteria which will be discussed in detail in this work. Areas where this original specification was not met included the time that CityScan could operate without operator intervention. The original target for this was set to be in the order of several months
however through the deployments discussed in this work it has been determined that the timescales over which CityScan can operate unmanned are in the order of two weeks.

Significant work is still required in order to fully optimise CityScan and the subsequent data analysis. However, this work will serve to show the potential of this technique and the improvements in understanding which are likely to develop owing to data from this new instrument.
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Wow, where to begin? So it’s finally complete (hooray!) and there are lots of people I should thank for helping to make that happen, so it here goes...

Firstly I would like to thank my supervisor Paul Monks, thank you for giving me this opportunity and for your invaluable advice and support along the way. I’d also like to acknowledge my supervisor at The Environment Agency, Rob Kinnersley, thanks for the interesting chats and insights into the goings on at the EA. To our head of group, John Remedios, thank you for always supporting my love of outreach and for giving me lots of great opportunities during my PhD.

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The retrieved NO$_2$ slant column is $4.79 \pm 0.34 \times 10^{16}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $-5.20 \pm 1.12 \times 10^{12}$ mol cm$^{-2}$, $1.68 \pm 2.31 \times 10^{18}$ mol cm$^{-2}$, $-8.63 \pm 2.10 \times 10^2$ mol cm$^{-2}$ and $8.43 \pm 19.8 \times 10^{14}$ mol cm$^{-2}$ respectively. The RMS of this fit is $2.01 \times 10^{-3}$. All measured spectra are plotted in red.

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AMAX-DOAS  Airbourne Multi AXis-DOAS
AMF        Air Mass Factor
AQMAs      Air Quality Management Areas
AURN       Automated Urban and Rural Network
BBCEAS     BroadBand Cavity Enhanced Absorption Spectroscopy
BL         Boundary Layer
BL0        LAQN site in Bloomsbury, Camden
CAD        Computer-Aided Design
CCD        Charge Coupled Device
CEN        European Committee for Standardisation
CG         Cloud to Ground
CH$_4$     Methane
CINDI      Cabauw Intercomparison Campaign of Nitrogen Dioxide Measuring Instruments
ClearfLo   Clean air for London
CNR        Italian National Research Council
CO$_2$     Carbon Dioxide
CS1, 2 and 3 CityScan Instrument 1, 2 or 3
DEFRA      Department of Environment, Food and Rural Affairs
DOAS       Differential Optical Absorption Spectrocopy
DSCD       Differential Slant Column Density
EA         Elevation Angle
EC         European Commission
ENEA       Agenzia Nazionale per le nuove tecnologie, l’energia e lo sviluppo economic sostenibile
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<tr>
<td>ENVISAT</td>
<td>ENVIronmental SATellite</td>
</tr>
<tr>
<td>ESA</td>
<td>European Space Agency</td>
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<tr>
<td>EU</td>
<td>European Union</td>
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<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
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<tr>
<td>GASCOD</td>
<td>Gas Analyzer correlating Optical Differences</td>
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<td>GM</td>
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<td>HSI-DOAS</td>
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<td>IC</td>
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<td>LED</td>
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<td>LEO</td>
<td>Low Earth Orbit</td>
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<td>LF</td>
<td>Low Frequency</td>
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<td>NASA</td>
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<td>NLLS</td>
<td>Non-linear Least Squares fit</td>
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<td>OMI</td>
<td>Ozone Monitoring Instrument</td>
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<td>PCB</td>
<td>Printed Circuit Board</td>
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<td>PEEK</td>
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<td>SVF</td>
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<td>TEC</td>
<td>Thermoelectric cooler</td>
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<td>TOA</td>
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Chapter 1

Introduction

Chapter 1 will introduce the critical concepts and theory which will be used as a foundation for the rest of the work described in this thesis; with topics ranging from a basic introduction to the atmosphere and dynamics within it to the chemistry related to air quality and the instrumentation which can be used to monitor it.

1.1 The Atmosphere

The atmosphere is a relatively thin envelope of gas, in comparison to the radius of the Earth, which surrounds our planet. This thin layer is critical to the survival of nearly all living species on our planet. The atmosphere can be split into four sections defined by changes in temperature. The lowest of these is the troposphere which extends to approximately 12 km from the Earth’s surface. The troposphere contains approximately 75% of the mass of the total atmosphere and is primarily composed of nitrogen (78%) and oxygen (21%). The main constituents of the atmosphere are shown in Table 1.1. The majority of the species listed in Table 1.1 have atmospheric residence times in excess of 100 years and are therefore considered “permanent” constituents. Exceptions to this are carbon dioxide (CO$_2$) methane (CH$_4$) and
nitrous oxide ($N_2O$). The area of the troposphere closest to the surface is affected by surface emissions and features, this region is called the boundary layer (BL) and extends up to 2 km from the surface. Beyond that is the free troposphere which covers from the top of the BL to the tropopause. BL chemistry will be the primary focus of this thesis. Figure 1.1 shows the structure of the atmosphere.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Chemical Formula</th>
<th>Mixing ratio vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>$N_2$</td>
<td>78.08</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$O_2$</td>
<td>20.95</td>
</tr>
<tr>
<td>Argon</td>
<td>$Ar$</td>
<td>0.93</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>$CO_2$</td>
<td>0.037</td>
</tr>
<tr>
<td>Neon</td>
<td>$Ne$</td>
<td>0.0018</td>
</tr>
<tr>
<td>Helium</td>
<td>$He$</td>
<td>0.00052</td>
</tr>
<tr>
<td>Methane</td>
<td>$CH_4$</td>
<td>0.00017</td>
</tr>
<tr>
<td>Krypton</td>
<td>$Kr$</td>
<td>0.00011</td>
</tr>
<tr>
<td>Xenon</td>
<td>$Xe$</td>
<td>0.00009</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$H_2$</td>
<td>0.00005</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>$N_2O$</td>
<td>0.00003</td>
</tr>
</tbody>
</table>

Table 1.1: The main constituents of the (unpolluted), dry atmosphere [63]

1.1.1 Urban Boundary Layer Structure and Dynamics

As the central study of this work will concentrate on measurements made in the urban environment, the structure and dynamics of the Urban Boundary Layer (UBL) will be discussed here to provide background understanding to the measurement environment. In order to allow discussion of the UBL there needs to be a short description of dynamical processes which occur in the BL which are summarised in Figure 1.2 [75]. The dominant dynamical process which occurs with the BL is the change that accrues diurnally. Diurnal changes in incoming radiation and therefore temperature cause structural changes in the BL. The BL is the lowest part of the troposphere which is beneath a capping inversion, as seen in Figure 1.2. In clear sky daytime conditions, a deep layer called the mixed layer (ML) develops as a results
of rising thermal plumes from the surface. This is topped with an entrainment zone caused by up drafts and downdrafts from the ML and fee atmosphere.

Under clear sky nighttime conditions, a stable boundary layer (SBL) forms with a temperature inversion close to the ground and a growing residual layer (RL) aloft. The SBL grows in depth during the night until sunrise when the surface is heated and convective mixing begins again. The residual layer seen in Figure 1.2 is a remnant from the previous day’s ML which continues to have weak mixing.

In order to interpret urban air pollution measurements, an appreciation of the complexities of the dynamical processes that occur in the urban environment is required. These dynamical processes will be briefly discussed here but more in-depth
Figure 1.2: Idealised schematic of the diurnal variations in the structure of the BL, image taken from Stull 2010 [75].

information can be found in Bailey et al. [4] and Barlow et al. [6]. Dynamics within the urban environment are especially important in this work, where measurements made on different spatial scales will be analysed and compared. The topography in urban environments is also vitally important in controlling the dynamics within the urban environment [4]. An example of the effect of topography on dynamics is illustrated in Figure 1.3 where the different scale of dynamical effects in the UL can be seen. The topography dominates the dynamics on a local and micro scale as is shown in Figure 1.3 with the buildings interrupting wind flows and creating recirculating flows within the street canyon itself.

The evolution of the boundary layer over the day will also need to be considered when analysing remote sensed measurements. In Barlow et al. [6] boundary layer dynamics have been studied over London during the REPARTEE-II campaign using Doppler lidar observations. The measured attenuated backscatter, vertical wind velocity and averaged vertical wind velocity variance for a given cloud-free day during the campaign are shown in Figure 1.4. This figure clearly shows the evolution of the mixing height over the day which will significantly impact upon the dynamics
Figure 1.3: Schematic diagram showing flows and dynamical processes with the UBL, set in the context of the Planetary Boundary Layer (PBL), Urban Canopy Layer (UCL) and the Sky View Factor (SVF). SVF is a measure of the degree to which the sky is obscured by surrounding buildings at a given point, which characterises the geometry of the urban canopy. The wide arrows indicate average wind direction and the narrow arrows indicate turbulent flow. Figure taken from [4] within the BL, which can be seen in Figure 1.5.

It is clear that an appreciation of the dynamical processes within the urban environment discussed here will be required when trying to compare remotely-sensed with in situ measurements.

1.2 Air Quality

Air quality can be defined as a measure of the concentration of pollutants in the air and is an important, trans-national issue. It is widely understood that air pollution can have a detrimental impact upon human health, buildings, agriculture and the natural environment [16]. The spatial scales over which these impacts are known to occur are wide ranging from regional through to global scales.
Air pollutants that are present in our atmosphere are produced by a wide range of both anthropogenic and biogenic sources some of these sources are shown in Figure 1.6. In this work the main focus will be anthropogenic sources as the subject of study is urban air quality. Examples of anthropogenic emissions include nitrogen oxides (NO$_x$) i.e. nitrogen dioxide (NO$_2$) and nitric oxide (NO), carbon monoxide (CO), volatile organic compounds (VOCs) and particulate matter (PM).

It is important to consider the distinction between primary and secondary pollutants. Primary pollutants are those species which are emitted directly by a source. Secondary pollutants are not directly emitted, but form as a result of reactions of primary pollutants in the atmosphere. An example of a secondary pollutant is ozone O$_3$ which forms in the troposphere as a result of reactions of hydrocarbons
with NO$_x$, CO and sunlight.

The major sources of primary anthropogenic pollutants is the combustion of fossil fuels for transport, energy generation and residential activities. NO$_2$ is produced during all combustion processes in air, through the oxidation of NO, and is therefore an important indicator of air quality. NO$_2$ will be the primary species measured in this work.

Directives both nationally and internationally aim to control the level of pollutants in the air which impact public health. Air quality legislation in the UK is driven by legislation set out by the European Commission. In 2008, the European directive 2008/50/EC [55] was published in order to merge most existing legislation into a single directive. This directive introduced new air quality objectives for PM$_{2.5}$ (Particulate matter with a diameter up to 2.5 $\mu$m) whilst keeping all existing objectives the same. It also introduced the possibility to discount natural sources
of pollution when assessing compliance. This legislation was made law in the UK through the Air Quality Standards Regulations 2010 \[65\], which stated limit values for NO$_2$ of 40 µg m$^{-3}$ annually, with an hourly limit at 200 µg m$^{-3}$; this should not be exceeded more than 18 times a year. These limit values were set to be met by the 1$^{st}$ January 2010, areas which failed to meet these targets have now been classified as air quality management areas (AQMAs). Within the UK there were 234 AQMAs declared by 2009; 218 have been declared for NO$_2$, while 78 have been declared for PM$_{10}$ and 10 for SO$_2$ \[24\].
1.3 Oxides of Nitrogen

1.3.1 NO$_y$ Chemistry

An overview of the main reactions of nitrogen containing species (NO$_y$) are shown in Figure 1.7 [63]. Much of the chemistry shown in Figure 1.7 is governed by concentrations of NO$_x$ species. As the subject of this work is measurements of NO$_2$, chemistry of species other than NO$_x$ will only be discussed in brief here.

![Figure 1.7: Overview of NO$_y$ chemistry](image)

For the purposes of this work the tropospheric boundary layer will be classified as either “clean” or “dirty”. Reactions of NO$_x$ in “clean” and “dirty” atmospheres impact the atmospheric chemistry in different ways. Reactions of NO$_x$ can act as production pathways of tropospheric ozone if the NO$_x$ concentrations are sufficiently high, whilst in the absence of NO$_x$ ozone destruction may occur.
Under clear sky conditions the daytime lifetime of NO\textsubscript{2} can be very short; in the order of two minutes owing to the following process \cite{12}:

\[ NO_2 + h\nu(\lambda < 420nm) \rightarrow NO + O(^3P) \] (1.1)

Reaction (1.1) is quickly followed by a recombination of O with O\textsubscript{2}

\[ O(^3P) + O_2 + M \rightarrow O_3 + M \] (1.2)

M denotes any atmospheric molecule, mainly N\textsubscript{2} and O\textsubscript{2} that absorbs excess vibrational energy stabilising the newly-formed O\textsubscript{3} molecule \cite{63} \cite{31}. Therefore, for each NO\textsubscript{2} photolysed, an ozone molecule is formed. However, ozone rapidly oxidises NO back to NO\textsubscript{2},

\[ O_3 + NO \rightarrow NO_2 + O_2 \] (1.3)

The reactions shown in Equations (1.1) to (1.3) are often referred to as the photostationary steady state and results in no net production or loss of any species.

The ratio of the concentrations of NO, NO\textsubscript{2} and O\textsubscript{3} can be determined by the Leighton relationship, as described by Equations (1.8) or (1.9) \cite{25}. Firstly the rates of reaction of the processes shown in Reactions (1.1) to (1.3) must be determined. The rate of Reaction (1.1) is determined by the photolysis rate of NO\textsubscript{2} as seen in the following equation, where \( j_{1.1} \) is the photolysis rate constant for reaction (1.1)

\[ Rate = j_{1.1}[NO_2] \] (1.4)

The rates of Reactions (1.2) and (1.3) are as follows, where \( k_{1.2} \) and \( k_{1.3} \) are the rate
constants for reactions 1.2 and 1.3 respectively:

\[ Rate = \frac{1}{2}k_{1.2}[O(3P)][O_2] \quad (1.5) \]

\[ Rate = k_{1.3}[O_3][NO] \quad (1.6) \]

At steady state, the loss of NO\(_2\) via photolysis shown in Reaction 1.4 is equal to the rate of NO\(_2\) production by Reaction 1.6, as shown in Equation 1.7

\[ j_{1.1}[NO_2] = k_{1.3}[O_3][NO] \quad (1.7) \]

which can be rearranged to give the Leighton Relationship:

\[ \frac{[O_3][NO]}{[NO_2]} = \frac{j_{1.1}}{k_{1.3}} \quad (1.8) \]

or

\[ \frac{[NO_2]}{[NO]} = \frac{k_{1.3}[O_3]}{j_{1.1}} \quad (1.9) \]

or

\[ \frac{k_{1.3}[O_3][NO]}{j_{1.1}[NO_2]} = 1 \quad (1.10) \]

\( j_{1.1} \) varies with solar zenith angle and cloud cover and therefore the ratio of the concentrations of NO, NO\(_2\) and O\(_3\) are also expected to change over the day. Figure 1.8 shows the variation in jNO\(_2\) over a clear sky day as measured on a field campaign in a chamber study in 2002 by Bohn et al. [12] alongside concentrations of NO, NO\(_2\) and O\(_3\). Figure 1.8 demonstrates that the peaks in NO and O\(_3\) concentrations and a minimum NO\(_2\) concentration coincides with a peak jNO\(_2\) at solar noon.
Figure 1.8: Upper panel: concentrations of NO₂, NO, and O₃ in an actinometric experiment ion 10th March 2002 under clear sky conditions. Lower panel shows the actinometric photolysis frequencies calculated using the photo-stationary (PS) and time-dependant (TD) approach. Image from [12].

The photostationary state does not result in a net production or destruction of ozone. However, in the atmosphere additional reactions occur which oxidise NO to NO₂ without consuming ozone. Therefore the level of NOₓ ultimately determines whether there is net production of ozone. The chemical oxidation reaction of a simple hydrocarbon such as carbon monoxide (CO) in the atmosphere, is shown in reactions 1.11 to 1.14.

\[ OH + CO \rightarrow CO_2 + H \] (1.11)
The reaction scheme shown in reactions (1.11) to (1.14) demonstrates the chemical pathway that occurs in remote regions with low NO\textsubscript{x} concentrations. The exact concentration of NO\textsubscript{x} at which ozone production occurs depends on chemical and meteorological conditions but has been shown in some studies to occur at concentrations above approximately 80 ppt [51] [39]. The so called compensation point, that describes the concentration of NO\textsubscript{2} at which ozone production occurs is shown in Figure 1.9. In a polluted atmosphere, i.e with levels of NO\textsubscript{x} above the compensation point concentration of 80 ppt, the reaction scheme that takes place is as follows.

\[ H + O_2 + M \rightarrow HO_2 + M \] (1.12)

\[ O_3 + HO_2 \rightarrow 2O_2 + OH \] (1.13)

\[ \text{Net: } CO + O_3 \rightarrow CO_2 + O_2 \] (1.14)

\[ OH + CO \rightarrow CO_2 + H \] (1.11)

\[ H + O_2 + M \rightarrow HO_2 + M \] (1.12)

\[ HO_2 + NO \rightarrow NO_2 + OH \] (1.15)

\[ NO_2 + hv \rightarrow NO + O \] (1.1)
Figure 1.9: Schematic representation of the dependence of the net ozone (N(O3)) production (regions B or C) or destruction (region A) on the concentration of NOx. The magnitudes reflect clean free tropospheric conditions. Image from [51].

\[ O + O_2 + M \rightarrow O_3 + M \]  
(1.2)

\[ Net: CO + 2O_2 + hv \rightarrow CO_2 + O_3 \]  
(1.16)

The two reaction pathways, shown for a “clean” or “dirty” environments respectively demonstrate that in a low NOx environment oxidation of hydrocarbons will lead to destruction of ozone whilst in a polluted atmosphere production of ozone occurs. In summary when the concentration of NO is high enough for the rate of Reaction 1.15 to exceed the rate of Reaction 1.13, HO2 preferentially reacts with NO rather than O3. Thus ozone destruction via Reaction 1.13 is suppressed and the
NO\textsubscript{2} product of Reaction [1.15] can go on to produce ozone. In regions influenced by industrial activities, where NO levels can reach many parts per billion (ppb), ozone production far exceeds ozone destruction. Although stratospheric ozone is vital to protect human health and biological systems from damaging UV rays; when it is formed in the troposphere it is shown to have adverse affects on human health [37] including inflammation of the airways and respiratory symptoms. Tropospheric ozone also acts as a greenhouse gas [25] and causes damage to trees and plants [78] [1].

Typical concentrations of NO\textsubscript{x} in urban environments vary greatly with emissions, the meteorology, day of the week and size of the urban environment. Owing to the short lifetime of NO\textsubscript{x} changes in emission sources are very quickly apparent in measured NO\textsubscript{x} concentrations. For large cities such as London the annual mean recorded at a kerbside monitoring site on Marylebone Rd for NO\textsubscript{2} in 2012 was 37.3 ppbv whilst the city centre monitor in the city of Leicester that is classified as an urban background site measured an annual mean of NO\textsubscript{2} for 2012 of 16.0 ppbv (as calculated from AURN data [20]).

1.3.1.1 Sinks of NO\textsubscript{x}

During the daytime, NO\textsubscript{2} can be oxidised by reactions with OH, when at typical [OH] of 2 x 10\textsuperscript{6} molecules cm\textsuperscript{-3} the lifetime of NO\textsubscript{2} owing to this reaction is approximately 16 hours [25].

\[
NO_2 + OH + M \rightarrow HNO_3 + M
\] (1.17)

At nighttime oxidation of NO\textsubscript{2} can occur through reactions with NO\textsubscript{3}, O\textsubscript{3} and
NO$_y$ with HNO$_3$ eventually forming as a sink for NO$_x$.

\[
NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1.18}
\]

\[
NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M \tag{1.19}
\]

\[
N_2O_5 + H_2O(l) \rightarrow 2HNO_3 \tag{1.20}
\]

The formation of HNO$_3$ seen in Reaction (1.19) only occurs during the daytime because most OH sources are photolytic. The night time formation of HNO$_3$ through the reaction of NO$_2$ with NO$_3$ does not occur in the daytime because NO$_3$ rapidly photolyses in the daytime. HNO$_3$ is then lost through wet and dry surface deposition and uptake onto aerosol as shown in Figure 1.7 [25]. HNO$_3$ is also one of the major contributors to acid rain.

### 1.3.2 Emissions of NO$_x$

The most prominent NO$_x$ production process is through combustion, the process of which is described by the Zel’dovich reaction.

\[
N_2 + O_2 \rightarrow 2NO \tag{1.21}
\]

The Zel’dovich mechanism is highly temperature dependent and NO$_x$ is only formed in significant quantities above 1800 K [49]. The temperature dependence of NO formation through this mechanism is demonstrated in Figure 1.10. The Zel’dovich mechanism requires high temperatures in order to break the triple bond in the nitrogen molecule and therefore this is the rate determining step.
The NO produced through the Zel’dovich mechanism quickly reacts with ozone in the atmosphere to produce NO\textsubscript{2}. There is also clear evidence that a larger fraction of NO\textsubscript{x} from vehicular emissions is being released as NO\textsubscript{2}. It is thought that the measured increase in NO\textsubscript{2} being produced as a primary pollutant is linked to the introduction of newer diesel vehicles (Euro 4 and 5) [17].

The Zel’dovich mechanism is also responsible for lightning produced NO\textsubscript{x}, the importance of lightning as a source of NO\textsubscript{x} is shown in Table 1.2. Another natural source of NO\textsubscript{x} is biomass burning, the importance of which as a source is also
latitudinal and seasonally dependent and is shown in Table 1.2.

Table 1.2 clearly shows soil emissions of NO\textsubscript{x} as a relatively large contributor of global NO\textsubscript{x}. The processes through which soil emissions of NO\textsubscript{x} occur are the microbially mediated nitrification and denitrification \[60\]. Nitrification is an aerobic process that is primarily carried out by autotrophic bacteria which results in the conversion of NH\textsubscript{4}\textsuperscript{+} to NO\textsubscript{3}\textsuperscript{−} through the intermediate NO\textsubscript{2} with autotrophic bacteria being those which can take carbon in from the atmosphere through fixation, reduction and incorporation of CO\textsubscript{2}. Denitrification is an anaerobic process which results in nitrogen oxides being reduced to N\textsubscript{2}. During denitrification significant amounts of N\textsubscript{2}O and small amounts of NO\textsubscript{x} can be emitted before complete reduction to N\textsubscript{2}. The rate of nitrification and denitrification in the soil is controlled by several factors including soil moisture content, concentration of mineral N, temperature and physical properties of the soil.

The main anthropogenic emission sources of NO\textsubscript{x} between 1980 and 2010 are shown in Figure 1.11 \[61\]. A clear decreasing trend in the emissions of NO\textsubscript{x} can be seen and the main emission sources have been attributed to transport and the energy industry.

1.4 Existing Techniques for the Measurement of Air Quality

A variety of techniques exist which can be used to measure air quality, specifically concentrations of nitrogen dioxide. A summary of the most common techniques are shown in Table 1.3; the techniques listed will be discussed further in the following sections.
Figure 1.11: Total UK NO\textsubscript{x} Anthropogenic Emissions by Category between 1980 and 2010. Image courtesy of [61]
<table>
<thead>
<tr>
<th>Class of Technique</th>
<th>Instrument</th>
<th>Measurement Area</th>
<th>Research or Commercial</th>
<th>Typical Sensitivity</th>
<th>Sampling Period</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Methods</td>
<td>Chemiluminescence NO/NO$_2$/NO$_x$ Analyser</td>
<td>In situ</td>
<td>Commercial</td>
<td>50 pptv</td>
<td>50 s</td>
<td>Cross contamination of measured species</td>
</tr>
<tr>
<td>Electrochemical Methods</td>
<td>Electrochemical NO$_2$ sensors</td>
<td>In situ</td>
<td>Research and Commercial</td>
<td>&lt;1 ppbv detection limit</td>
<td>0.2 s</td>
<td></td>
</tr>
<tr>
<td>DOAS$^a$ Methods</td>
<td>LP-DOAS</td>
<td>Remote Sensing</td>
<td>Research</td>
<td>50 pptv</td>
<td>50 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Imaging-DOAS</td>
<td>Remote Sensing</td>
<td>Research</td>
<td>Unspecified, routinely measures at stack sources</td>
<td>3-7.5 s exposure, Up to 17 mins total image</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AMAX-DOAS</td>
<td>Remote Sensing</td>
<td>Research</td>
<td>120 pptv</td>
<td>2 s</td>
<td>Errors introduced due to cloudy/foggy conditions. Needs sunlight to work.</td>
</tr>
<tr>
<td></td>
<td>Broadband Cavity Enhanced Absorption Spectrometer (BBCEAS)</td>
<td>In situ</td>
<td>Research</td>
<td>50 pptv</td>
<td>50 s</td>
<td>Errors introduced due to cloudy/foggy conditions. Needs sunlight and a plane to work.</td>
</tr>
</tbody>
</table>

Table 1.3: Air Quality monitoring instrument specifications $^a$ Differential Optical Absorption Spectroscopy (DOAS)
1.4.1 Operational Air Quality Monitoring Techniques

Throughout the UK there is an extensive air quality monitor network. This includes both automatic and non-automatic monitoring systems. The automatic network produces hourly pollutant concentrations for key air pollutants such as $O_3$, CO, NO, NO$_2$, total NO$_x$, PM$_{10}$, PM$_{2.5}$ and SO$_2$ with data being collected wirelessly. Some of the sites have been collecting data since 1972. The non-automatic network instruments measure less frequently and samples are collected by some physical means, for example the use of diffusion tubes. These samples require off-line analysis in order to produce determine concentrations. For NO$_2$ measurements in non-automatic networks historically (1993–2005) diffusion tubes were the employed technique; more recently this method has been replaced with data from the Automated Urban and Rural Network (AURN) and modelling.

The European Committee for Standardisation (CEN) has produced a series of standard methods for monitoring air pollutants. These standards prescribe a specific measurement for each regulated pollutant. In the case of NO$_2$ this is a chemiluminescence method. The standards also describe minimum performance characteristics for a monitoring instrument.

Chemiluminescence monitors such as the Ecophysics CLD 780TR are routinely used by local authorities to monitor concentrations of NO and NO$_2$ using a single channel NO analyser. The sample air is switched regularly so that it alternately passes through a photolytic converter. The photolytic converter uses a xenon light source to convert NO$_2$ to NO and thus concentrations of ambient NO$_2$ can be measured by subtracting the concentration of NO without the photolytic converter switched on from the total NO when NO$_2$ has been converted to NO. In the main reaction chamber $O_3$ is reacted with NO resulting in a chemiluminescence signal which can then be measured using a photomultiplier tube (PMT). Chemiluminescence
monitors using the photolytic converter are relatively new and have replaced older versions which used a heated molybdenum catalytic converter. These monitors are installed throughout the UK in a variety of locations including roadside, kerbside, urban background, industrial and rural. Data from these instruments are readily available at the DEFRA website (http://uk-air.defra.gov.uk/data/) and the London Air Quality Network (LAQN) website (http://www.londonair.org.uk/london/asp/datadownload.asp).

1.4.2 Research Instruments

There are several scientific research instruments which are capable of measuring air quality; specifically NO$_2$, which will be discussed here and have been separated into ground and space-based.

1.4.2.1 Ground-Based Methods

There are several DOAS-based techniques which are being more commonly used as methods for air quality monitoring. These include Long-Path DOAS (LP-DOAS), Imaging DOAS (I-DOAS), Airborne MAX-DOAS (AMAX-DOAS) and Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS). DOAS will be explained more completely in the next section; here the different techniques and their strengths and weaknesses will be discussed. Specifications of the techniques are listed in Table 1.3; also shown in the Table are the specifications of the operational in-situ monitors.

It is clear from Table 1.3 that each technique has its own advantages and disadvantages. First, the chemiluminescence monitors have both a low detection limit and high temporal resolution, although values are often reported as hourly averages. The main weakness of this technique is its low spatial sampling as it measures at a point; although in many ways this can be seen as a weakness it can also be very advantageous if the aim of the measurement is to monitor individual emission sources.
It is also important to note that when networks of these sensors are combined with dispersion models concentrations of pollutants can be characterised over large urban areas.

The LP-DOAS measurements also have the same temporal resolution and detection limit as the chemiluminescence monitors but the measurements are taken over an integrated line of sight. This allows the concentrations to be representative over a larger area but it is more difficult to identify individual point sources using this technique. The I-DOAS instrument has lower time resolution than the other techniques discussed thus far, owing to the extensive field of view which it covers, but does have the advantage of imaging over large areas. AMAX-DOAS offers the advantage of being capable of covering large spatial areas whilst also offering relatively good temporal resolution and sensitivity; however flying the instrument aboard aircraft is both expensive and infrequent. The major disadvantage as with all DOAS instruments is that the concentrations measured are integrated over a line of sight, hence it is difficult to separate emitters within that column area.

The BBCEAS technique provides both excellent sensitivity and temporal resolution, however this again is a point measurement which provides little information over large urban areas. The BBCEAS instrument has been used aboard research aircraft which offers the chance to take measurements over larger spatial scales [38].

Another point, research-quality instrument which has recently been developed is the electrochemical sensor which is described in Mead et al. [50] which has been shown to have ppbv sensitivity and is also described as a low-cost sensor. The advantages of this technique are high sensitivity to several trace gases, excellent temporal resolution and being low cost they can be used in large networks of sensors. The electrochemical sensors have been shown to be low-power which makes them suitable to be used as a network as well as a mobile sensor unit which can be carried
by individuals. This not only offers the opportunity to look at large scale urban air quality but also personal exposure.

### 1.4.2.2 Space-Based Methods

There are several satellite instruments which measure NO\(_2\) columns. Whilst providing the opportunity for global coverage the major disadvantage of these instruments is that they have a large footprint; meaning poor spatial resolution relative to many of the ground-based sensors. The Ozone Monitoring Instrument (OMI) aboard NASA’s AURA satellite is one of the most commonly used space based instruments used for air quality monitoring as, for a satellite instrument, it has a relatively small footprint at 13 x 24 km. An example output of global NO\(_2\) concentrations that can be achieved using the OMI instrument are shown in Figure [1.12](#), highlighting the usefulness of a satellite method for pin-pointing the highest global emitters of NO\(_2\), including the identification of large power plants and shipping lanes. However the spatial resolution is not fine enough to resolve individual emission sources within urban environments.

The major strength of space-based instruments lie in their use for monitoring global transport of air pollutants, which is especially important for longer-lived trace gases such as CO\(_2\) rather than the short-lived NO\(_2\) whose transport is relatively limited. A final point regarding space-based instrumentation is with regard to sampling times. Many of the instruments used to monitor NO\(_2\) from space are aboard satellites with a sun-synchronous orbit; meaning that they revisit a given location once a day at the same time each day. The lack of measurements collected throughout the rest of the day means that spaced-based instruments are mostly limited to monitoring long-term trends as opposed to monitoring diurnal cycles. Also many satellite instruments used to monitor air pollutants measure visible light and thus do not work in cloudy conditions; this renders as much as 50% of the observations useless.
in summer and 80% in winter over the UK.

Figure 1.12: Global NO$_2$ concentration as an annual average for 2007 as measured by the OMI instrument. Image courtesy of Mark Kroon, KNMI

1.5 An Introduction to Absorption Spectroscopy

Absorption Spectroscopy makes use of the absorption of electromagnetic radiation by matter. Electromagnetic radiation is known to take many forms which can be distinguished by wavelength or frequency, such as microwave, x-ray, visible and infra-red for example. In this thesis the focus will be on the ultra violet (UV) and visible parts of the electromagnetic spectrum. Figure 1.13 shows the full electromagnetic spectrum.

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. When an atom or molecule absorbs energy electrons are promoted from their ground state to an excited state.

For over 100 years spectroscopy has been used to study the atmosphere of our
planet. Absorption spectroscopy initially concentrated on the strong absorbers such as ozone which are easily identifiable in a solar light absorption spectrum. Strong absorptions from ozone in the Huggins band and weaker features in the Chappuis band were quickly discovered with further signals being identified over the following years [29]. Much work continued investigating ozone absorption, discovering the existence of the ozone layer [23] and invention of the Dobson spectrometer in 1931 [21].

Steps towards measuring the weak absorption of atmospheric trace gases were made in 1975, when Noxon measured the intensity of the solar spectra over a continuous wavelength interval in the region where NO\textsubscript{2} absorption appears [53]. Secondly, he removed the strong Fraunhofer structure in the solar spectra by dividing a measured spectrum (during dusk or dawn) by a spectrum measured around noon. This became the basis for many DOAS techniques which have since been developed.
1.6 Differential Optical Absorption Spectroscopy (DOAS)

1.6.1 Theory of the DOAS Method

Scattered sunlight DOAS techniques use the unique absorption structures in solar radiation that are present after light has passed through the atmosphere, resulting from interactions of molecules with incident radiation, to give an absolute measure of their concentration. Other DOAS methods use artificial light sources in place of solar radiation. The basis of all DOAS techniques is the Beer-Lambert law. For a given molecule of interest the Beer-Lambert Law states that incident light intensity at a given wavelength ($I_\lambda$, where the molecule of interest is an active absorber) is a result of the transmitted intensity at the same wavelength ($I_{0(\lambda)}$), the absorption cross section of the molecule of interest at the same wavelength ($\sigma(\lambda)$), the concentration of the target absorber ($N$) and the path length through the gas ($l$).

The Beer-Lambert law can be expressed by the following equation [59]:

$$\frac{I_\lambda}{I_{0(\lambda)}} = e^{(-\sigma(\lambda)Nl)}$$

Equation 1.24 can be rearranged to allow calculation of the concentration of a target species, when using a wavelength where only the species of interest absorbs to give.

$$-\ln \left[ \frac{I_\lambda}{I_{0(\lambda)}} \right] = \sigma N l$$

(1.23)

However, Equation [1.25] [5] is only valid in scenarios where there are no absorption features from species other than the one of interest or broadband extinction. Broadband extinction results from scattering and is significant in scattered sunlight.
spectroscopy. The DOAS method can be used to calculate the concentration of a specific absorber in situations where there are more than one absorber within a bandwidth and/or extinction causing broadband features. In order for the DOAS technique to be used measurements must be collected over a broad spectral bandwidth.

In order to explain the DOAS method completely one must begin by first looking at the simplest scenario, where one structured molecular absorber and an unstructured broadband extinction process are present. This situation will result in a spectrum containing a slowly varying broadband extinction ($\alpha_{BB}$) and a structured absorption feature centred around $\lambda_2$ from absorber A. The spectrum resulting from this scenario ($I_{meas}(\lambda)$) is shown in Figure 1.14.

![Figure 1.14: The DOAS method for one structured absorber in the presence of broadband extinction. Image take from [5]](image)

In an ideal situation a reference spectrum ($I_0(\lambda)$) would be collected by measuring the light intensity as a function of wavelength before it enters the sample. However,
in the case of scattered sunlight DOAS methods this is not possible and thus a reference spectrum is collected that contains light that has traveled the shortest distance through the atmospheric sample; often this is a zenith measurement at noon. Now Equation 1.25 can be arranged to give:

\[ I_{\text{meas}}(\lambda) = I_0(\lambda) \exp(-\sigma_A(\lambda) N_A l - \alpha_{BB}(\lambda) l) \]  

(1.24)

By collecting measurements at wavelengths where A does not absorb (\(\lambda_1\) and \(\lambda_3\) shown in Figure 1.14) an estimate of the light transmitted through the sample in the presence of all other absorbers except A can be determined (\(I_0'(\lambda)\)). Resulting in:

\[ I_0'(\lambda) = I_0(\lambda) \exp(-\alpha_{BB}(\lambda) l) \]  

(1.25)

The broadband extinction that remains in Equation 1.27 can then be removed by producing a polynomial interpolation for \(I_0'(\lambda)\) using all wavelengths where A does not absorb. The optical depth of A is then determined using \(I_{\text{meas}}(\lambda_2)\) and \(I_0'(\lambda_2)\) from the following:

\[ OD_A = -\ln \left[ \frac{I_{\text{meas}}(\lambda_2)}{I_0'(\lambda_2)} \right] = \sigma(\lambda_2) N_A l \]  

(1.26)

The concentration of A can then be obtained through a rearrangement of Equation 1.28, providing the absorption cross section of molecule A and the path length are known.

\[ N_A = \frac{1}{\sigma_A(\lambda_2) l} \ln \left[ \frac{I_0'(\lambda_2)}{I_{\text{meas}}(\lambda_2)} \right] \]  

(1.27)

In scenarios where there are multiple absorbers with overlapping absorption structure the previously described method can be used to determine the concen-
ttation of a first absorber, B. One such scenario is shown in Figure 1.15 where there are two structured absorbers (A and B) and broadband structure.

![Figure 1.15](image)

**Figure 1.15**: The DOAS method for two structured absorbers in the presence of broadband extinction. Image take from [5]

The concentration of B can be calculated using the following equation.

\[
N_B = \frac{1}{\sigma_B(\lambda_3)} \ln \left( \frac{I_0(\lambda_3)}{I_{\text{meas}}(\lambda_3)} \right)
\]

(1.28)

The concentration of A can now be determined as \(N_B\) and \(\sigma_B(\lambda_2)\) are now known using Equation 1.31

\[
OD_{A+B} = -\ln \left( \frac{I_{\text{meas}}(\lambda_2)}{I_0(\lambda_2)} \right) = (\sigma_A(\lambda_2)N_A + \sigma_B(\lambda_2)N_B) \times l
\]

(1.29)

This method can then be extended to multiple absorbers providing the number of absorbers does not exceed the number of individual wavelengths measured. The
generalised Equation to describe this can now be expressed as:

\[ OD_{\text{absorbers}} = -\ln \left( \frac{I_{\text{meas}}(\lambda)}{I_0(\lambda)} \right) = \sum_{\text{absorbers}} (\sigma_i(\lambda)N_i \times l) \]  

\hspace{1cm} (1.30)

### 1.6.2 Application of DOAS

The application of the theory described in Section 1.6.1 will now be discussed.

A complication of the application of the DOAS method is that the absorption cross sections can be both pressure and temperature dependent. Therefore, reference cross sections \((\sigma_i(\lambda,p,T))\) must be included in the Beer-Lambert law at specific temperature and pressures representative of the measurement scenario. Raman and Mie extinction by molecules and aerosols respectively are included and are described by \(\epsilon_R(\lambda)\) and \(\epsilon_M(\lambda)\) respectively. A further term, \(A(\lambda)\) is included to account for instrument spectral characteristics. The modified version of the Beer-Lambert Law is now as follows.

\[ I(\lambda) = I_0 \cdot exp \left[ -L \cdot \left( \sum (\sigma_i(\lambda,p,T) \cdot N_i) + \epsilon_R(\lambda) + \epsilon_M(\lambda) \right) \right] + A(\lambda) \]  

\hspace{1cm} (1.31)

Passive, scattered sunlight DOAS must be given further consideration owing to the complicated light paths through the atmosphere that are followed by the measured light. The path followed depends on the solar position, the viewing direction of the telescope and the distribution of air molecules and aerosol particles.

Scattering occurs when photons interact with matter resulting in one of two outcomes. Either the energy of the photon and matter is unchanged or there is conversion of energy during the interaction. These two scattering effects are known as elastic or inelastic scattering respectively. During inelastic scattering there can be complete absorption of the photon or, after a collision, a photon of a different
energy to the incoming one can be emitted. There are three types of scattering processes depending on the type of matter that interacts with the photon. These are Rayleigh scattering, Mie scattering and Raman scattering.

Elastic scattering due to collisions with air molecules is known as Rayleigh scattering. Mie scattering is elastic scattering owing to collisions with aerosol particles present in air. Both of these processes can change the direction of an individual photon but not its energy.

Raman scattering describes inelastic scattering between photons and air molecules. Similar to elastic scattering the direction of the photon is changed however here the energy of the photon is also altered. The energy of the photon can either be reduced and some energy be transferred to the scattering molecule (Stokes scattering) or energy can be transferred from the thermally excited molecules to the photon increasing the amount of energy for a given photon(anti-Stokes scattering) [63].

In order to remove all of the scattering effects it is necessary to fit a polynomial which removes the broadband structure in the resulting differential spectrum as has previously been discussed in Section 1.6.1. The broadband component \( (\sigma_{BB}(\lambda)) \), that is accounted for by fitting a polynomial to the object spectrum, is made up of contributions from \( \varepsilon_R \) and \( \varepsilon_M \). When the broadband polynomial is subtracted from the object spectrum, the result is \( I'(\lambda) \), which comprises of the narrowband absorption features \( (\sigma_{ij}(\lambda)) \) of \( I_0(\lambda) \). Now the intensity of light measured can be compared at multiple wavelengths with trace gas absorption cross sections at the same wavelengths in order to separate the absorption from each trace gas of interest by the unique absorption patterns of the cross sections.

The differential optical density \( (\tau_I) \) can now be derived following the fitting of the polynomial, where \( I'_o(\lambda) \) is the measured absorption spectrum after subtracting
the unstructured broadband absorption’s polynomial from the measured spectrum.

\[ \tau' = \log \frac{I'_o(\lambda)}{I(\lambda)} = \sum_i (\sigma'_i(\lambda) \cdot N_i) \times l \]  

(1.32)

The concentration, \( N \), of absorber \( i \) is calculated using linear regression, fitting a reference absorption cross section from the literature \( (\sigma'_i(\lambda)) \) to the differential absorption features in the measured spectrum. Fitting multiple absorbers at the same time is made possible, by fitting several absorption cross sections over the same wavelength range, owing to differences in the absorption spectra of each trace gas of interest. After deriving \( N \), it is then possible to arrive at an average density for the absorber along the path, \( L \), which is referred to as a Slant Column Density (SCD) with the units of molecules per cm\(^2\) (mol cm\(^{-2}\)).

\[ SCD = \frac{\tau'}{\sigma_i} \]  

(1.33)

DOAS instruments usually focus light of intensity \( I(\lambda,L) \) onto the entrance of a grating spectrometer with a multi-channel detector (eg CCD) recording the spectrum. The limited resolution of a spectrometer causes the shape of spectrum \( I(\lambda,L) \) to be altered as the instrument cannot fully resolve the spectral features. This process is described mathematically by convolution of \( I(\lambda,L) \) with the instrument function \( (H) \) to give \( I^*(\lambda,L) \).

\[ I^*(\lambda,L) = I(\lambda,L) \times H \]  

(1.34)

Therefore, all of the reference cross sections used in the DOAS fitting procedure must also be convolved with the ILS.

The Beer Lambert Law \( (1.33) \) can now be combined with Equation \( 1.36 \) in order to account for instrumental issues. Also included are pressure and temperature
dependencies of the absorber cross sections and scattering (\(\epsilon_R\) and \(\epsilon_M\)) at point \(l\) integrated along the measured light path \(L\) within a layer of thickness \(dl\), resulting in:

\[
I^*(\lambda, L) = I(\lambda, L) \times H = \int_{-\Delta \lambda}^{\Delta \lambda} I_0(\lambda - \lambda', L) \exp\left(\int_0^L \sum_i (\sigma_i(\lambda - \lambda', p, T) \cdot c_i(l)) + \epsilon_R(\lambda - \lambda', l) + \epsilon_M(\lambda - \lambda', l) dl\right) \times H
\]

(1.35)

Integration over the entire atmospheric path length, \(L\), is valid in clear sky conditions; where the path of the photons to the detector is assumed to be constant over the bandwidth of the instrument.

1.6.2.1 Instrument Line Shape

The instrument line shape is an instrument specific parameter which describes the instrument response to a monochromatic signal at a given wavelength. The ILS causes broadening of the narrow-band features in the measured spectrum. For visible light spectrometers the magnitude of the broadening is dictated by the entrance slit width and the properties of the diffraction grating. The ILS also varies as a function of wavelength owing principally to chromatic aberration. Chromatic aberration describes the effect caused by the wavelength dependence of refraction causing light of different wavelengths to be refracted at different angles with respect to the lens.

The reference cross sections are convolved with the ILS in order to remove artefacts which would be introduced because the instrument cannot fully resolve the absorption features in the measured incident radiation. The ILS of CityScan was calculated during this work using the QDOAS calibration tool as shown in Section 2.4.1.
1.6.2.2 The Ring Effect

Fraunhofer lines are absorption lines seen in solar spectra caused by absorption by gases in the outer regions of the sun such as iron, hydrogen or helium. Raman scattering by molecules in the Earth’s atmosphere leads to an effective filling-in of the Fraunhofer lines in the light received at ground level, due to inelastic scattering and this complicates the removal of the Fraunhofer structure from the object spectrum and is described as the ring effect [27]. The reduction in intensity is in the order of a few percent and therefore needs to be corrected for as this can be many times greater than the absorption from trace species of interest.

Light intensity that is scattered in to a passive DOAS system can be expressed as:

\[ I_{\text{meas}} = I_{\text{Rayleigh}} + I_{\text{Mie}} + I_{\text{Raman}} = I_{\text{Elastic}} + I_{\text{Raman}} \]  \hspace{1cm} (1.36)

In order to determine \( I_{\text{elastic}} \) and \( I_{\text{Raman}} \) accurately, radiative transfer calculations need to be performed for each individual observation. However, by including a so called “ring spectrum” in the DOAS fitting process as a pseudo absorption cross section this step can be approximated; this method was first proposed by Schmeltekopf et al. in 1987 [63].

1.6.2.3 \( I_0 \) Correction

Owing to the instrument line shape of a typical DOAS instrument, typically a few tenths of a nanometer, the solar and atmospheric absorption lines cannot be spectrally resolved. The observed intensity can be described as:

\[ I^*(\lambda) = H \ast I(\lambda) \]  \hspace{1cm} (1.37)
Where the * denotes the convolution of the solar spectrum with the instrument line shape. Interference occurs between the spectral absorptions structures and the highly structured solar spectrum. Thus, dividing the measured spectrum by the convolved Fraunhofer spectrum fails to completely remove the Fraunhofer structures \[86\]. This phenomenon is known as the I_0 effect. An example of the residual structure that remains when observing NO\textsubscript{2} absorption spectra calculated for a smooth light source and a highly structured solar spectrum can be seen in Figure 1.16. The two NO\textsubscript{2} absorption spectra look very similar however the difference between the two shows residual structures which results from the interference of the atmospheric absorption with the Fraunhofer lines in the solar spectrum. Figure 1.16 demonstrates the spurious spectral structures that can potentially be introduced if a non-I_0 corrected cross section is used.

Figure 1.16: The I_0 effect. The blue and violet curves represent NO\textsubscript{2} absorption spectra, one calculated for a smooth light source and the other for the highly structured solar spectrum, both convolved with the same ILS (left-hand axis). The residual of the difference between these two spectra is shown in red (right-hand axis). Image taken from \[86\], data unavailable to be replotted to more than one significant figure.
In order to remove the I₀ effect, firstly the highly resolved solar spectrum is convolved with the ILS. A modelled absorption spectrum for the trace gas of interest is also convolved with the ILS. The modelled spectrum is calculated from the highly resolved solar spectrum and a highly resolved absorption cross section. In order to derive this modelled cross section, an atmospheric column density (S) has to be assumed for all strong absorbers in the fitting window. The calculation of the I₀-corrected cross section is shown in Equation 1.40.

\[ \sigma_{\text{corrected}}(\lambda, S) = -\ln \left( \frac{I^*(\lambda, S)}{I_{0*}(\lambda)} \right) \]

In this work an I₀ corrected cross section will be used for NO₂ with S (the assumed slant column density) set to 1x10¹⁶ mol cm⁻². The value of S was chosen because it was used by Vandaele et al. [81] in their intercomparison of several MAX-DOAS instruments and is representative of a clean urban environment. As the I₀ component is approximately two order of magnitudes smaller than the measured absorption cross section, as seen in Figure 1.16, variations in retrieved SCD from the assumed SCD in the I₀ correction will result in errors of less than 1% and therefore be considered to negligible.

1.6.2.4 Absorption Cross Sections of Trace Gases in the Region of Interest

The absorption cross section describes the ability of a trace gas to absorb incoming radiation as a function of wavelength. An important specification required for DOAS measurements is that the trace gas of interest must include some narrowband structure in order that its absorption signal can be separated from the broadband structure. The molecular absorption structures need line widths typically less than 10 nm [63], or substantially narrower than the bandwidth of the measurements. In
order to be able to separate individual absorbers, they must also have a unique spectral structure. All trace gases known to absorb within the fitting window must have their absorption cross sections included in the DOAS fit in order to retrieve their concentrations and remove their spectral contributions from the spectrum. The reference cross sections used in this work will be discussed further in Section 2.3.4.2.

1.6.3 The DOAS fit

SCDs are retrieved in QDOAS by performing a linear least squares fit of the differential spectra to reference absorption cross sections and a polynomial. QDOAS is DOAS software which runs on linux machines, version 2.0 is used here, written by Fayt et al. [18]. The first stages of the fitting process are treated as a non-linear least squares problem owing to shift, stretch and offset parameters applied to the measured spectrum that are mathematically solved using a Marquardt-Levenberg (M-L) algorithm [18]. In QDOAS the M-L algorithm is used to find the set of parameters that minimises the weighted sum of squares (F) using the following relationship. Using a value of the instrumental errors, $\sigma^i$, is optional in QDOAS and if unspecified $\sigma^i$ is set to 1.

$$F(\vec{\alpha}) = \frac{1}{2} \sum_{i=1}^{M} \left( \frac{f_i(\vec{\alpha})}{\sigma^i} \right)^2 =$$

$$\frac{1}{2} \sum_{i=1}^{M} \left( \frac{ln(I_i(\vec{\alpha}))) + \sum_{j=1}^{n} S^j c_j + \sum_{k=0}^{d} b_k(\lambda_i)^k - ln(I_0)}{\sigma^i} \right)^2$$

(1.39)

where $\vec{\alpha} = (\vec{a}, \vec{b}, \vec{c})$ is the vector containing all fitted parameters;

$\vec{a}$ is the set of parameters describing the shift, stretch and offset of the measured spectrum;

$\vec{b}_{k, k=1,...,d}$ are the fitted polynomial coefficients, of the polynomial used to subtract the broadband extinction caused by scattering;

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\( \vec{c}_j, j=1,...,n \) are the fitted SCDs of all fitted molecules;

\( \lambda, i=1,...,M \) is the wavelength grid of the reference spectrum \( I_0 \), which is calibrated with respect to the Fraunhoffer structures in a high resolution solar spectrum;

\( \Gamma_i(\vec{a}) \) is the measured spectrum including shift, stretch and offset corrections, interpolated at wavelength \( \lambda_i \);

\( S^{ij} \) is the absorption cross section of the absorber species \( j \), as measured in a laboratory, interpolated at wavelength \( \lambda_i \) which is the same as the \( \sigma(i) \) in Equation 1.37;

\( I_{i0} \) is the reference spectrum at wavelength \( \lambda_i \)

In each iteration of the fitting algorithm new values will be chosen for the parameters using the M-L algorithm and the sum of squares, \( F \), will be recomputed. The algorithm assumes it has converged to a solution when the difference between two succeeding values of \( F \) is smaller than a fixed convergence criterion, \( \epsilon \), which can be specified by the user but is usually set to a value of \( 10^{-3} \) or \( 10^{-4} \). In this work \( \epsilon \) is set to \( 10^{-4} \).

For any given value of the non-linear parameters \( \vec{a} \), the determination of the parameters \( c_j \) and the polynomial coefficients \( b_k \) is a linear least squares problem. Equation 1.41 can now be rewritten as:

\[
F = \frac{1}{2} \sum_{i=1}^{M} \left( \frac{\ln(I_i(\vec{a})/I_{i0}) + (A \cdot \vec{x})^i}{\sigma^i} \right)^2 \quad (1.40)
\]

where the matrix \( A \) contains the polynomial basis \((\lambda_i)^k, k=0,...,d\) and the absorption cross sections \( S^{ij}, j=1,...,n \) and \( \vec{x} \) represents the combined linear parameters \( \vec{b} \) and \( \vec{c} \). QDOAS exploits this in order to limit the parameter space of the M-L algorithm to the non-linear parameters. Once a new set of non-linear parameters are chosen \((\vec{a}')\) the linear parameters \( b_k \) and \( c_j \) are updated using a linear least squares algorithm minimising the sum of squares for the given values of the non-
linear parameters (see, Equation 1.41). The linear least squares problem is solved in QDOAS using a singular value decomposition (SVD).

Further parameters which can also be included in Equation 1.41 include the width of the instruments slit function and the wavelength shifts in the reference spectrum. Mathematically they play the same role as the shift, stretch and offset parameters, \( \vec{a} \).

The quality of the DOAS fit can be estimated from the magnitude of the ‘residual’ signal which remains after the fitting process. The Root Mean Square (RMS) residual is calculated using the following relationship:

\[
RMS = \sqrt{\frac{\sum_{0}^{n} x_i^2}{n}}
\]  

(1.41)

Where \( n \) is the number of pixels in the spectrum and \( x_i \) is the value of the residual spectrum which remains after the fitting procedure, at a given pixel \((i)\), as calculated by QDOAS. Calculation of a single RMS value to represent the magnitude of the residual provides a simple method for quantifying the quality of the DOAS fit and is a commonly used metric within the DOAS community [68] [81].

1.6.4 Imaging DOAS (I-DOAS)

I-DOAS is a passive DOAS technique which is based on the MAX-DOAS method where several vertical elements within an azimuthal field of view can be measured either concurrently or sequentially.

I-DOAS systems use a 2D detector to image spatial information versus spectral information. Each row of the detector provides spectral information for a separate spatial element. The instrument or just the entrance optics are then moved in the direction perpendicular to the entrance slit in order to produce a data-set of absorption spectra in a 2D field of view.
Previous work by Lohberger et al. [22] and Bobrowski et al. [10] have shown the potential for using I-DOAS to measure NO$_2$ at point emission sources. Work by Lohberger uses a push-broom spectrometer to achieve a vertical field of view of 13.1° with a resolution of 0.104° and a horizontal resolution of 0.087°. An example of the data presented in Lohberger et al. [22] is shown in Figure 1.17 where an I-DOAS instrument has been used to monitor a stack emission source.

![Figure 1.17](image)

Figure 1.17: Visualisation of an NO$_2$ plume of a power stations exhaust fume stack under calm wind conditions [22].

Figure 1.17 shows the potential of I-DOAS methods for use at point emission sources to track plumes and the additional information they provide on plume dispersion.

1.7 Summary

This chapter has introduced the topics of air quality and DOAS, the focus of this thesis will be measurements of NO$_2$. Whilst both global distributions and emissions at point sources can be relatively well monitored with current techniques, the spatial
distribution of NO\textsubscript{2} on sub-urban scales is difficult to quantify even when combining modelling with networks of sensors.

The instrument developed during this work, CityScan, will provide a new tool for monitoring NO\textsubscript{2} concentrations with improved time and spatial resolution compared with both operational air quality monitors and other DOAS techniques. This instrument has the ability to link down wind pollution with original emission sources in complex urban environments. Results from this study look to demonstrate the capability of the CityScan technique whilst also adding to knowledge in the areas of emission sources, chemistry and transport of NO\textsubscript{2}.
Chapter 2

Instrument Design and Performance

This chapter provides an overview of the design process, instrument build and subsequent characterisation of the CityScan instruments which has taken place during this work. The data from the instruments that are described in this chapter will be used in the ensuing chapters with the aim of improving knowledge of emissions, transport and dynamics within an urban environment.

2.1 Design Motivations

Current methods of monitoring NO$_2$ concentrations include in situ chemiluminescence monitors, satellite instruments and ground-based DOAS instruments. There are limitations to all of these methods; the in situ monitors used throughout the UK have a temporal resolution in the order of minutes however they measure at a single point, which often is not representative of a wider area. Modelling is required in order to derive air quality information over a larger spatial domain [20] and the uncertainties in these models is still relatively high owing to all of the dynamical
and chemical processes not being fully understood. At the opposite end of the scale, low earth orbiting (LEO) satellite based instruments normally have relatively poor temporal resolution with only one overpass per day and also have a spatial footprint which is typically the size of an entire city. The Ozone Monitoring Instrument (OMI) onboard NASA’s AURA satellite has one of the highest spatial resolutions of the satellite instruments used for measurements of NO$_2$, and at 13 x 24 km this resolution provides little or no information on the sub-city scale. There is a clear gap in knowledge in terms of the spatial dispersion of NO$_2$ within city scales and this lack of understanding makes source apportionment and air quality management problematic.

Somewhere between the two aforementioned techniques in terms of spatial resolution are DOAS methods. There are many design for DOAS instruments ranging from single line of site instruments to imaging systems. Many of these imaging systems adopt a method of moving entrance optics in order to provide a large field of view. One example of this method is described in Lohberger et al. This Heidelberg ground-based imaging DOAS system uses a stationary grating spectrometer which images a 13.1° vertical field of view onto a two dimensional CCD. A scanning mirror is then used in order to move the field of view in a horizontal direction in order to build up imaging data of large areas. The limitation of this technique is the length of time it takes to scan the instrument across the area of interest in order to build up an image. It is upon this point which the HSI-DOAS instrument (CityScan) aims to improve.

The original design concept for the CityScan units was to create an instrument that consisted of a sealed, imaging spectrometer with a large continuous field of view mounted within a rotating, weatherproof and thermally-stable casing. This design enables the whole spectrometer to be rotated in order to give full hemispherical
imaging on a six minute time-scale. Moving the whole instrument offers the additional benefit that issues related to changing the alignment between the entrance optics and spectrometer are removed. Full hemispherical imaging will provide unprecedented information on the spatial variability of NO$_2$ with urban areas; if more than one of these instruments were to be deployed with overlapping fields of views, the option of producing 3D gas fields would also be possible through the use of tomography.

2.2 Design Drivers

The design for the CityScan instruments was devised using a number of performance criteria. These include a large instantaneous field of view, which can be used to build up hemispherical imaging; the spatial resolution of this field of view was also crucial to the design as it is important to have a large number of vertical and azimuthal elements in order to achieve the high spatial resolution which is necessary in order to provide air quality information on a sub-urban scale. In order to be able to use these instruments for DOAS analysis, a high spectral resolution was also necessary as the DOAS method relies on being able to resolve narrowband molecular absorption features within a broadband spectrum.

Other design drivers include that the instrument should be fully autonomous and weatherproof in order to make long deployments in remote regions possible. CityScan also needed to be transportable as it was not intended to be deployed permanently in a single location but for a wide range of time periods at several locations. Outlined in Table 2.1 are some of the target specifications which were hoped to be achieved during the design and build process.

As with all instrument design and development projects some compromises were necessary in order to make an instrument build possible within both budget and
Table 2.1: Target Specifications of the CityScan instrument.

<table>
<thead>
<tr>
<th>Component</th>
<th>Target Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral range</td>
<td>420 to 590 nm</td>
</tr>
<tr>
<td>Field of View (elevation)</td>
<td>Zenith to -5 °</td>
</tr>
<tr>
<td>Field of View (azimuth)</td>
<td>1 °</td>
</tr>
<tr>
<td>Spatial Resolution (azimuth)</td>
<td>1 °</td>
</tr>
<tr>
<td>Spatial Resolution (elevation)</td>
<td>0.19 °</td>
</tr>
<tr>
<td>Scanning field of view (azimuth)</td>
<td>360 °</td>
</tr>
<tr>
<td>Azimuthal scanning speed</td>
<td>1 ° per second</td>
</tr>
<tr>
<td>Mean Spectrometer temperature</td>
<td>25.0 °C ± 0.1°C</td>
</tr>
<tr>
<td>Mean Detector temperature</td>
<td>-10.0 °C ± 1.0°C</td>
</tr>
<tr>
<td>Entrance Slit width</td>
<td>90 µm</td>
</tr>
<tr>
<td>Full Width Half Maximum of the ILS</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>Spectral Sampling</td>
<td>0.2 nm</td>
</tr>
<tr>
<td>Running time without maintenance</td>
<td>1 yr</td>
</tr>
</tbody>
</table>

time constraints; these decisions which required design trade-offs will be discussed further in this and subsequent chapters.

### 2.3 Realisation of the HSI-DOAS Design

CityScan is a novel Hemispherical Scanning Imaging DOAS (HSI-DOAS) instrument. CityScan is designed to concurrently measure 500 resolved viewing geometries over a 95° field of view which spans from the zenith to 5° below the horizon. CityScan also scans in an azimuthal direction for a full 360° view at a rate of 1° per second. This scanning pattern combined with the improved field of view could give unprecedented information on the spatial distribution and vertical profiles of a species measured. Figure 2.1 shows the final design for the CityScan instrument.

The CityScan instrument comprises of two primary subsystems; the head unit and base unit. The head unit contains the spectrometer, environmental sensors and a computer. The base unit remains stationary and houses the computer which controls the movement of the head unit and the transfer of data between the spectrometer
computer and a remote server or a hard drive stored in the base unit. The internal functional architecture of CityScan is shown in Figure 2.2.

The spectrometer is mounted onto an aluminium heater plate which is fixed to a beam that can be adjusted to change the angle and height of the spectrometer with reference to the casing. The heater plate is used to maintain a constant temperature within the head unit and the spectrometer itself. This mounting system can be seen in Figure 2.3. Two fans are also visible on this view under a protective cover these are used to push warm air out of the head unit to maintain a stable temperature. The temperature of the spectrometer, head-unit and head-unit casing are all recorded to allow diagnostics in this area.

A second view of the head unit is shown in Figure 2.3 on the left. From this view the entrance window can be seen along with the webcam window and com-
Figure 2.2: Block diagram showing the structure of CityScan computer mounting position. There is an external shutter that can be closed when the spectrometer is not in use in order to keep the external window as clear as possible.
2.3.1 The Concentric Imaging Spectrometer

CityScan uses a concentric Offner-based spectrometer designed by Dan Lobb of Surrey Satellite Technology Limited (SSTL). The final design of this spectrometer, as used in the CityScan instruments, is shown in Figure 2.4. The spectrometer is housed within a powder-coated steel box, made from 1 mm thick steel plate on which the CCD control electronics are mounted and feedthroughs into the spectrometer are fitted. The walls of the spectrometer needed to be very thin whilst also being very strong in order to allow the spectrometer window to be positioned very close to the front window of the CityScan casing. The optical elements are mounted on a 19.5 mm aluminium plate containing pre-drilled fixing points and dowel holes; the dowel holes have a precision of 5 µm. The precision of the dowel holes ensured that the optical mounts would be positioned very accurately, thus removing the need for much adjustment during the alignment process. This plate provides a rigid base on which all of the optics can then be mounted. This optics mounting plate is then fixed to a second aluminium plate which forms the base of the spectrometer box.
2.3.1.1 Offner Relay Spectrometers

The standard Offner spectrometer comprises three spherical elements; two concave mirrors and one convex mirror. This design was originally proposed by Offner in 1975 [56]. Thevenon modified the original design a few years later by suggesting that the secondary mirror was replaced with a diffraction grating to form an imaging spectrometer [66]. Imaging spectrometers of this sort have previously been proposed for remote-sensing applications [82]. The spectrometer is made up of two sub-systems. The first receives the radiation and images the target onto the entrance aperture. The second sub-system is a grating spectrometer which disperses the radiation that has passed through the slit as a function of wavelength and records the two-dimensional image on a detector. Offner relays offer several advantages over other spectrometers in push-broom spectrometry; they have low chromatic aberrations, are compact in size and have a low optical distortion [48]. Push-broom
spectrometers are classified by consisting of a slit which is dispersed and imaged onto an area detector array, the columns of which are considered here parallel to the slit, with the rows thus providing the spectral information\textsuperscript{[52]}. Each row is effectively a separate spectrometer.

2.3.1.2 Calibration Subsystem

The calibration subsystem consists of a mercury lamp for wavelength calibration and several LEDs for absolute radiance calibration. The reverse side of the entrance shutter has been designed to be mirrored, so that when this shutter is closed, the light from the calibration lamps is reflected back off the reverse of the shutter onto the entrance mirrors. The entrance mirrors will then focus the light into the spectrometer to allow the calibrations to take place in the field and at any time of day. The calibration subsystem was found to be unusable for calibrations as the lamps installed did not provide sufficient illumination for calibrations to be performed in this manner. It was also found to cause internal reflections resulting in shadowing of the lamp signal upon the detector. These effects are shown in Figure\textsuperscript{2.5} where there are spectra shown as measured using the internal calibration lamp and an external mercury lamp. In the spectra measured using the internal lamp it can be seen that the intensity of the light source is very low and therefore the signal to noise ratio is poor; whilst the external lamp provides sufficient signal that the detector is illuminated adequately. Also evident in Figure\textsuperscript{2.5} are the additional peaks in the spectra of the internal lamp; with two peaks surrounding each peak of the external lamp separated by approximately 45 pixels.

2.3.1.3 Entrance Optics

A two-mirror Schwarzschild telescope configuration provided this instrument with a 95\(^\circ\) field of view (FOV). The diamond turned mirrors have been manufactured
to a surface roughness of 3 nm by Kaleido Technology, with the primary mirror being convex and the secondary mirror concave. These mirrors and their mounting systems are shown in Figure 2.6. The spectrometer was tilted at 42.5° above the horizontal to provide a FOV extending from 5 degrees below the horizon, to the zenith. After 16-pixel binning in the spatial domain, the resolution of resulting measurements varied from 0.07° in the centre of the images, to 2.5° at the extremes of the field of view.

The field of view from the 2-mirror Schwarzchild system was curved with the central point offset azimuthally by approximately 6° from the extreme viewing angles at +/- 47.5° from the centre of the entrance slit. This curvature of viewing angle was characterised within the laboratory and is shown in black in Figure 2.7. The slight asymmetry of the field of view is a result of minor misalignments in the entrance optics; which could be improved with a more extensive alignment procedure. In order
to reduce absolute photon fluxes, and reduce the azimuthal resolution, the azimuthal field of view of the spectrometer optics was constrained by an external baffle to $0.2^\circ$. The baffled field of view was applied in the reconstruction of hemispherical data sets.

The instantaneous field of view of the spectrometer was constrained azimuthally to approximately $0.2^\circ$ for all measurements in this study, as measured in the laboratory. Given the scanning speed of the spectrometer of $1^\circ s^{-1}$, and image integration times of 2 s, azimuthal resolution was dictated by scanning motion rather than instrument field of view. The resolved field of view of the instrument was a product of the time over which images were integrated (2 s), and the total time taken to integrate and store captured data. The resolved field of view was approximately $2.5^\circ$ for the deployments discussed in this thesis. These fields of view are shown in Figure 2.7 where the green shading shows the 2.5 s integrated FOV for the baffled
Figure 2.7: The measured instantaneous field of view of the spectrometer (black), the instantaneous field of view of the instrument once an external baffle was added (red) and the effective field of view of the instrument once the 2.5 second integration time is accommodated; black shading is the original FOV of the spectrometer and the green shading is the 2.5 s FOV for the baffled version. Calculations and measurements were performed in partnership with Alex Webb.

0.2° FOV (the width of which is shown in the red lines) and the black shading shows the original FOV of the spectrometer without the baffle.

2.3.1.4 Entrance Slit

The entrance slit position is one of the major design constraints with this spectrometer design. The centre of the slit needs to be 7 mm away from the edge of the focal plane. The total size of the entrance slit mount therefore needs to be small in width whilst also measuring 33 mm in length. This makes manufacture very difficult and thus the entrance slit would be very expensive to manufacture. Ideally, a laser etched entrance slit would be used but owing to budget constraints this was not possible in this phase of the project.
The width of the entrance slit is directly related to the instrument line shape (ILS); the wider the entrance slit the larger the ILS will be. In our case the entrance slit was made by pushing two precision razor blades together leaving a desired gap of 90 µm between them. This method of creating an entrance slit proved to be very difficult as the edges of the razor blade were very easily damaged and thus they could not just be pressed up hard against a guide. So the width of the entrance slit required characterisation as there were inconsistencies in the width of the slit causing potential variations in the ILS.
Figure 2.8: The entrance slit of CS1 imaged using a microscope on 5x zoom, showing the bottom (top panel), middle (middle panel) and top (bottom panel) of the entrance slit. The scale in the bottom right hand corner of the individual images is 200 µm.

Shown in Figure 2.8 are images of the entrance slit taken using an Olympics BX51 microscope on 5x zoom. Measurements of the entrance slit width were made...
at regular intervals along the slit. These images show that the entrance slit width is vastly different to the desired width at the top and bottom and much closer to 90µm in the middle. This is presented more clearly in Figure 2.9 which shows the measured slit width at all measured points along the entrance slit. It is clear that in the middle of the slit the width is relatively constant and close to the desired value whilst at the top and bottom the values are very large with the first measurement at the bottom of the slit being 666% above the desired value.

Figure 2.9: The measured slit width with point 1 being at the bottom of the slit and point 86 the top.

The mean slit width measured is 117.9 µm with minimum and maximum values of 82.41 and 602.45 µm respectively and a standard deviation of 64.05 µm. When the first measured point at the bottom of the entrance slit is excluded from analysis the mean slit width is 112.2 µm with minimum and maximum values of 82.41 and 249.59 µm respectively and a standard deviation of 36.4 µm. The original target ILS, of 90µm, will therefore be unachievable across most of the measurements in this instrument without some corrective optics. The external baffle acts as a corrective
optic in this case, reducing both the ILS and spatial resolution simultaneously. However, fitting the external aperture also complicates instrument calibrations as the internal calibration sub-system is no longer relevant to measurements made using ambient light. Figure 2.10 shows spectra of an external mercury lamp taken before and after the external baffle was fitted.

![Figure 2.10: Measured spectra of a mercury emission lamp with (black, bottom x-axis) and without (red, top x-axis) the corrective entrance aperture fitted.](image)

Figure 2.10 clearly shows the improvement seen in the ILS width and shape when the entrance aperture is fitted. The two x-axis correspond to the two spectra where the black line has been measured with four pixel binning on the detector and the spectra without the baffle (red) recorded with two pixel binning. Without the external baffle the line shape is wider and asymmetric whilst the ILS when the aperture is fitted is much narrower and more symmetrical. It is also now possible to resolve the doublet centred at approximately pixel 800, which corresponds to the
doublet in the mercury emission spectrum at 576.9 and 579.0 nm.

2.3.1.5 Shutter

The design of the entrance shutter was also affected by space constraints around the focal plane and therefore a small solenoid was used to control the shutter as this was one of the smallest options available. The shutter itself is a metal component, actuated by the solenoid, which is shaped to close off the entrance slit whilst the the previous frame is read off the CCD. The shutter design was shown in Figure 2.6 (right hand side). Owing to the shutter only being held at the bottom, the design has been found to be prone to wear and tear problems which cause the shutter to get jammed for several frames at a time. The barrel of the solenoid gets worn unevenly owing to the weight of the shutter being unsupported at the top. This dramatically reduces the quality of the measurements which can be made because the automatic exposure time control over-exposes images immediately following the shutter jamming and takes several frames to correct itself. This degradation takes approximately 2 weeks to become obvious in the measurements, which is equivalent to over 9 million repetitions of the shutter. A solution to this problem would be to use a frame transfer CCD; however they were prohibitively expensive for this project. Another alternative is to use the current CCD as a frame transfer CCD by blanking out half of the CCD, however this causes the field of view that can be measured to be halved and thus would also not meet the design criteria for the FOV of the instrument. If a design where the shutter could be supported at the top as well as the bottom could be devised this would also offer a solution.

2.3.1.6 Optical Elements of the Spectrometer

All of the optical elements of the spectrometer were mounted in anodised aluminium mounts. All of the mounts were designed to have very little adjustment in them
but instead contained reference faces onto which the optics themselves could be referenced. The mounts also contained dowels which could be use to align the mount onto the optics bench. The three main optics of the spectrometer are shown in their individual mounts in Figure 2.11. The mounts needed to be custom designed again due to space constraints within the spectrometer. The grating and lens sit only a few millimetres apart in the final design and thus required mounts which only supported them on three sides whilst still holding them firmly in place.

Figure 2.11: CAD images of each of the three main optical elements of the spectrometer, shown here in their mounts. Image courtesy of Christopher Whyte and Roland Leigh.

The optical elements of the spectrometer include a spherical meniscus lens, a concave spherical mirror and a diffraction grating. Of these bespoke optical elements the diffraction grating was the most difficult to manufacture as it has the largest impact on instrument throughput and therefore the manufacturing tolerances are more exacting than for the other optical components. The grating was manufactured by a French-based company Horiba Jobin Yvon and has a grating frequency of 1800 grooves/mm.

The lens and mirror were both manufactured by Jenoptik Ltd, a Florida based
company. The lens was anti-reflection coated and it has been demonstrated that the reflectivity was less than 3.0% for the majority of the bandwidth up to 500 nm [88]. The mirror was coated with a dielectric–protected aluminium layer provided by Universal Thin Film Labs. The reflectivity of this was shown to be between 91–93% for the total bandwidth of 420–590 nm by the manufacturer.

The compact size of the spectrometer makes assembly difficult as mounting points become unreachable once the next optical element is fixed in place. Thus an assembly plan was devised in order to ensure that all of the optics could be mounted securely upon the optics bench. An image showing the spectrometer under assembly is shown in Figure 2.12 this image highlights the space limitations.

### 2.3.1.7 Detector and Focal Plane

The focal plane assembly was shown in Figure 2.6. The CCD used in the CityScan spectrometer is an E2V CCD230-42 front illuminated scientific CCD sensor. This CCD has 2048 (horizontal) x 2064 (vertical) pixels with a pixel size of 15 µm x 15 µm giving a total imaging area of 30.7 mm x 31.0 mm. The CCD is mounted onto a PCB which is then held in place within the focal plane wall by an assembly of a thermoelectric cooler (TEC), PEEK (Polyether Ether Ketone) board and a copper cold finger. These four components are pressed against the focal plane; this design can be seen in Figure 2.6. Between the CCD and the cold finger a platinum resistance thermometer (PRT) is used to measure the temperature of the detector and the TEC then draws heat from the CCD to the cold finger. All of the junctions between components use either thermal grease or thermally conducting films to improve the thermal connections. Springs are used to encapsulate the screws that hold the focal plane assembly together in order to prevent too much force being applied to the CCD whilst still holding it firmly in place. PEEK board is used to hold the cold finger because it is strong, easy to manufacture and a good thermal
Figure 2.12: A photograph of the spectrometer being assembled, visible here are the diffraction grating, lens and the back of the mirror mount.

insulator. The cold finger protrudes through the spectrometer box wall where there is a large heat sink fixed to it.

The CCD is capable of 4 node read out which speeds up the time between scans. Owing to time constraints it was only possibly to get the CCD working in the 2-node mode for this work.
The quantum efficiency of the detector is defined as the ability of the detector to convert incoming photons into electrons which can be readout. The quantum efficiency of the detector is known to vary with wavelength and therefore this will affect measured signal across the detector. The variation in quantum efficiency is shown in Figure 2.13. The fitting window used in this work for the DOAS fit is 428 – 495 nm and it is clear in this plot that the quantum efficiency in this region is relatively poor ranging from approximately 10 – 25 %. Knowledge of this is crucial in order to be able to successfully perform DOAS fits on this data. In order to maximise the signal measured in this region the automatic exposure time control was only performed using the area of the CCD where the fitting window was imaged. This meant that the exposure time was optimised for the signal in this region instead of at the higher wavelength end of the CCD.

Figure 2.13: The percentage quantum efficiency of the detector as a function of wavelength as measured by the manufacturer.

![Graph showing percentage quantum efficiency against wavelength. The graph shows a smooth curve with the efficiency increasing from approximately 10% at 428 nm to 25% at 495 nm.](image)
2.3.2 Hemispherical Imaging

In order to achieve hemispherical imaging the instantaneous field of view provided by the spectrometer needed to be rotated. Thus a housing design was developed which allowed the spectrometer to be mounted at the specified angle and to rotate at the stated speed. The instantaneous field of view of -5° below the horizon to the zenith and footprint provided by the instrument rotation are shown in Figure 2.14. This Figure shows the extent over which the measurements are representative assuming a 5 km visibility; it is clear that this technique will be able to provide information over entire urban areas as the footprint of the two instruments has covered the city centre of Bologna and surrounding areas.
Figure 2.14: Shows the two FOV and footprints for the two deployed instruments during the PEGASOS campaign, with the top panel showing Bologna city centre which is enclosed within a circular ring road, seen in yellow on the map.

The CityScan housing was designed and constructed by Magna Parva Ltd of Coalville UK, and is designed to be weatherproof and thermally stable. A fundamental element of the design was the rotation of the head unit. The base unit remains stationary whilst the head unit rotates at a rate of one degree per second.
in a smooth rotation. This rotation speed and direction can be controlled using the programmable stepper motor. In order to make power available in the head unit, a slip ring runs through the pillar which joins the head and base together. A further design feature is that the head and base units can be separated to make the instrument more portable. Along all panel edges rubber seals were used to ensure that the instrument was waterproof and any panels which weren’t required to be removable had silicon sealant applied.

2.3.2.1 Instrument Control

The rotation of the head unit is controlled using a stepper motor which can be programmed to rotate in a single direction continually or to rotate between two angles. The ability of the instrument to move back and forth between two discrete points is particularly useful in deployment locations where some of the field of view is obstructed, e.g. by tall buildings, and hence in a full rotation there would be large areas of data which would have to be discarded.

All processing and data collection within the head unit is controlled using software written by Roland Leigh, Oliver Blake, Duncan Ross and Tony Abbey at the University of Leicester in IDL v7.0. The main instrument control software is used to manage all components within the instrument including the operation mode, the exposure time, the integration time, the temperature of the instrument, the temperature management systems, the CCD settings (including binning and readout modes), the shutter settings, the calibration unit settings, the TEC power and the external shutter. The spectral collection software also contains automatic exposure time control which, depending upon the saturation level of the previous frame collected, will adjust the exposure time of the next frame accordingly within a minimum and maximum range.
2.3.2.2 Data Collection and Transfer

Within the CityScan instrument a network is created which both head and base computers connect to. This allows the data collected in the head unit to be transferred to the base unit computer wirelessly, where it can be saved to either an external hard drive or uploaded to a server depending on the availability of an Ethernet connection in the deployment location. The spectral data collected in each exposure is co-added for the specified integration time and then saved as a .tiff file which can then be analysed at a later date. A log file is also recorded which contains information relating to each saved .tiff file including the azimuth angle, integration time, all of the temperature information. Spectral data and environmental data are all transferred along with webcam images. This method was developed in order to prevent the head unit computer needing to manage both data collection and storage.

2.3.3 Environmental Monitoring and Control

In order to maintain a stable environment in which the spectrometer and computers can operate, temperature stabilisation features were included in the design such as heaters, fans and temperature and humidity monitors. The environmental monitor data which are collected in the head unit, i.e temperature and humidity sensors are analysed in real-time to control the heating systems within the head-unit. Feedback loops control the fans or heaters depending on the temperature recorded. There are temperature sensors both inside the spectrometer and the head unit. Within the spectrometer the temperature of the CCD and cold finger were also both recorded in order to monitor the effectiveness of the CCD cooling method. In order to help to achieve a thermally-stable system, the instrument casing has a brushed aluminium finish to reflect as much light as possible. Figure 2.15 shows temperature data recorded over a three day period during June on a field campaign held in Bologna,
Italy. The temperature control was found to be less effective than originally envisaged with the initial design stating a CCD operating temperature of 10 °C and a mean measured temperature over this period of 17.9 °C. As the temperature of the CCD is higher than originally planned the CCD dark current will also be higher than the specification. Some potential reasons for the CCD cooling being less effective than originally specified are that the TEC may have been operated at too low a voltage, there might be an air gap between the CCD or cold finger and that the external heat sink did not dissipate the heat as effectively as it needed to.

Two webcams are mounted in the CityScan head unit below the spectrometer window. They provide a combined vertical field of view of 120°. Webcam images are collected at regular intervals from two webcams mounted below the main entrance window of the instrument providing useful context to the measurements. These images are collected every 15 seconds and can be used to reconstruct an image of the situation in which the measurements have been taken. They can also be used to monitor any variation in the horizontal measurement position of the instrument. The head unit was designed to stay level after continuous use but the webcams provide a method of monitoring this. An example panoramic image which can be built up from six minutes of web cam data is shown in Figure 2.16. This data is very useful in order to provide some context to the trace gas measurements taken with the CityScan instruments, showing the location of obstructions in the field of view or areas of cloud cover.

2.3.4 The Data Processing Chain

The steps between raw count data to final slant column concentrations are shown in the flowchart in Figure 2.17. The first step in the processing chain is to perform a rough wavelength calibration using an instrument-specific wavelength correction.
Figure 2.15: Top plot: temperature measurements from CS1’s internal temperature monitors, including CCD and cold finger temperatures. Bottom plot: shows ambient temperature.

which will be described in section 2.4.1

Following this, the spectra are extracted by row for a specific wavelength window and saved as .spe files to be analysed using QDOAS, a DOAS analysis software.
which runs on Linux machines. The .spe file and previously calculated .ref, reference file, are then imported into QDOAS for analysis using an instrument specific .xml settings file. The .ref file has been created separately and consists of a row specific wavelength calibrated wavelength grid and spectra from a relatively unpolluted and clear sky day during the current campaign. The .xml defines the fitting parameters used which will be discussed in the following section. QDOAS then outputs a file of predefined output parameters per binned row of the CCD. An azimuthal correction is then applied within the data analysis software which is dependent on the time stamp of the instrument. This correction needs to be applied to correct for errors in the rotation time for the instrument. The approximate error in the instrument rotation is $5^\circ$/hr. The curved FOV is then corrected using the calibration data which has been collected and has been discussed in Section 2.3.1.3. The resulting data is then finally smoothed by averaging over $3^\circ$ azimuthally to produce a panorama of CityScan data every six minutes.

Figure 2.16: Six minutes’ worth of webcam data collected from two webcams with an image taken every 15 seconds built up to give a full panoramic ($360^\circ$ image.)
Figure 2.17: Flow chart of the data processing chain used in the CityScan data analysis
2.3.4.1 Fitting Parameters used for Analysis

QDOAS version 2.0 [9] was used to perform the DOAS fit for the CityScan instrument in this work. The fitting parameters used in the QDOAS fit are shown in table 2.2. Where a wavelength dependent Gaussian has been applied this is calculated by QDOAS during the wavelength calibration that outputs the FWHM which can then be applied to the cross sections by QDOAS during the analysis.

<table>
<thead>
<tr>
<th>Fitting Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting Window</td>
<td>428 to 495 nm</td>
</tr>
<tr>
<td>Reference File</td>
<td>A row specific reference taken from the afternoon of the 'clean', clear sky day of the 9th June 2012</td>
</tr>
<tr>
<td>Line Shape</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Solar Reference</td>
<td>Kurucz solar atlas [43]</td>
</tr>
<tr>
<td>Wavelength Calibration</td>
<td>NLLS fit of object and reference spectrum to solar reference.</td>
</tr>
<tr>
<td>Order of Polynomial</td>
<td>Fourth order</td>
</tr>
<tr>
<td>Cross Sections</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Wavelength Dependent Gaussian with I$_0$ correction ($1 \times 10^{16}$ mol/cm$^2$ at 294 K [80])</td>
</tr>
<tr>
<td>O$_4$</td>
<td>Wavelength Dependent Gaussian [28]</td>
</tr>
<tr>
<td>Ring</td>
<td>QDOAS Calculated Wavelength-Dependent Gaussian pre-convolved with the instrument line shape</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Wavelength-Dependent Gaussian, from the HITRAN database [69]</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>Wavelength-Dependent Gaussian</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Wavelength-Dependent Gaussian with I$_0$ correction ($1 \times 10^{20}$ mol/cm$^2$ at 223 K [111])</td>
</tr>
</tbody>
</table>

Table 2.2: Fitting parameters used for the DOAS fit in QDOAS specified in the .xml file.
2.3.4.2 Trace Gas Cross Sections

The Beer-Lambert Law outlined in Equation 1.24 is the basis of the DOAS technique. This equation includes the absorption cross-section $\sigma$. The absorption cross-section describes the extent to which photons are absorbed by gaseous species at different wavelengths. In the wavelength region of interest in this study the main absorbers are NO$_2$, the oxygen dimer (O$_4$), ozone, water vapour and glyoxal. In order to improve the DOAS fit for a trace gas of interest, a fitting window must be selected which maximises the absorption features of the trace gas of interest whilst minimising the effect of the other trace gas absorbers; the window chosen should also ideally avoid strong Fraunhofer signatures present in the solar radiation. Discussed in the following section are the absorption cross sections of the absorbers within the chosen fitting window. The absorbers included in this analysis are shown in Figure 2.18.

Within the fitting window used in this work, NO$_2$ has both broadband and fine structure, and this narrowband structure makes NO$_2$ an ideal candidate for DOAS as the DOAS method relies upon being able to separate narrow structures from broadband features. It is important to note that the absorption cross section has a strong temperature dependence, and that changes in temperature result in changes in depth of the fine absorption structure [79], see Figure 2.19. As this work focuses on urban air quality, the 294 K temperature dependent cross section was used in this work’s analysis.

The NO$_2$ absorption cross section is convolved with an I$_0$ correction within QDOAS the result of this convolution is shown in Figure 2.20.

O$_4$ is the oxygen dimer, a collisional complex which has a well-defined profile only slowly varying with changes in atmospheric pressure [28]. This makes measurements of O$_4$ very useful when using the DOAS method as it gives an indication of the photon path length through the atmosphere [84]. When this derived path length
Figure 2.18: The trace gas absorption cross sections used in this work, top row left to right: NO$_2$ at 293 K, O$_4$, middle row from left to right: the ring spectrum glyoxal and bottom row from left to right: water vapour and ozone at 223 K. Highlighted on each is the fitting window use in this work.

is used in conjunction with radiative transfer modelling, O$_4$ measurements provide information on the scattering properties of the atmosphere and thus also give aerosol information. Within the fitting window used in this work, O$_4$ has some strong
Figure 2.19: NO$_2$ absorption cross sections recorded at 203 (pink) and 294 K (blue), demonstrating the temperature dependence of the NO$_2$ absorption features.

Figure 2.20: NO$_2$ absorption cross section used convolved with an $I_0$ correction.
absorption features, these can be seen in the cross section summary shown in Figure 2.18.

The ozone absorption cross section used in this work is seen in Figure 2.18; this cross section contains both narrow and broadband features. This part of the ozone absorption cross section is within the Chappuis bands. The absorption bands for ozone within the UV, visible and near-infrared regions are seen in Figure 2.21 to put this part of the cross section into a wider context. Similar to NO$_2$, ozone has a temperature dependent cross section thus the correct cross section for the measurement situation needs to be identified and selected. For the results in this thesis, the main ozone absorption occurs in the stratosphere and therefore the O$_3$ cross section measured at 223 K were applied to these analyses.

![Ozone absorption cross section over the visible region](image)

Figure 2.21: Ozone absorption cross section over the visible region [58].

Water vapour is also a significant absorber in the fitting window used in this work and must therefore be accounted for. The water vapour cross section used here is shown in Figure 2.18; it is clear that there are several note-worthy absorption features centred around 445 nm and 470 nm.
The final trace gas absorption cross section used in this work is that of glyoxal which has a highly structured absorption cross section in the 420–460 nm region of the fitting window. However glyoxal is a weak absorber at standard concentrations in this fitting window. Standard concentrations of glyoxal in polluted urban environments such as Mexico City rarely exceed 1 ppbv whilst NO₂ often measures over 50 ppbv [83].

2.3.5 Deployment Design Considerations

An important part of the instrument design was that CityScan should be easy to deploy in various locations. To this end, each CityScan unit can be separated into three parts which are more transportable than moving it as a complete unit. CityScan has three mounting points on its base, these are shown in Figure 2.22. The instruments feet also contain anti-vibration mounts which mean that it is possible to install the instrument in a variety of locations, including airports.

The fixing points on the base of the CityScan units were then fixed to an aluminium frame that could be secured in a deployment location. An example of a CityScan unit deployed on a rooftop is shown in Figure 2.23. This Figure shows the mounting system developed that was used for several deployment locations. This image is from a deployment in Bologna, Italy which will be discussed later in this work in Chapters 4 and 5. In order to aid temperature stabilisation in the height of summer in Italy an air conditioning unit was attached to the base unit in order to try to maintain a temperature that was suitable for the spectrometer and computers to operate in. The ducting for the air conditioner can be seen in the image as can the tarpaulin which was used to keep the air conditioning unit waterproof.

Another important deployment feature was the use of an uninterpretable power supply. This meant that the CityScan units would continue to work in the event of
Figure 2.22: The design of the fixing points for CityScan, viewed from beneath the instrument.

2.4 Design Performance

Due to time constraints only one of the three CityScan instruments was characterised fully here. This instrument will be referred to as CS1 throughout this work. Data presented from the two other instruments in this work should be considered to be preliminary data.

2.4.1 Wavelength Calibration

Performing an accurate wavelength calibration before performing a DOAS fit is crucial as misalignment of wavelength grids between the reference and object spectrum...
can cause large errors in the retrieved DSCD. The wavelength calibration of the instrument has been briefly studied using a spectrum taken of the internal mercury calibration lamp. This spectrum cannot be used to look at the FWHM of the instrument line shapes as it was taken internally, whereas all external measurements used further in this work were performed after an external aperture had been installed in front of the entrance optics. This entrance aperture significantly improved the ILS of the instrument. The spectra collected using the internal mercury lamp however gives a good indication of the wavelength shift that needed to be applied to the measured spectra and are also good indicators of the very small instrument smile discussed in the following section.
Figure 2.24: Top: A mercury emission spectrum as measured by the CityScan spectrometer. Bottom: The modelled emission spectrum.
The measured mercury internal lamp spectrum is shown here in Figure 2.24 with a modelled version of what a mercury emission spectrum should look like when imaged using the CityScan spectrometer below it. The strongest mercury emission lines are imaged at 435.8, 546.1 and a doublet centred around 578.2 nm (576.96 and 579.06 nm). A small wavelength shift needs to be calculated and applied to these measurements in order for them to exactly match the modelled spectrum, however it is very clear that the levels of smile in the spectra are very low; this will be quantified in the following section.

A rough wavelength calibration is performed before analysis in QDOAS. This is calculated by plotting a scattered sunlight spectrum measured using each of the CityScan instruments against a reference solar spectrum pre-convolved with the instrument line shape. Through an iterative process the two spectra are matched by adjusting the starting wavelength and sampling of the CityScan instrument. This calculation is performed for each individual instrument. The corrected wavelength grids for all three of the CityScan instruments are plotted in Figure 2.25. This demonstrates how small differences in instrument alignment can have a significant impact upon the wavelength calibration, with there being 12 nm shift between CS1 and 3.

An investigation into the effectiveness of the wavelength calibration procedure in QDOAS was performed. It was important to assess whether this calibration was necessary as it significantly lengthens the time taken to perform the DOAS fit in QDOAS. Six minutes’ worth of CityScan data were analysed using QDOAS, from elevation angle 5° on the 6th of June 2012; with just the reference spectra being wavelength calibrated and with both the object spectrum and reference being calibrated. The resulting NO₂ differential slant column densities and RMS values were assessed. Figure 2.26 shows the result of this test.
It is clear that there is a significant increase in RMS values when the wavelength calibration isn’t performed (an average of 32.3% increase in RMS is measured in this six minute period); this will cause larger errors in the retrieved DSCDs and thus it was determined that it was necessary to use wavelength calibrated object spectra. By comparing the subsequent DSCDs it is clear that by enabling the wavelength calibration the very high variability structure is removed. This can be seen in Figure 2.27. The variability in the NO$_2$ DSCD measured over this six minute period is relatively large owing to the elevation angle that has been chosen to study. The 5° elevation angle measures on the top border of the boundary layer and as such can be highly variable dependent on boundary layer height with azimuth.

The instrument line shape has been characterised over the fitting window selected using QDOAS for CS1. This is performed in six discreet sub-windows between 428 and 495 nm. ILS values are recorded for each individual row during the QDOAS calibration procedure. The results of this are shown in figure 2.28. It is clear that the
Figure 2.26: Difference in RMS when QDOAS analysis is performed with and without the wavelength calibration procedure for the object spectrum. Shown are the values of the RMS with a wavelength calibration (red), without a wavelength calibration (blue) and the difference between the two (pale blue).

The instrument line shape varies both with wavelength and row upon the detector usually between 1.5 and 2.5 nm. The variation seen with row is thought to be attributable to the changes in entrance slit width. The calculated ILS for the bottom 5 rows is much larger than for the rest of the detector owing to the entrance slit width at this point being very large. The measured instrument line shapes are higher than the original target FWHM specified, however they are shown in this work to be sufficient to perform a DOAS fit for a highly structured absorber such as NO₂.
Figure 2.27: DSCDs produced by QDOAS with (blue) and without (red) the object spectrum wavelength calibration feature and the difference between the two (pale blue).
Figure 2.28: Instrument Line Shape FWHM by row over the DOAS fitting window in six discreet sub-windows.
2.4.2 Instrument Smile

The ‘smile effect’ can also be referred to as the spectral line curvature. It is an effect seen in imaging spectrometers and describes the non-uniform imaging of the spectral range across the detector. There are several possible causes of this including spatial distortions caused by the dispersive element, in this case the grating, or by aberrations in the focusing optics. The smile effect needs to be characterised and corrected for in order to establish a consistent wavelength grid across the detector. The instrument smile has been evaluated by studying the spectral shift seen by row. This analysis has been performed by looking for specific minima in a scattered sunlight spectrum taken by CS1 associated with Fraunhofer lines. The original CCD image is shown in Figure 2.29 and it is clear from visual inspection that there is minimal smile associated with the spectrometer, however more thorough investigation is required as very small differences in wavelength grid by row would be difficult to see in this figure.

The lines studied here are those at 434, 486 and 518 nm. these lines were chosen as they are some of the strongest Fraunhofer lines within the wavelength range measured. These signals were identified by pin pointing the measured minima within a given window surrounding the theoretical Fraunhofer line wavelength. These points were recorded for each row of the detector which allows the shift between individual rows to be seen, thus giving a measure of the instrument smile. It is clear that there is very little smile seen using this spectrometer as demonstrated in Figure 2.30. the shift between rows is generally within 1 nm, except for the first few rows of the detector. The spectral shift from the first 10–20 rows are likely to be unreliable as a measure of instrument smile as there is very little illumination at the bottom of the detector as seen in Figure 2.29, this will produce a very weak spectral signature thus making peak positioning less accurate; hence the bottom 10 rows will be ignored in
Figure 2.29: Example CCD Image of Measured Scattered Solar Spectra used to Investigate the Instrument smile

the smile analysis.

A second measure of the instrument smile has been collected within the QDOAS calibration procedure with the spectral shift being measured by row over the fitting window in six sub-windows. The results of this analysis is shown in Figure 2.31.
Figure 2.30: Individual Fraunhofer lines plotted by Row of the Detector; chosen lines are 434 nm (black), 486 nm (red) and 518 nm (green).
Figure 2.31: Spectral shift by row as calculated by the QDOAS calibration procedure over the DOAS fitting window in six discreet sub-windows.
The spectral shift shown in Figure 2.31 is consistently below 1 nm and shows little evidence of instrument smile, with the changes variation following the changes in ILS rather than showing obvious curvature in the wavelength grid.

### 2.4.3 Measurements of Stray Light

Stray light within the instrument can be caused by reflections of incident photons off both optical and non-optical elements of the spectrometer such as the optical mounts and spectrometer walls and feedthroughs. It can also originate from higher diffraction orders from the grating. If this stray light is imaged by the CCD it can cause errors in the retrievals. The main source of stray light was observed to be along the edge of the CCD at the lowest wavelength end of the CCD, as can be seen in Figure 2.29. The cause of this stray light is a gap along the edge of the CCD allowing light from the entrance optics to be seen. This source was minimised using a rapid prototyped baffle. As this part of the CCD is not used in the DOAS fitting window, it should not affect the retrieved slant columns and can therefore be ignored. Other stray light appears to have very little effect on the DOAS fit and so is assumed to be negligible.

### 2.4.4 Measurements of Dark Current

Dark current causes there to be a non-zero baseline in conditions where there is no light entering the spectrometer. This is caused by thermal energy within the CCD creating electrons. Dark current has been found to vary from pixel to pixel and also over time. Reducing the operating temperature of the CCD minimises the dark current. Unfortunately here the active cooling was less effective than originally planned and therefore the dark current was higher than specification. The effect of temperature on dark signal can be seen in Figure 2.32 which shows the dark signal as
calculated from the manufacturer’s performance testing. A measure of dark signal at 248K was provided as 0.285 e⁻/pix/s. This value can be used in conjunction with equation (2.1) (provided by the manufacturer) to calculate dark signal at various temperatures.

$$\frac{Q_d}{Q_{do}} = 1.4 \times 10^6 T^3 e^{-9080/T}$$

(2.1)

Where \(Q_{do}\) is the dark current at 293 K and \(Q_d\) is the dark signal at temperature \(T\). This relationship is only valid between temperatures of 248 and 300 K.

Figure 2.32: Calculated dark current of the detector using the manufacturers performance test results.

Measurements of the dark signal on the detector were taken in a blacked out laboratory. Due to the software used to control the CityScan spectrometer the dynamic exposure time control meant that exposure times were automatically set to
the maximum value of 10 seconds. The dark signal changes with different exposure times and so this measurement cannot be applied to spectra taken with other exposure times. An alternative method for calculating the dark signal was developed which took a dark signal measurement from a CCD image captured during normal operation where the bottom part of the CCD was not exposed to light. This dark signal spectrum was then used as a template for measurements from different rows of the detector. Using the spectra measured in the blacked out laboratory, a function was calculated which accounted for the change in dark signal across the detector. It was assumed that the relative dark signal between rows would change linearly with changes in time and thus this function could be applied to the dark current template. The output from this calculation is shown in Figure 2.33.

Figure 2.33: Calculated Dark Signal

It is clear that there is a step change in the magnitude of dark signal with the different nodes of the detector. This is clarified in Figure 2.34 which is the calculated dark signal for a single row and column of the detector. The detector has four nodes and the step changes between these are seen in both lines. The main source of stray light is also very clear in both plots. Along the left hand edge of the detector there is a significant stray light signal. As this area is not within the fitting window it is assumed not to be a source of significant error in any derived slant columns. It is also important to note that the structured narrow-band features which are visible in Figure 2.34 are not caused by dark current as described previously but are due
to power supply noise. This power supply noise varies over time and was therefore very difficult to remove from the measurements.

![Calculated Dark Signal for a Single Row and Column of the Detector](image)

Figure 2.34: Calculated Dark Signal for a single row (black) and column (blue) of the detector taken as cut-throughs of Figure 2.33

2.5 Discussion of CityScan Spectral Fits

The spectral fits produced in QDOAS are analysed in this section to access the performance of the DOAS fitting process. Spectral fits are completed for NO\textsubscript{2}, O\textsubscript{4}, H\textsubscript{2}O, glyoxal, O\textsubscript{3} and the ring spectrum. Representative examples of the QDOAS fits have been chosen for the 6th and 13th of June 2012. The two example days are of interest for comparison because the 6th of June was a clear sky day whilst the 13th of June was a cloudy day with a high pollution event. These two days should
offer contrasting scenarios that provide a useful comparison. Spectral fits will also be shown for several viewing angles (elevation) on these days.

The spectral fits for the 6th of June at 11:57 are shown in Figures 2.35 and 2.36 for rows 15 and 40 of the detector respectively. Rows 15 and 40 of the detector correspond to elevation angles 7° and 25° respectively. These two elevation angles have been chosen to study because the 7° elevation angle is a line of sight that has a major absorption component in the boundary layer, whilst the 25° elevation angle measures a line of sight with a smaller boundary layer component. Therefore, the two views offer a useful contrast in terms of pollution levels. The most distinct difference between the spectral fits for these two elevation angles is seen in the NO₂ spectral fit. The retrieved NO₂ SCD for the 7° elevation angle (4.79 x 10^{16} \text{ mol cm}^{-2}) is more than double that of the 25° elevation angle (1.29 x 10^{16} \text{ mol cm}^{-2}) with slant column errors of 3.36 x 10^{15} \text{ mol cm}^{-2} and 3.52 x 10^{15} \text{ mol cm}^{-2} for row 15 and 40 respectively. An assessment of the quality of the fit is made by looking at the magnitude of the residual structure which remains after the fitting process. The residual structure, as quantified by the RMS of the residual spectrum, is approx 5.5% smaller in the 7° angle’s fitted spectra than for the 25° angle.

The spectral fits for ozone, water vapour and glyoxal are poor and therefore will not be used further in this work because the retrieved column amounts for these absorbers are regularly below the retrieval uncertainties on their slant column amounts, error bars are shown on slant column amounts for all species in Figures 2.35 to 2.40. The O₄ spectral fit quality varies with atmospheric conditions, mainly changes in cloud cover and as such will be discussed further in the rest of this work. The O₄ spectral fits provided in Figures 2.35 and 2.36 are negative. Negative values in the spectral fit indicate that the slant column amount of O₄ is greater in the reference used owing to a longer path length at the reference time period. This
longer path length may be a result of higher aerosol loading leading to increased scattering or very low aerosol loading leading to high visibility during the period at which the reference was collected.

In order to assess the performance of the DOAS fitting procedure in different scenarios a contrasting day (the 13th of June), in terms of meteorology and pollution, has been chosen to compare to the spectral fits from the 6th of June. The conditions on this day will be discussed in greater detail in Chapter 5, but in brief the meteorology was dominated by a large hail and lightning storm at approximately 13:00 local time. This storm was preceded by a build up of thick cloud and was followed by a high-pollution event that was observed in all azimuth angles in the lowest 10-25° elevation angles.
Figure 2.35: Spectral fits for data taken at 11:57 of the 6th of June 2012 on row 15 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO$_2$ at 293 K, O$_4$, the ring spectrum, water vapour, the fitted polynomial, O$_3$ at 223 K, the residual structure and glyoxal. The retrieved NO$_2$ slant column is $4.79 \pm 0.34 \times 10^{16}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $-5.20 \pm 1.12 \times 10^{22}$ mol cm$^{-2}$, $1.68 \pm 2.31 \times 10^{18}$ mol cm$^{-2}$, $-8.63 \pm 2.10 \times 10^2$ mol cm$^{-2}$ and $8.43 \pm 19.8 \times 10^{14}$ mol cm$^{-2}$ respectively. The RMS of this fit is $2.01 \times 10^{-3}$. All measured spectra are plotted in red.
Figure 2.36: Spectral fits for data taken at 11:57 of the 6th of June 2012 on row 40 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO$_2$ at 293 K, O$_4$, the ring spectrum, water vapour, the fitted polynomial, O$_3$ at 223 K, the residual structure and glyoxal. The retrieved NO$_2$ slant column is $1.29 \pm 0.35 \times 10^{16}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $-1.08 \pm 0.12 \times 10^{43}$ mol cm$^{-2}$, $-5.97 \pm 2.43 \times 10^{18}$ mol cm$^{-2}$, $-8.76 \pm 2.21 \times 10^2$ mol cm$^{-2}$ and $-3.51 \pm 2.08 \times 10^{15}$ mol cm$^{-2}$ respectively. The RMS of this fit is $2.12 \times 10^{-3}$. All measured spectra are plotted in red.
Figures 2.37, 2.38 and 2.39 respectively show fits for rows 15, 40 and 60 from data collected during the main storm activity at 13:05. Row 60 of the CCD equates to approximately 40° elevation angle. As seen in the previous example the NO\textsubscript{2} fit improves with an increased slant column density of NO\textsubscript{2}. In the row 15 example in Figure 2.37 the fit is significantly better both visually and in terms of RMS than the row 40 spectral fits in Figure 2.38 with the RMS improving from 5.19 x 10\textsuperscript{-3} to 4.54 x 10\textsuperscript{-3} with decreasing elevation angle. The error on the NO\textsubscript{2} slant column in all rows at this time period is between 8.18 x 10\textsuperscript{15} mol cm\textsuperscript{-2} and 8.9 x 10\textsuperscript{15} mol cm\textsuperscript{-2}. The error on the NO\textsubscript{2} slant column seen here is more than double the error on the spectral fits shown for the 6th of June. A likely cause of this increase in error is the thick clouds in the field of view at this time on the 13th of June that alter the scattering properties significantly and introduce further errors into the spectral fit. The likely cause of the increase in errors in the fit is the reduced solar intensity measured during cloudy periods resulting in lower signal on the CCD and therefore a lower signal to noise ratio. The O\textsubscript{4} spectral fits plotted in Figures 2.37, 2.38 and 2.39 shows an improvement with increasing elevation angles owing to an increasing retrieved column amount. The error on these O\textsubscript{4} DSCDs remain relatively constant for all three rows studied (varying from 2.54-2.89 x 10\textsuperscript{42} mol cm\textsuperscript{-2}). The spectral fit for O\textsubscript{4} is significantly improved in the row 60 plot where there is the highest column amount of O\textsubscript{4} retrieved. The likely cause of this is that there is thick cloud in the field of view of the row 60 plots and therefore the light path of the measured photons has been lengthened owing to additional multiple scattering. This path length enhancement causes retrieved amounts of O\textsubscript{4} to increase owing to the longer light path through the absorber.

Finally, Figure 2.40 shows a spectral fit for a pollution event observed on 13th June. The spectrum was acquired on row 15 of the detector at 14:59:53, and at this
Figure 2.37: Spectral fits for data taken at 13:05 of the 13th of June 2012 on row 15 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO$_2$ at 293 K, O$_4$, the ring spectrum, water vapour, the fitted polynomial, O$_3$ at 223 K, the residual structure and glyoxal. The retrieved NO$_2$ slant column is $6.60 \pm 0.82 \times 10^{16}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $2.43 \pm 0.25 \times 10^{13}$ mol cm$^{-2}$, $2.52 \pm 0.53 \times 10^{19}$ mol cm$^{-2}$, $-2.96 \pm 48.3 \times 10^{4}$ mol cm$^{-2}$ and $4.99 \pm 4.62 \times 10^{15}$ mol cm$^{-2}$ respectively. The RMS of this fit is $4.54 \times 10^{-3}$. All measured spectra are plotted in red.
Figure 2.38: Spectral fits for data taken at 13:05 of the 13th of June 2012 on row 40 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO\textsubscript{2} at 293 K, O\textsubscript{4}, the ring spectrum, water vapour, the fitted polynomial, O\textsubscript{3} at 223 K, the residual structure and glyoxal. The retrieved NO\textsubscript{2} slant column is 6.50 ± 0.86 x 10\textsuperscript{16} mol cm\textsuperscript{-2}, with O\textsubscript{4}, O\textsubscript{3} at 223 K, Water Vapour and Glyoxal being retrieved at 3.21 ± 0.29 x 10\textsuperscript{43} mol cm\textsuperscript{-2}, 2.02 ± 0.60 x 10\textsuperscript{19} mol cm\textsuperscript{-2}, 1.07 ± 0.54 x 10\textsuperscript{3} mol cm\textsuperscript{-2} and 2.54 ± 0.51 x 10\textsuperscript{16} mol cm\textsuperscript{-2} respectively. The RMS of this fit is 5.19 x 10\textsuperscript{-3}. All measured spectra are plotted in red.
Figure 2.39: Spectral fits for data taken at 13:05 of the 13th of June 2012 on row 40 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO$_2$ at 293 K, O$_4$, the ring spectrum, water vapour, the fitted polynomial, O$_3$ at 223 K, the residual structure and glyoxal. The retrieved NO$_2$ slant column is $4.42 \pm 0.89 \times 10^{16}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $4.36 \pm 0.26 \times 10^{13}$ mol cm$^{-2}$, $1.50 \pm 5.52 \times 10^{18}$ mol cm$^{-2}$, $1.38 \pm 0.51 \times 10^{3}$ mol cm$^{-2}$ and $1.63 \pm 0.49 \times 10^{16}$ mol cm$^{-2}$ respectively. The RMS of this fit is $4.12 \times 10^{-3}$. All measured spectra are plotted in red.
time the pollution was confined to elevations below 30°. The NO\textsubscript{2} fit shown in Figure 2.40 has less than a 3% error on it (1.62 x 10\textsuperscript{17} mol cm\textsuperscript{-2} with a slant column error of 4.31 x 10\textsuperscript{15} mol cm\textsuperscript{-2}) and is considerrably more reliable than the fits from days with lower NO\textsubscript{2} SCDs such as those measured the 6th of June (approximately 1-5 x 10\textsuperscript{16} mol cm\textsuperscript{-2}), where the error on a retrieved slant column of NO\textsubscript{2} is between 10 and 25%. Of the three clear sky scenarios shown in this section (on the 6th of June and at 14:59 on the 13th of June) the slant column errors remain between 3.36 x 10\textsuperscript{15} mol cm\textsuperscript{-2} and 4.31 x 10\textsuperscript{15} mol cm\textsuperscript{-2} with RMS values of 2.01 x 10\textsuperscript{-3} to 2.59 x 10\textsuperscript{-3}. This result indicates that CityScan has a NO\textsubscript{2} detection limit of approximately 4 x 10\textsuperscript{15} mol cm\textsuperscript{-2} on clear sky days. As discussed previously in relation to the measurements shown in Figures 2.37 to 2.39 the error on the NO\textsubscript{2} slant column increases in cloudy situations and the detection limit in cloudy conditions is calculated to be more than double that on clear sky days at 8.6 x 10\textsuperscript{15} mol cm\textsuperscript{-2}.

The difference between the spectral fits of NO\textsubscript{2} during a high pollution event and on an average day indicate that the best error on the slant column of NO\textsubscript{2} retrieved which can be achieved using CityScan is a 3% error on a DSCD of 1.62 x 10\textsuperscript{17} mol cm\textsuperscript{-2}. This error can be up 25% on days without high pollution events, where retrieved DSCDs are as little as 1.29 x 10\textsuperscript{16} mol cm\textsuperscript{-2}. The slant column error for NO\textsubscript{2} in both of these scenaros shows very little variation with the extremes being 3.36 and 4.31 x 10\textsuperscript{15} mol cm\textsuperscript{-2} reinforcing the stated detection limit of 4 x 10\textsuperscript{15} mol cm\textsuperscript{-2} on clear sky days.
2.6 Initial Measurements

CityScan was deployed in Bologna, Italy throughout June 2012 as described in Chapter 4. The deployment location, instrument performance and data processing chain will not be discussed here as they will be covered elsewhere in this work in Chapters 4-6. The purpose of this section is to introduce and describe the data output format which will be used when presenting CityScan data in subsequent chapters of this thesis.

2.6.1 Nitrogen Dioxide Measurements Data Output

Each CityScan instrument produces very large volumes of data, up to 2.5 GB per day of data from the CCD alone; with extra data being recorded by the webcams and other environmental sensors. Due to these large data volumes a method of visualising the data in an easily accessible format needed to be devised. The method chosen was to plot out six minutes’ worth of CityScan data as a full hemispherical panorama. This method produces a concentration map of the trace gas of interest which can be very illustrative of the spatial variability of trace gas concentrations within an urban environment. An example set of the panoramas produced in the CityScan analysis software is shown in Figure 2.41 with the measured DSCD of NO$_2$ being seen in the top panel.

This Figure shows several panoramas within separate panels. These panoramas show the potential range of information which can be available using a CityScan instrument. Currently the data analysis has been optimised primarily for NO$_2$, O$_4$ and H$_2$O and therefore the other DSCD products should be taken as preliminary data; they are only shown here to demonstrate the potential wealth of information which in future, it may be possible to obtain. The RMS error, ratio and intensity plots are also robust outputs which will be used later in this work. There are
Figure 2.40: Spectral fits for data taken at 13:05 of the 13th of June 2012 on row 40 of the CCD (binned). Top panel shown the measured spectrum (red) with the reference spectrum (black). Panels left to right from top to bottom are fitted NO$_2$ at 293 K, O$_4$, the ring spectrum, water vapour, the fitted polynomial, O$_3$ at 223 K, the residual structure and glyoxal. The retrieved NO$_2$ slant column is $1.62 \pm 0.043 \times 10^{17}$ mol cm$^{-2}$, with O$_4$, O$_3$ at 223 K, Water Vapour and Glyoxal being retrieved at $3.14 \pm 0.14 \times 10^{43}$ mol cm$^{-2}$, $1.57 \pm 0.29 \times 10^{19}$ mol cm$^{-2}$, $7.53 \pm 2.70 \times 10^2$ mol cm$^{-2}$ and $2.67 \pm 25.5 \times 10^{14}$ mol cm$^{-2}$ respectively. The RMS of this fit is $2.59 \times 10^{-3}$. All measured spectra are plotted in red.
also some artefacts which are visible in these panoramas including the patches of missing data around the sun; this is caused by the instrument saturating when looking towards the sun, which prevents a successful DOAS fit in this region. In order to explain the format of the panoramas further, shown in Figure 2.42 is just a NO$_2$ DSCD panorama for the same time period. Marked on this panorama are the viewing directions with north being in the centre of the panorama and the viewing elevation angles. It is clear in this panorama the level of information that can be obtained about the spatial variability of NO$_2$. Here, there are areas of high NO$_2$ concentrations in the southern half of the panorama, with the northern region showing cleaner air masses become obvious. The causes of this will be discussed in greater detail in chapter 4. Another issue clear in the panoramas is horizontal striping of the data in the higher elevation angles, the cause of which is unknown but it is almost certainly an instrument artefact, potentially caused by changes in the width of the entrance slit and thus variations in the instrument line shape along the CCD.

This panoramic format has been shown to be useful for scanning through large amounts of data quickly, more in depth analysis will be preformed in subsequent chapters to study trends and spatial distributions of trace gases in more detail.

2.7 Instrument Design and Performance Summary

Three CityScan instruments have been constructed and deployed as part of this study. Many of the design features which were originally outlined have been achieved, such as the FOV of the instrument. However the largest challenge during this work has been to minimise the impact on the measurements of those specifications which have not been met. During this project hemispherical DOAS measurments have successfully been made, collected and analysed. These measurements have proven
the design concept to be sound even where some of the target specifications have not been met. The specifications which haven’t been met include the instrument line shape of the instrument (without the corrective aperture), the entrance slit width and the temperature stabilisation system. The major spectrometer characteristics which have been discussed in this chapter are summarised in table 2.3.
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Table 2.3: Specifications of the CityScan spectrometer used in this work with the target specifications where applicable; coloured text indicates whether target specifications were met (green), not met (red) or partially met (orange).
Figure 2.41: Example CityScan output. Shown in the top panel is NO$_2$ DSCD with (moving from left to right and top to bottom) the webcam images, O$_4$ DSCD ($\times 10^{44}$), RMS error, water DSCD, the ratio of the spectral pixels 100:400, the intensity of pixel 100, O$_3$ DSCD and glyoxal DSCD.
Figure 2.42: Example NO$_2$ DSCD panorama as produced by CityScan.
Chapter 3

Hemispherical Radiative Transfer Modelling

3.1 Motivation for a Modelling Study

When using a scattered sunlight measurement it is very difficult to calculate the path length of the measured light, which is classically, the basis of using absorption spectroscopy as an analytical technique. Therefore, in order to interpret the scattered sunlight measurements which are the subject of this work correctly, an understanding of the radiative transfer through the atmosphere is required. The SCD measured by an off-axis scattered sunlight DOAS measurement, such as a MAX-DOAS method, or in this work CityScan, depends upon several geometric parameters, the solar zenith angle (SZA), solar azimuth angle (SAA) and the elevation angle (EA). Each one of these parameters will influence the light path and the contribution of the tropospheric and stratospheric gases to the final concentration measured [63]. Figure 3.1 shows a typical geometry of a MAX-DOAS instrument and demonstrates the difficulty in characterising the light path through the atmosphere with an infinite number of possible light paths dependent upon the solar conditions.
Also clear in Figure 3.1 is the effect the SZA and EA have on the contribution of the troposphere/stratosphere composition to the SCD. The SZA controls the contribution of the stratospheric column to the measurement whilst the EA controls that of the tropospheric contribution. In order to increase sensitivity to tropospheric composition lower elevation viewing angles are used.

Figure 3.1: Geometry of Multi-Axis DOAS (MAX-DOAS) showing radiative transport through the atmosphere. Realistically there are an infinite number of light paths. Image taken from Platt and Stutz, 2008 [63].

As the main subject of this work is the analysis and interpretation of CityScan data, a modelling study has been performed in order to assist in the understanding and interpretation of the results. Questions to be addressed here include what is the effect of changing the viewing angle and solar zenith angle on the retrieved DSCD of NO\textsubscript{2}? What is the consequence of changing the NO\textsubscript{2} profile? Finally, the question of whether it is possible to separate near-field emissions from background concentrations within a complex urban environment will be discussed.
3.2 Background to Radiative Transfer Modelling Studies

With scattered sunlight measurements becoming an ever more widely applied method of monitoring point source emissions, urban air quality and atmospheric composition in remote environments, much work has recently been focused on understanding and interpreting measurements taken using this technique. Some of the most recent work will be discussed here.

Wagner et al. [85] demonstrated the effect the relative solar azimuth angle has on the normalised radiance and air mass factor (AMF). The AMF is a quantity that describes the sensitivity of measurements taken with a remote sensing instrument to atmospheric trace gases concentrations at particular levels of the atmosphere, and thus gives an indication of the change which will be seen in the calculated SCD when varying several geometric parameters.

Hönninger et al. [33] discussed various geometric conditions and the effect these can have on both the AMFs and SCDs when using a variety of trace gas profile shapes. The modelling in the Hönninger study is performed using the RTM “Tracy”.

In Hönninger et al. AMFs were calculated for eight profile shapes, P1-P8. The profile shapes used are shown in Figure 3.2. The calculated AMFs for profiles 1-6 are shown in Figure 3.3, and it is clear that changing the viewing direction has a different effect of the AMF depending upon the profile shape. The AMF is strongly dependent upon the viewing direction when the absorber is close to the ground, with the AMF increasing continuously as the elevation angle increases (P1, 2, 3 and 5). This effect is understood to be caused by path length changes. As the elevation angle increases the absorption path length will decrease where the absorption path length describes the path length through the absorbing trace gas layer. P4 is a profile
Figure 3.2: Profile shapes used in the sensitivity studies performed by Höninger et. al [33] with an elevated layer and shows a maximum AMF at an elevation angle of 5°. This can be very simply understood, at elevation angles less than 5° the instrument looks ‘below’ the layer. Conversely, the elevation angle is almost independent of viewing angle for the stratospheric profile, P6.

Aerosol load and surface albedo are known to play a significant role in the radiative transfer, especially in the troposphere. The effect of these on the calculated AMFs are shown in Figure 3.4. The calculations with a low aerosol load are not different in shape to the Rayleigh case shown in Figure 3.3. However, the values of the AMFs are smaller at elevation angles below 10° and in the case of high aerosol
loading the increase of the AMF at lower elevation angles becomes much weaker. The variation with elevation angles is also much less pronounced.

Profiles that extend to higher levels such as P 4 and 5 have lower AMF values in comparison with the Rayleigh case. This is because of the shorter mean free paths of the photons owing to aerosol extinction. The mean free path describes the average distance travelled by a moving particle between collisions. Hence, the absorption path in the lowest atmospheric layers is shorter in these cases and a more vertical path through higher layers is probable. With increasing aerosol loading the effect of a shorter mean free path becomes even more dominant. The maximum AMF can also shift to a higher elevation angle owing to this as seen in P4 in the high aerosol cases. Increasing albedo causes enhancements in AMFs for profiles extending to
Figure 3.4: AMF as a function of elevation angle for P1-6 for low (left column) and high (right column) aerosol load and 5% (top panels) and 80% (bottom panels) ground albedo respectively. Calculations were performed for a wavelength of 352 nm and 30° SZA from Höninger et. al [33].

the ground because longer absorption paths in the lowest layers are favoured by scattering at the ground.

3.2.1 SCIATRAN

SCIATRAN is a radiative transfer model (RTM) based upon GOMETRAN with an extended spectral range to cover the eight spectral channels of the SCIAMACHY instrument. SCIAMACHY is the SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY which was a spectrometer onboard ESA’s ENVISAT (ENVIronmental SATellite) that measured reflected, transmitted and scattered sunlight from the Earth’s surface in the UV, visible and near infra-red wavelength re-
Table 3.1: SCIATRAN Settings used for RT Modelling

<table>
<thead>
<tr>
<th>SCIATRAN Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTM Type</td>
<td>Pseudo spherical atmosphere</td>
</tr>
<tr>
<td>Numerical Method</td>
<td>CDI</td>
</tr>
<tr>
<td>RTM Mode</td>
<td>Slant Col</td>
</tr>
<tr>
<td>Wavelength Range</td>
<td>420–630 nm</td>
</tr>
<tr>
<td>Internal Wavelength Step</td>
<td>0.01 nm</td>
</tr>
<tr>
<td>Profile</td>
<td>Standard profile for lat and lon for June with varying concentrations of NO\textsubscript{2} at the bottom of the boundary layer (lowest 1 km)</td>
</tr>
<tr>
<td>Aerosol Profile</td>
<td>Urban aerosol profile taken from [7] and [47]</td>
</tr>
<tr>
<td>Trace Gas Cross Sections</td>
<td>(\text{O}_3) at 203, 223, 243, 273 and 293K, (\text{NO}_2) at 203, 223, 243, 273 and 293K, (\text{O}_2), (\text{IO}), (\text{CHOCHO}), (\text{O}_4) and (\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Line Absorbers</td>
<td>(\text{NO}_2), (\text{H}_2\text{O}), (\text{O}_3), (\text{SO}_2) and (\text{O}_4)</td>
</tr>
<tr>
<td>FOV size</td>
<td>0.5°</td>
</tr>
<tr>
<td>Clouds</td>
<td>Not Included</td>
</tr>
</tbody>
</table>

3.2.2 SCIATRAN settings used in Radiative Transfer Modelling

In this thesis NO\textsubscript{2} and O\textsubscript{4} slant column files were produced for the wavelength range 420–630 nm for elevation angles (EA) 0–89°, all solar azimuth angles (SAA) and solar zenith angles (SZA) 15–95° in 20° intervals. For further settings see Table 3.1.

Full hemispherical images were built up using all EA and SAA for a given SZA. Full details of the geometric and atmospheric composition of the different SCIA-
### Table 3.2: SCIATRAN Geometry and Composition Settings Used for RT Modelling

<table>
<thead>
<tr>
<th>Run</th>
<th>SZA/°</th>
<th>NO₂ Box Profile</th>
<th>Visibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15, 35, 55, 75, 95</td>
<td>5 ppb</td>
<td>5 km</td>
</tr>
<tr>
<td>6</td>
<td>15, 35, 55, 75, 95</td>
<td>10 ppb</td>
<td>5 km</td>
</tr>
<tr>
<td>11</td>
<td>15, 35, 55, 75, 95</td>
<td>5 ppb</td>
<td>10 km</td>
</tr>
<tr>
<td>16</td>
<td>15, 35, 55, 75, 95</td>
<td>10 ppb</td>
<td>10 km</td>
</tr>
<tr>
<td>21</td>
<td>15, 35, 55, 75, 95</td>
<td>5 ppb</td>
<td>15 km</td>
</tr>
<tr>
<td>26</td>
<td>15, 35, 55, 75, 95</td>
<td>10 ppb</td>
<td>15 km</td>
</tr>
</tbody>
</table>

NO₂ profiles are the box model concentration up to 1km altitude, beyond this height the standard SCIATRAN profile for this latitude is used. The visibility is defined by the extinction coefficient which is calculated using the relationship; Extinction coefficient \((1/\text{km}) = 3.0/\text{Visibility (km)}\).

TRAN scenarios are shown in Table 3.2. SCIATRAN version 3.1.27 was used in this work.

The NO₂ profiles used during this work were adapted from the standard latitude and month profiles supplied as .mpi files with SCIATRAN; the profiles were used as standard with the bottom 1 km being a box profile of a specific NO₂ concentration, defined for this work. The chosen standard SCIATRAN profile was for June and at 45°N to be most representative of the conditions during the main measurement period in Bologna, where CityScan was deployed (for information on the deployments see chapter 4). The two box profile concentrations used here were 5 and 10 ppb, as shown in Figure 3.5, the profile used also includes a large stratospheric concentration of NO₂ as can be seen in the Figure.

### 3.3 Results and Discussion

Modelled NO₂ and O₄ slant columns were produced for each viewing direction of the CityScan instrument simulation and then plotted into the panorama format used for visualising the CityScan data. In these visualisations, the position of the sun is modelled at the centre of the panorama. O₄ slant columns are considered to be a
good indication of the path length of the measurement as its concentration varies little within the atmosphere. In the following Chapters of this work the CityScan slant columns of NO₂ and O₄ are ratioed in order to provide some indication of the enhancement of the NO₂ within the slant columns which cannot be attributed to increased path length and instead can be assigned to increased emissions. The robustness of this assumption will be explored here.

3.3.1 Viewing Angle Dependence of Modelling

The influence of varying the relative azimuth angle of the measurement was explained by examining a single modelled panorama. The relative azimuth angle is discussed here as the viewing direction of the instrument is constantly changing as
it rotates. At low relative azimuth angles (i.e. when the measurement is taken close to the direction of the sun) the slant columns are smaller than those taken when viewing predominantly scattered light in the opposite direction to the sun. A modelled \( \text{O}_4 \) panorama is shown in Figure 3.6 demonstrating this azimuthal variability which is very distinct in this example.

Figure 3.6: Modelled \( \text{O}_4 \) SCD for SZA 35 with a 5ppb box profile and 15km visibility.

The variability of SCD with azimuth can be attributed to the change in path length when the viewing angle is varied. When measurements are taken in the direction of the sun this will give the shortest light path and owing to less distance travelled through the atmosphere lowest retrieved SCD. Assuming no near field emission sources, as is possible for \( \text{O}_4 \), this effect can be attributed to the strong forward peak in Mie scattering as discussed in [34]. Conversely, when the instrument view faces the opposite way to the sun, the light path is extended and thus the slant column densities are modelled with higher values. Therefore the azimuthal angular dependence of the \( \text{O}_4 \) DSCDs is explained in Figure 3.1. Changes in retrieved SCD with variation of the azimuth angle is shown more clearly for both \( \text{NO}_2 \) and \( \text{O}_4 \) in Figures 3.7 and 3.8 respectively.

In the case of \( \text{NO}_2 \) it is clear that the SCDs increase with increasing solar azimuth
Figure 3.7: Modelled NO$_2$ SCD as a function of elevation angle for visibilities 5 (black), 10 (Blue) and 15 km (red) and at azimuth angles 0°, 90° and 180° from top to bottom, with a box profile of 5 ppbv of NO$_2$. 
angle whilst the general shape of the profile remains the same. It is also clear in this example that the sun position is seen in the 0° SAA plot as all the curves have a minima in the direction of the sun, in this scenario that position is at 55° elevation angle.

The modelled O4 SCD displayed in Figure 3.8 show more variation in the shape of the gradients for the various azimuth angles than the modelled NO2 SCDs. The minima is very clear in the 0° SAA at the viewing angle of the sun position. There is also a very clear cross-over point observed between the different visibility scenarios where the scenario with the highest modelled SCDs at low elevations becomes the highest and vice versa. The point of this cross-over moves higher vertically with increasing SAA. The reasons for this cross-over are somewhat unclear as it is difficult to untangle the effect of multiple scattering from single scattering. The gradient which occurs vertically changes with azimuth and this is hypothesised to be caused by the scattering point varying with azimuth, elevation and visibility, a schematic which visualises the effect that visibility can produce is shown in Figure 3.9.

Figure 3.9 provides an explanation for the more pronounced gradient in concentrations which is seen at higher visibilities such as the modelled 15 km visibilities. It can be seen that the paths through the boundary layer with 5 km visibility when looking towards the sun and away from the sun are very similar whilst the 15km visibility scenario has markedly different tropospheric paths in the two viewing directions. When the SAA is 180° with a visibility of 15 km the path of the photon will be relatively long through the boundary layer before the scattering point is reached and thus there will be a large tropospheric component to the measured column. The cause of the cross-over point moving with azimuth is the change in the profile of O4 retrieved with azimuth which manifests itself in the pattern which is clear in the panorama data. This pattern is caused by the viewing angles in the direction of the
Figure 3.8: Modelled O$_3$ SCD as a function of elevation angle for visibilities 5 (black), 10 (Blue) and 15 km (red) and at azimuth angles 0°, 90° and 180° from top to bottom, with a box profile of 5 ppbv of NO$_2$. 
Figure 3.9: Schematic showing photon paths through the boundary layer under different visibility conditions. Shown in red are the paths at 15 km visibility and grey is for 5 km visibility.

sun being the minimum concentrations; having the shortest light path. There is a gradient of increasing concentration which spreads out from this minima.

Variation of path length is also the source of the vertical structure seen in the panoramas, with the lowest viewing angles providing the longest light path through the atmosphere, again this is visualised in Figure 3.1. Both of these geometric effects are seen in the modelled NO\textsubscript{2} slant columns as well as the O\textsubscript{4} for these idealised cases. An example NO\textsubscript{2} panorama is shown in Figure 3.10.

Figure 3.10: Modelled NO\textsubscript{2} SCD for SZA 35° with a 5 ppb box profile and 15km visibility.
3.3.2 Solar Zenith Angle Dependence of Modelling

In order to understand the effect of changing solar zenith angle on modelled slant columns, several modelled scenarios were performed for SZAs of $15^\circ$, $35^\circ$, $55^\circ$, $75^\circ$ and $95^\circ$. The outcome of this modelling for a single atmospheric composition scenario (of a 5 ppbv box profile of NO$_3$ and 10 km visibility) is shown in Figure 3.11.
Figure 3.11: Modelled NO$_2$ SCD for solar zenith angles $35^\circ$-95$^\circ$ with a 5 ppb box profile and 10 km visibility.
It is clear that changing the solar zenith angle causes a change in the shape of the concentration gradient of the SCD in modelled panorama, with the lowest SCD found to be in the direction of the sun and the SCD increasing with distance from the sun. The panorama for solar zenith angle 95° is just shown here for reference but it is unlikely to be used in further analysis as CityScan measurements after dusk are not possible.

The magnitude of the SCD also changes with SZA. As the solar zenith angles increases the SCD also increases. This is a result of the light path travelling further through the troposphere in comparison to lower SZAs where the light path will travel through more of the upper atmosphere. This explanation is visualised in Figure 3.12; it is clear that at higher SZAs the light path through the atmosphere will be dominated by the lower levels of the atmosphere whilst, for low SZAs much of the light path will be through higher levels of the atmosphere.

Figure 3.12: The effect of solar zenith angle upon the light path through the atmosphere and thus the retrieved SCD.

The effect of a change in SZA is more pronounced for O$_4$ SCDs in comparison
with NO$_2$ this can be seen in a comparison between Figures 3.13 and 3.14. The gradient for the O$_3$ SCDs show very clear minima at the point of the sun and this obviously moves with changing SZA. The SCD values also increase in magnitude with increasing SZA, this can be attributed to longer tropospheric paths at higher SZAs.
Figure 3.13: The effect of varying the solar zenith angle upon the modelled NO$_2$ SCDs for 15°, 35° and 55° SZA. The SAA for these plots is 0°.
Figure 3.14: The effect of varying the solar zenith angle upon the modelled O$_4$ SCDs for 15°, 35° and 55° SZA. The SAA for these plots is 0°.
The reason for the more subtle changes seen in the NO₂ SCDs are likely to be due to the atmospheric profile of NO₂ being dominated by the high concentrations in the troposphere and thus at higher elevation angles with the shortest tropospheric path lengths changes are less dramatic. Again it can be seen that the values of the NO₂ SCDs increase with increasing SZA; this is likely to be for the same reason as discussed for the O₄ SCDs.

It is important to note that in high and low SZA scenarios there is very little variation azimuthally of the modelled gas profile. In order to produce an indication of the errors which are likely to be introduced if radiative transfer effects are ignored in the CityScan analysis, the variation of the modelled DSCD retrieved at a given EA and at opposing SAA (0 and 180°) was assessed. For a variety of scenarios where the SZA was between 35 and 55°, the percentage difference in NO₂ and O₄ DSCDs was calculated. In the modelled NO₂ cases, the retrieved DSCD varied azimuthally up to 18% and for O₄ this was between 13 and 20%. This analysis will enable features which vary by more than this percentage change azimuthally to be attributed to changes in the concentration of a given trace gas spatially and not be entirely caused by radiative transfer effects.

3.3.3 The Effect of Changing the NO₂ Profile

The NO₂ profiles used during the modelling are the 5 and 10 ppbv box profiles shown in Figure 3.5. A brief examination of the results obtained with each profile will be discussed here.

The effect of changing the concentration of NO₂ in the box profile used for this modelling is very much as expected; increasing BL concentrations produce higher SCDs of NO₂ across all scenarios. An example of this is shown in Figure 3.15.

It can be seen in this example that doubling the boundary layer concentration in
Figure 3.15: The effect of varying the concentration of NO$_2$ upon the modelled NO$_2$ SCDs for 35° SZA. The SAA for these plots is 180° in order to remove effects of direct sun viewing.
turn doubles the DSCD of NO\textsubscript{2} measured. Here, only box profiles of NO\textsubscript{2} have been modelled however in reality the profile of NO\textsubscript{2} is more likely to be exponential. Oversimplifying the profile as a box in this way allows the change in NO\textsubscript{2} concentration to be analysed more easily. However it also makes the results less representative of a complex urban boundary layer.

3.3.4 Retrieval of Near-Field Emissions in an Urban Environment

In order to definitively assign spatial patterns seen in CityScan data to near-field emissions it is important to be able to separate changes in SCDs from radiative transfer effects from those caused by increased concentrations of trace gases of interest. Here, we investigate the effectiveness of using O\textsubscript{4} SCDs as a proxy for path length and thus a ratio of NO\textsubscript{2} to O\textsubscript{4} could provide an indication of enhancements in the NO\textsubscript{2} SCDs not caused by changes in path length. Panoramas of ratios of NO\textsubscript{2} and O\textsubscript{4} are produced for all SCIATRAN scenarios. Examples of some of these outputs are shown in Figures 3.16 and 3.17.

In order to review the effectiveness of the ratio for removing geometric dependence of retrieved SCDs Figure 3.18 shows the change in SCDs of NO\textsubscript{2} and O\textsubscript{4} with elevation angle at 0° SAA; the variation is clearly different for the two gases. However, the changes are least pronounced at the lowest elevation angles and thus the ratios may still be valuable when considering emissions just above the horizon.
Figure 3.16: From top panel to bottom, NO$_2$ SCD, O$_4$ SCD and a ratio of the two, for SZA 15° with a box profile of NO$_2$ of 5 ppb and 15 km visibility.

3.4 Comparison of Modelled Data to Measured Data

The modelled SCD produced in Section 3.3 can be compared to measured CityScan data in order to better understand the limitations and strengths of this modelling study and to help to interpret CityScan data. The spatial patterns in both the O$_4$ and NO$_2$ SCDs modelled here are very rarely recreated in the measured SCDs taken
Figure 3.17: From top panel to bottom, NO$_2$ SCD, O$_4$ SCD and a ratio of the two, for SZA 55° with a box profile of NO$_2$ of 10 ppb and 5 km visibility.

by CityScan. The morning of the 8th of June has been identified as producing a smoothly varying change in SCD with a minima in the direction of the sun as seen in the modelled data. On this morning there is a thin layer of white cloud seen uniformly across the hemisphere measured by CityScan. Data collected at 10:41 will be presented here alongside the modelled scenario that best represents the time of day and the atmospheric conditions, this comparison is seen in Figure 3.19.
Figure 3.18: Modelled NO$_2$ (top) and O$_4$ (bottom) SCDs for 0° SAA and 15° SZA.
Figure 3.19: Measured NO$_2$ and O$_4$ DSCDs ($\times 10^{40}$) and the NO$_2$/O$_4$ ratio (left hand-side, top to bottom) and modelled NO$_2$ SCDs, O$_4$ SCDs and NO$_2$/O$_4$ ratio for 35° SZA, with a 5 ppbv box profile of NO$_2$ from the ground up to 1 km, and 10 km visibility (right hand-side, top to bottom). All SCDs are in mol/cm$^2$. The sun position is located at 180° in the modelled data and on the right hand side of the measured data plot above the University of Leicester logo.
Both the modelled and measured panoramas plotted in Figure 3.19 show a distinct minima in the NO$_2$ panorama surrounding the sun. The sun can be identified in the measured data as an area with no data on the right hand side of the plot above the University of Leicester logo, whilst in the modelled data the sun is located in the centre of the panorama at 180°. The reduction in SCD is less prominent in the measured O$_4$ surrounding the sun than in the modelled counterpart, however is still present. Both modelled and measured data are plotted on the same colour scale to assist with the comparison, in doing so it becomes apparent that the magnitude of the SCDs when measured are markedly larger than the modelled O$_4$ SCDs in the majority of elevation and azimuth angles. A potential explanation for the difference in the modelled and measured O$_4$ SCDs is the presence of cloud in the measured data. It is likely that cloud in the FOV smooths out geometric effects that would be expected to be seen more prominently on a clear sky day. Clouds in the FOV will increase the O$_4$ DSCD measured owing to additional scattering of the incoming solar radiation.

The percentage difference between the modelled and measured data for this time period is shown in Figure 3.20 alongside the measured and modelled O$_4$ SCDs. Figure 3.20 highlights that the largest difference in magnitude of the O$_4$ column is seen in the lowest elevation angles, approximately below 20° where the percentage difference is over 60%. In higher elevation angles than this the difference remains below 50% with a minimum in error in the elevation angle of the sun (centred around 50° elevation). The largest disagreement between modelled and measured columns of O$_4$ in the lowest elevation angles are thought to be caused by additional emission sources at the ground causing elevated aerosol concentrations which also cause light scattering and enhance the path length.

Comparisons of modelled and measured O$_4$ SCDs on clear-sky days have not
Figure 3.20: Measured O\textsubscript{4} DSCDs on the 8th of June at 10:41 (top), modelled O\textsubscript{4} SCDs (middle) and the percentage difference between modelled and measured (bottom). All SCDs are in mol/cm\textsuperscript{2}.
produced any strong correlations in terms of the spatial patterns. It is hypothesised that the reason for this is the measurement environment where the data has been collected. The data presented in this work has all been taken in urban environments which are a complex mix of emissions which cannot be represented in SCIATRAN as the user can only input uniform profiles of trace gases and aerosol profiles. This is likely to cause the largest differences closest to the ground.

The SCIATRAN modelling does potentially offer a scenario which is representative of background unpolluted conditions, such as a site downwind of a large city where the air mass is well mixed within the boundary layer rather than the situation that occurs in a city, where emission sources are distinct from one another. Plotted in Figure 3.21 are O$_4$ DSCDs modelled (dashed line) and measured on the 8th of June at 10:41 (solid line) at four elevation angles for all azimuth angles. Direct comparison of modelled versus measured FOVs shows some common features and also some marked differences. The smoothly varying shape that is indicative of the modelled data is reproduced in the measured data as broadband structure. There is narrowband structure that is superimposed on this in the measured data which is caused by changes in atmospheric composition or instrument noise and therefore would not be present in the modelled data. The difference in the magnitude of the SCDs between modelled and measured increases with a decreasing elevation angle. As there are likely to be additional emission sources in the measurements at ground level which are not represented in the model the SCIATRAN modelling will calculate a background scenario. The difference between maximum SCDs for high ($50^\circ$) and low elevation angles ($10^\circ$) for modelled and measured are $0.75 \times 10^{44}$ and $5.75 \times 10^{44}$ mol/cm$^2$ respectively. This increasing disagreement with decreasing elevation angles strongly indicates that the aerosol profile at the ground level is underestimating the amount of aerosol present in the measurement scenario. Therefore the standard
urban aerosol profile used in this modelling under represents the aerosol loading in Bologna.

With further time this work would benefit from extending the number of model runs to include scenarios with different aerosol profiles at which point the model runs may prove to be a realistic proxy for the background atmospheric conditions. The comparison of modelled and measured data here demonstrates that CityScan measures larger than expected O$_4$ DSCDs in the lowest elevation angles owing to path length enhancement caused by increased aerosol loading. The elevated O$_4$ DSCDs indicate that the NO$_2$ DSCDs will also be enhanced because of path length enhancement. However, it is not possible within the timescales of this work to fully untangle the enhancement caused by increased path length from the increased NO$_2$ signal caused by the local ground-based NO$_2$ emissions. The ratio of NO$_2$/O$_4$ has been used in the subsequent chapters of this work in an attempt to minimise the enhancement in NO$_2$ DSCDs caused by increased path length.

3.5 Hemispherical Radiative Transfer Modelling

Summary

It has been demonstrated in this modelling study that radiative transfer effects cannot be ignored when analysing CityScan data. Both the biggest advantage and disadvantage of CityScan is its hemispherical viewing geometry. This allows the instrument to monitor spatial distributions of gases with unprecedented levels of information but also complicates the considerations of radiative transfer required to interpret the measurements.

It is clear that changes in SAA and SZA can dramatically change the retrieved SCD when there is no change in the atmospheric situation. It has been shown that
at high and low SZAs, where the sun is not directly in the FOV, that the SAA dependence of the modelling is minimised. The effect caused by changes in SAA are the most important to this work, because the rotation of the CityScan unit means that the effective SAA is constantly changing and thus comparisons of SCDs within a single panorama can be misleading. Where there is a uniform atmospheric profile in all viewing directions one would expect to see spatial patterns in SCDs corresponding to the modelled panoramas such as in Figure 3.16. However, the measurements discussed here are unlikely to have been collected under homogeneous atmospheric conditions because the CityScan deployments were in urban environments where there were likely to have been a considerable number of distinct emission sources. The main difficulties with analysing the CityScan data will not be in identifying a
plume in a specific direction, as this will be quite different to the diffuse patterns modelled here, but being able to compare the magnitude of the SCD within that plume to another plume at a different viewing position.

As has been shown the geometry of a measurement can have a marked effect upon the magnitude of the DSCD measured. In order to attempt to set a threshold that can be used to separate features caused by radiative transfer effects from changes in trace gas concentrations the difference between the retrieved DSCDs for a given scene at SAAs 0 and 180° was calculated at a single elevation angle. This calculation demonstrated that the retrieved DSCD for a single atmospheric scene could vary by as much as 18% and 20% for NO₂ and O₄ respectively in a sza 55° scenario with 15 km visibility, and thus any features that are identified in the CityScan data in the following chapters that show larger concentration changes than this azimuthally can be attributed to changes in concentrations of trace gases. This threshold will only apply in clear sky conditions as modelling the effect of clouds on the DSCDs is beyond the scope of this work.

Several limitations of this modelling study should be highlighted, principally the use of box NO₂ profiles and the homogeneous boundary layer structure which has to be used in SCIATRAN. Both of these factors mean that the results shown here will be more applicable to well mixed boundary layers such as those seen in rural locations rather than a complex urban boundary layer, the likes of which were measured in this work. However the modelled outputs presented in this Chapter go some way to demonstrating the difficulty that arises from radiative transfer effects when analysing CityScan results. This modelling study is not exhaustive and in future work other factors which would need to be considered would include the effect of changing the NO₂ profile shape, aerosol type, aerosol profile, introducing clouds and investigating the components caused by multiple and single scattering.
separately. Additionally, the use of a model which allows the introduction of a heterogeneous boundary layer would also make these results more representative of an urban environment.
Chapter 4

HSI-DOAS Measurements During the PEGASOS Campaign

4.1 The Pan-European Gas-AeroSOl-climate interaction Study (PEGASOS) Project

PEGASOS is a large European funded project which brings together many European research groups in both observational and modelling fields. The PEGASOS project aims to improve knowledge of the interactions of atmospheric chemistry and climate change in the past, present and future. It hopes to provide better estimates of air pollution in Europe and its impact on climate, to support the EC/Thematic strategy on air pollution and air quality regulation, and to better quantify regional and global links between air quality and climate change to underpin mitigation options and policy initiatives. The overriding aims of the project are:

- To quantify the magnitude of regional to global feedbacks between atmospheric chemistry and a changing climate and to reduce the corresponding uncertainty of the major ones.
• To identify mitigation strategies and policies to improve air quality while limiting their impact on climate change.

The project combines the development of anthropogenic and biogenic emission inventories, laboratory studies, field measurements over Europe using a Zeppelin combined with mobile and fixed ground platforms, air quality models and policy analysis to achieve its objectives. Further information regarding the PEGASOS project can be found on the PEGASOS website (http://pegasos.iceht.forth.gr/). As part of the PEGASOS project, ground measurements were recorded at three main ground sites around Bologna during June 2012; Bologna city centre, San Pietro Capofiume and Monte Cimone. The location of each of these sites is shown in Figure 4.1. The two CityScan instruments were all deployed in Bologna city centre and the exact locations will be discussed in the following section.

Figure 4.1: Map showing the locations of the three main measurement sites during PEGASOS
In combination with the ground-based measurements collected in Bologna, the PEGASOS zeppelin was flown over the Po valley during June to provide measurements of trace gases and aerosol at 700 m altitude. Bologna was selected as a ground-based campaign site because it is located within the Po Valley, which is one of the most polluted areas within Europe owing to the high concentration of cities within the valley and the surrounding hills and mountains that trap pollution in the valley. A map of NO\textsubscript{2} concentrations over Europe for 2007 as measured by NASA’s OMI satellite is shown in Figure 4.2. This map shows the areas in Europe which are most affected by poor air quality and the Po Valley in the North of Italy is clearly one of the most polluted areas.

Figure 4.2: Map of NO\textsubscript{2} concentrations over Europe as vertical column densities as measured by the OMI instrument and produced by KNMI. This is an annual average for 2007.
4.2 Instrument Locations

Two HSI-DOAS instruments were deployed in Bologna from the 5th-28th June 2012. The first instrument was located on the roof of Instituto di Scienze dell’Atmosfera e del Clima (ISAC) at the Italian National Research Council (CNR) approximately 40 m above the ground (lat 44.523429, lon 11.338564) and the second on a tower at Agenzia Nazionale per le nuove tecnologie, l’energia e lo sviluppo economico sostenibile (ENEA), Monte Cuccolino in the hills south of the city centre (lat 44.463823, lon 11.329084) approximately 250 m above sea level. The two locations are shown in Figure 4.3.

Figure 4.3: Map showing the location of the two CityScan Deployment Sites

Site one (ISAC) provided uninterrupted views over the full 360° of rotation with the city centre to the south east and the airport to the west. Site two (ENEA) allowed distant views of the city to the north and uninterrupted views in all directions. CS1 was sited at ISAC and CS2 was sited at ENEA. On both sites the instruments
were raised on platforms to remove local obstructions from the field of view. At site two the instrument was also tilted at an angle of 4° downwards in the north facing direction to provide a better field of view into the valley in which the city centre is located.

4.3 Bologna City Centre In-situ Monitors

In and around Bologna city centre there are six operational air quality monitors which measure NO$_2$ concentrations. The locations of these are shown in Figure 4.4 in relation to the two CityScan instruments.

![Map of Bologna with locations of all of the in-situ monitors and the CityScan instruments.](image)

The monitor sited at Porta San Felice (PSF) is a roadside monitor on a busy road junction of the ring road in Bologna. The Via Giardini Margheritti (GM) monitor is within a large park, set about 200 m away from the ring road. Via Chiarini, San Marino and Villa Torchi are all urban background sites, positioned away from main
roads. San Lazzaro is situated beside a large road. Data from all six instruments have been collected for the entire campaign period with one hour time resolution and a detection limit of 12 $\mu$g m$^{-3}$ which is approximately 6.38 ppbv (using the conversion 1 ppbv equals 1.88 $\mu$g m$^{-3}$ of NO$_2$).

4.3.1 Improving the Field of View of CS2

The roof of ENEA, where CS2 was deployed, is surrounded by safety railings. These railings were initially in the field of view of the instrument therefore on the 8th of June the instrument was raised above these to allow for a clear field of view. It was also noted in early data analysis that, because of the hillside location of CS2, very little below the horizon was being seen and so the instrument was also tilted downwards by 4° in the northerly direction to provide a clearer view of the city which is visible in the valley.

4.4 Meteorological Conditions During PEGASOS

The meteorological conditions in Bologna were recorded for the duration of the campaign from several sites in the centre of the city. Here, only the wind speed, wind direction, relative humidity and temperature are examined as these are likely to have the most bearing on our measurements. The meteorological measurements were recorded at Torre Asinelli in the city centre. Owing to instrument down-time there are only wind speed measurements from the 6th-16th of June.
Figure 4.5: Meteorological conditions during the PEGASOS campaign, top: temperature (black) and relative humidity (red) bottom: wind speed (red) and wind direction (black)
The campaign meteorological conditions are shown in Figure 4.5 with temperature and relative humidity in the top panel and wind speed and wind direction in the bottom panel. The temperature measurements show two clear regimes during the campaign. The first part of the campaign has relatively low daily maxima of approximately 26-27 °C whilst from the 15th of June onward the peak temperatures begin to increase until the 21st June where the recorded highest daytime temperature was 35 °C. The daily maxima in temperature remain relatively high for the rest of the campaign period in comparison to the average high temperature in Bologna in June which is 28 °C. The %RH is anticorrelated with temperature for the duration of the month peaking at over 90% (during the night-time early in the campaign), with a daytime minimum during the later half of the month at 40%.

The wind measurements show that the wind speeds were relatively low for the duration of the data, rarely exceeding 4 ms$^{-1}$. The wind direction is dominated by Westerlies for the whole of June (over 30% of the measured wind direction is Westerlies), this can be seen more clearly in Figure 4.6 where the percentage frequency of a given wind direction and wind speed are plotted. It is very clear that there are rarely Southerlies (less than 1% of the measured wind direction during the month) with a very small fraction of Northerlies (11%) and North Easterlies (15%).

4.5 Instrument Modifications During the Campaign

4.5.1 Application of window film

Window film (Abode window films, Daylight natural-light) was applied to CS2 on the afternoon of the 8th of June as even with the shortest exposure time the CCD was saturating for a substantial part of each rotation. This window film is quoted to
reduce the transmission of visible light to 65%. Before the film could be applied it was important to check the transmission curve for any narrow band features which might interfere with the DOAS fit.

The film was characterised using a QTH lamp and a spectral radiometer in the laboratory; the setup is shown in Figure 4.7. A baffle was used in order to isolate the direct light from the lamp. A control experiment was performed without the window film in place to measure the QTH lamp intensity without the film. Measurements were taken over a ten minute period with a three-minute lamp warm-up period. The first three minutes of data during this warm up period were therefore excluded from further analysis. The experiment was then repeated but this time with the window film covering the gap in the baffle.
The data for both experiments were averaged over the seven-minute measurement period to minimise any bias caused by fluctuations in the light source. The measured counts for each experiment are shown in Figure 4.8 with the difference between the two experiments also plotted. The percentage transmission of the window film was calculated and is plotted in Figure 4.9. It can be seen that the percentage transmission varies with wavelength between 62% at 375 and 700 nm and 87% at 275 nm. Within the wavelength range used by CityScan the variation is less with the percentage transmission between 64 and 76%. There is no narrowband structure with a FWHM of less than 10 nm seen in the transmission of the window film within the DOAS fitting window used in this work and as such it has been concluded that the broadband features seen within the fitting window will be removed by the DOAS fit and thus no correction needs to be applied to the CityScan data.

4.6 Results

4.6.1 Analysis of CityScan Data

4.6.1.1 The DOAS Fit

The settings used for the DOAS fit were as outlined in Section 2.3.4.1. Briefly, the main features of the DOAS fit will be outlined. The fitting window used was 428–495 nm, with NO$_2$, O$_4$, Ring, H$_2$O, CHOCHO and O$_3$ cross sections being
fitted. The reference spectra used to analyse the PEGASOS campaign data is a row-specific reference which was taken at 15:11 on the 9th June 2012. This reference was chosen because it was a relatively unpolluted clear sky period as identified during preliminary analysis of the data.

In order to access the uncertainty in the results obtained during the PEGASOS campaign, analysis of the fitting errors has been performed using the errors output by QDOAS. The QDOAS fitting procedure outputs the RMS and slant column errors for each spectrum which is analysed, these have been used to access the uncertainty in the data. Two hour long periods have been investigated, the first under relatively ‘normal’ atmospheric conditions (on the 6th of June) and the second during a high pollution event (on the 13th of June). These two time periods were chosen to demonstrate the difference in errors that arise in markedly different conditions. The

![Plot of the measured counts for the QTH lamp with and without the window film and the difference between them.](image-url)
When comparing data from the two days it should be noted that the scale on the y axis of the plots has been altered for clarity. The errors seen for the data on the 6th of June are approximately 25-30% errors with some variation between the rows. The RMS for this time period is highest for row 30 of the detector at approximately $5 \times 10^{-3}$ on average over the hour and a lower RMS for row 10 at approximately $3.5 \times 10^{-3}$. Rows 10, 20 and 30 on the detector were selected for error analysis as they are at low viewing angles which are most sensitive to changes in the concentration of trace gases in the troposphere and thus would give a good indication of the change in errors caused by changes in NO$_2$ concentration.
Figure 4.10: NO$_2$ DSCD with associated error bars (top panel) and RMS of the data (bottom panel), for the 6th of June 2012.
Figure 4.11: NO$_2$ DSCD with associated error bars (top panel) and RMS of the data (bottom panel), for the 13th of June 2012.
DSCDs of NO\textsubscript{2} measured on the 13th of June are significantly higher than on the 6th of June for reasons which will be discussed in Chapter 5, peaking at over 2.5x10\textsuperscript{17} mol cm\textsuperscript{-2} on the 13th compared to less than 1.5x10\textsuperscript{17} mol cm\textsuperscript{-2} on the 6th of June. As such the percentage errors which can be seen in Figure 4.11 are significantly lower with errors of less than 5% at peak concentrations and up to 15% errors at the lowest concentrations measured at this time. The average RMS values by row are similar to those seen on the 6th with more variability seen in the RMS for row 10. The fitting error calculated here is comparable in some circumstances to the fitting error found in the literature of 5% [46]. However this is the best fitting error for the scenarios analysed and thus it is probable that the majority of the data has larger fitting errors than found in the literature.

Here, only the error associated with performing the DOAS fit has been discussed. However it is important to note that there are other factors which may cause errors in the retrieved NO\textsubscript{2} DSCDs from CityScan. Although time constraints do not allow a full error budget to be calculated the main error sources are outlined in Table 4.1 and discussed here.

Cross section errors describe the accuracy of the measurement and account for the errors caused by the temperature dependence of cross sections. Errors also arise when the cross section is convolved to the instrument line shape. The DOAS bias
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describes the uncertainty in the DOAS technique which could be caused by using a narrow fitting window for example. The error in the scattering represents the range of potential scattering scenarios which could influence the measured NO$_2$ DSCDs. Path length uncertainties are caused by the path length of the photon paths being unknown. The pointing accuracy of the instrument defines the error which is created by not having accurate pointing information for the rotation of the instrument. The viewing direction of the instrument is calculated by co-locating webcam images with the NO$_2$ data and then using the solar position and the location of obstructions the viewing direction was determined. The error in the pointing angle is estimated to be $\pm 5^\circ$ both azimuthally and for the elevation angle. This error could potentially lead to large or small errors dependent upon the spatial inhomogeneity of the scene which is being analysed. If the spatial inhomogeneity is low then the error caused by this is small because neighbouring FOVs will have similar NO$_2$ concentrations along the light path and the opposite would be true if neighbouring FOVs had very differing NO$_2$ concentrations along their light paths.

4.6.2 Panoramic data from instruments CS1 and CS2

Data was collected from both CS1 and CS2 instruments from the 6th to the 29th of June with breaks in data caused by instrumental errors between the 16th and 20th June for CS1. Data from CS2 suffered more interruptions with a break on of June the 14th and from the 22nd of June onwards, owing to frequent power disruptions connected with lightning strikes in the locality. An example of data recorded from each of the CityScan instruments, in the panorama format, are shown in Figures 4.12 and 4.13.

Clearly observable in Figures 4.12 and 4.13 are the differences in data quality between the two instruments, demonstrating the requirement to optimise the DOAS
fit and to fully characterise the instrument in order to produce usable data. There are very few artefacts in the data from CS1, such as gaps in data caused by the DOAS fitting procedure failing. The proportion of data with an RMS below the acceptable threshold of $9.5 \times 10^{-3}$ is significantly lower for CS2. Furthermore a number of artefacts are also evident in the CS2 data. The RMS threshold set here is higher than is usually seen in DOAS measurements, with literature values of RMS being as low as $4 \times 10^{-4}$ [63]. However here $9.5 \times 10^{-3}$ was considered usable as NO$_2$ is a strong absorber in the fitting window used and is found at elevated concentrations in urban environments. It has been shown previously in this work that the errors on the DSCD are kept within a reasonable range during the campaign, usually between 5 and 30%, hence the threshold of $9.5 \times 10^{-3}$ appears to be stringent enough to keep the errors to an acceptable level. Owing to time constraints the DOAS fit was only optimised for CS1 and instrument characterisations were not fully analysed for CS2 and as such the data shows many gaps caused by the DOAS fit failing. Even spectra which do appear to be successfully fitted produce very noisy data. Hereafter, data will only be shown from CS1 because CS2 data is too noisy to be useful scientifically at this stage of its analysis.

The panorama data displayed in Figures 4.12 and 4.13 also highlights the ob-

![Figure 4.12: Panorama of CityScan NO$_2$ DSCD data collected by CS1 at 11:53 on the 6th of June 2012](image)
structions in the FOV of the two instruments. The FOV of CS1 is almost entirely clear above the horizon except for a sunblocker of another instrument sited neighbouring CS1 on the roof of ISAC which partially obstructs the FOV near North. The panorama shown for CS2 in Figure 4.13 was taken before the instrument FOV had been adjusted and therefore contains obstructions caused by the safety railings for the full 360° FOV.

Figure 4.13: Panorama of CityScan NO\textsubscript{2} DSCD data collected by CS2 at 11:53 on the 6th of June 2012

In order to demonstrate the improvement in FOV which was implemented on the 8th of June, webcam images collected on the 9th June are displayed in a panorama format in Figure 4.14. After the adjustments to the FOV there are minimal obstructions in the foreground of the CityScan FOV, with mountains in the distance. Bologna city centre is seen in the valley to the northeast.

4.6.3 Degradation of Data with Time

The length of the PEGASOS campaign allowed the performance of the CS1 spectrometer to be monitored over a relatively long time period of 24 days. The data quality was seen to deteriorate over the campaign owing to the shutter within the spectrometer jamming. This degradation is shown to begin after the 15th of June after ten days of constant use. The result of the shutter jamming is that the data is
intermittent at the bottom part of the CCD as the shutter did not always open fully, getting stuck at the bottom; this is visible as the missing data along the horizon in Figure 4.15. Also clear in Figure 4.15 are the higher number of gaps in the data recorded in the bottom 15° in comparison with the panorama taken on the 6th of June displayed in Figure 4.12. There is also more vertical striping visible in the panorama from the 27th; the cause of this is likely to be that the exposure time changes significantly between frames owing to the shutter not clearing the entrance slit, which would result in the exposure time being automatically increased and thus overexposure of the CCD.

Figure 4.14: Panorama of CityScan webcam data collected by CS2 at 11:53 on the 9th of June 2012

Figure 4.15: Panorama of CityScan NO\textsubscript{2} data collected by CS1 at 11:53 on the 27th of June 2012
4.6.4 Spatial Variability of Nitrogen Dioxide Concentrations within Bologna

In order to establish the spatial variability of the NO$_2$ concentrations during the campaign and potentially to identify weekly trends or correlations with wind data, the 5° field of view has been plotted radially by time of day. These radial plots allow the movement and development of air masses to be monitored over a day. A radial plot for CS1 on the 6th of June is shown in Figure 4.16. Various significant features are labelled on this plot and will be discussed here. Visible on the radial plot (Figure 4.16) is the movement of the sun over the day which is seen as a black line spiralling outwards radially from East in the morning (Point 1). No valid data is produced in the direct LOS of the sun owing to saturation of the CCD which prevents a successful DOAS fit being completed.
Figure 4.16: Radial summary plot of NO$_2$ DSCDs (x10$^{17}$) (top) measured by CS1 data on the 6th June 2012, with the scale from blue to red representing 0 - 1.5x10$^{17}$ mol cm$^{-2}$ respectively. The 5° elevation angle data is plotted azimuthally with time over the day starting in the centre, prominent features in the plot are labelled (numbers 1-5) and are discussed in the text. The bottom panel shows the radial summary plot for O$_4$ DSCDs (x10$^{14}$).
Other features which merit discussion that are visible in Figure 4.16 are the spatial variation which is seen azimuthally in the data (Points 2 and 3), dilution of NO\textsubscript{2} potentially caused by BL rise (Point 4) and that much of the data is significantly above the noise. Spatially, the areas of highest pollution are seen to move over the course of the day. In the early morning the direction which shows the highest in concentrations of NO\textsubscript{2} is in a northerly direction from CityScan towards the tangenziale (motorway) which is north of the city. Traffic travelling into Bologna is the likely cause of this. As the working day begins and the rush hour subsides the area of highest NO\textsubscript{2} concentrations is seen to move from the north to a south/south east direction; this can be attributed to an increase in activity in the city centre during the working day. Visible in Figure 4.16 and all subsequent radial plots that will be shown in this work is the overall reduction in measured NO\textsubscript{2} concentrations that occurs at approximately midday and can be seen uniformly over the measurement area in the afternoon owing to an increase in BL height. Mixing in of cleaner air from the free troposphere dilutes the measured NO\textsubscript{2} concentrations. A radial plot for O\textsubscript{4} is shown beneath the NO\textsubscript{2} in Figure 4.16 to demonstrate that the reduction in concentration in the NO\textsubscript{2} plot seen at approximately midday also appears in the O\textsubscript{4} DSCDs. A reduction in the O\textsubscript{4} concentrations supports the explanation that there is a dilution in trace gas concentrations in the BL as the BL height increases during the day. Features which have been discussed are shown to be well above the noise, which is visible as the speckled effect in the radial plots, as they are large scale features which are well defined above this. At dusk it can be seen that there are relatively uniformly high DSCDs of NO\textsubscript{2}, in terms of azimuth angle, measured this is owing to the increased light path at dusk and dawn.

After dusk the data cannot be considered to be accurate as the illumination upon the CCD is too low and thus produces noisy results. Figure 4.16 also demonstrates
the value of this plotting method as the spatial variability of DSCDs of NO$_2$ with time become very clear. The change in spatial patterns over the day can be attributed to effects other than radiative transfer effects, which result from the change in geometry and thus path length over the day because the spatial features seen in the both the panoramas and radial plots do not show the same spatial patterns as those modelled in Chapter 3. The modelled patterns are smooth variations over the hemisphere with minima in NO$_2$ concentrations in the viewing direction of the sun whilst the panoramas produced with the CityScan data and the subsequent radial plots show azimuthally distinct features which do not have a concentration minima in the direction of the sun.
Figure 4.17: Radial summary plot of NO$_2$ concentrations measured by CS1 data for June 2012 taken during the PEGASOS campaign. 5° elevation data is plotted azimuthally with time over the day starting in the centre.
Radial plots for the entire campaign for CS1 are shown in Figure 4.17. These radial plots show that lower DSCDs of NO$_2$ are measured at the weekends. It is difficult to correlate NO$_2$ DSCDs with the measured wind direction as there appear to be very few similarities between days with the same measured wind fields, suggesting that the overriding influence upon the NO$_2$ DSCDs measured are the emissions rather than meteorology.

4.6.5 Comparison with in situ monitors

In order to evaluate the spatial variability of the NO$_2$ DSCDs which is evident in the CityScan data, a comparison has been performed to standard monitoring techniques. Individual lines of sight have been plotted against in situ monitor data. The difference between these two monitoring techniques should be highlighted at this point as it is important to appreciate the effects the different methodologies for measuring air quality have on the comparison. The in situ monitors measure at a single point on the ground which makes them excellent instruments to use when wanting to understand emissions from a specific source. However the area over which the measured value is relevant can be very small for multiple emission sources and inhomogeneous conditions in urban environments. Whilst CityScan is a remote-sensing instrument and thus is not ideally suited for separating out individual emission sources within an urban environment but it will provide concentrations along integrated lines of sight which may offer some indication of the background/average concentration of NO$_2$ over the city.

The position of all six Bologna in situ monitors were calculated as lines of sight from the CityScan instrument located at ISAC. These lines of sight were then turned into regions of interest by averaging the bottom 10° of CityScan data and taking a 10° region azimuthally centred around the line of sight with 5° either side. The LOS
for the in situ monitor at Porto San Felice is displayed over an example panorama in Figure 4.18 because this is the closest sensor geographically to CityScan. Two examples of the resulting data are shown in Figures 4.19 and 4.20 where CityScan data in the region of interest surrounding a particular in situ monitor collected for the length of the campaign is plotted with the in situ monitor data plotted alongside. It is important to note that the temporal resolution of the in situ monitors is lower than that of CityScan, with a CityScan measurement every six minutes in comparison with hourly averaged data recorded by the in situ monitors and a single CityScan measurement actually only lasting a fraction of second and then being averaged temporally to cover a larger area azimuthally. In order to make the two instrumental methods as comparable as possible the stratospheric component of the CityScan DSCDs needed to be removed. In order to do this for each panorama a stratospheric component was calculated by averaging all of the LOS’s in the top 10° of the FOV measured by the instrument for all azimuths. The stratospheric DSCD could then be subtracted from all the regions of interest to leave an assumed tropospheric SCD.
Figure 4.18: Top panel shows the position of PSF in relation to CS1 installed at ISAC with the bottom panel showing the LOS which was therefore defined for PSF.
GM and PSF are situated in very different locations, PSF is a very busy road junction whilst GM is several hundred meters from a road within a park in the city centre. It is expected that measurements from PSF will dominated by emissions from the major road neighbouring the monitor whilst GM is likely to show background concentrations of NO$_2$ in Bologna. Figures 4.19 and 4.20 show the differences between the measurements from the two in situ monitors but the similarity between the CityScan measurements in the two lines of sight. The lines of sight between the two in situ monitor are 35° apart and so there could be some similarity in the airmasses which are being sampled by CityScan. It seems most likely that CityScan is actually measuring the background concentrations rather than picking up the traffic emissions which are dominant in the PSF measurements, as CityScan measurements are DSCDs this theory is more robust as the measurements represent a line of sight across a large area and thus effects of individual emission sources will be smoothed out.

The comparison between CityScan and PSF shown in Figure 4.20 also highlights that CityScan does not always measure high concentrations around the evening rush hour which are evident in the in situ monitor data. The reasons for this are unclear as on the days when CityScan detects a statistically-significant increase in NO$_2$ during the evening rush-hour (7th, 22nd and 25th) there are no similarities between the meteorological measurements collected. It is hypothesised that the boundary layer height on these days must be relatively low in comparison to the rest of the campaign which will keep concentrations within a confined space vertically and thus increase the concentration of NO$_2$ which would be measured.

Correlations between each of the in situ monitors and CityScan data within the line of sight of them have also been analysed using CityScan data which is temporally binned to the same time resolution as the in situ monitors.
Figure 4.19: CityScan NO$_2$ DSCD ROI over the duration of the PEGASOS campaign (black) with in situ monitor measured NO$_2$ concentrations at the in situ monitor at Giardini Margheretti (blue). Each plot shows a calendar week from Monday on the left to Sunday on the right.
Figure 4.20: CityScan NO$_2$ DSCD ROI over the duration of the PEGASOS campaign (black) with in situ monitor measured NO$_2$ concentrations at the in situ monitor at Porta San Felice (blue). Each plot shows a calendar week from Monday on the left to Sunday on the right.
In order to be able to discuss the comparison of in situ monitors and CityScan data some appreciation of the assumptions which need to be made is required. Described in the rest of this section is a methodology which could be used to quantitatively compare the two measurements if it was possible to parametrise several unknowns such as path length, chemistry, dilution rates and dynamics. It is not possible to parametrise these within the time constraints of this work and therefore this is outlined here as thought experiment. To allow a quantitative comparison of measured concentrations from both techniques, the SCD measured by CityScan needs to be converted into the same units as used by the in situ monitors, $\mu g m^{-3}$. This calculation requires an assumed path length; here we will assume a path length of 10 km which is considered to be normal in urban areas [77]. The method used for this calculation is shown in Equation 4.1.

$$ VMR = SCD \times PL $$

(4.1)

Where the path length (PL) is in cm. Equation 4.1 will return a mean volume to mixing ratio (VMR) along the path length of CityScan in ppbv. To convert ppbv to $\mu g m^{-3}$ this value is multiplied by 1.88. Where the SCD measured is $1x10^{17} mol cm^{-2}$ the mean VMR along the path length at 3, 5 and 10 km is calculated as 25.47, 15.28 and 7.64 $\mu g m^{-3}$ respectively. The calculated mean concentration along the light path is lower than that measured by any of the in situ monitors, therefore, it is evident that in this scenario CityScan measurements are influenced by background fields of NO$_2$ more than the in situ monitor with the extent of this dependent upon the path length assumptions and the representativity of the ground-based sensors.

Correlation plots have been produced, based on a 1:1 relationship where 100 $\mu g m^{-3}$ is equal to $1x10^{17} mol cm^{-2}$, which, using the relationship outlined in Equation 4.1 is representative of a path length of 764.23 m. This is significantly lower
than would be expected in an urban environment and therefore indicates that some smoothing of the influence emission sources may be taking place as CityScan is heavily influenced by background fields. If we now assume that there is a 5 km path length and in situ monitors measure 100 µg m$^{-3}$ while CityScan measured a SCD of 1x10$^{17}$ mol cm$^{-2}$, then CityScan would be showing an approximately seven times lower concentration (5 km/764.23 m), between the points where the in situ monitor measured the NO$_2$ and where CityScan does. Again it is important to note that this method does not account for chemistry or dynamics and as such this value cannot be deemed accurate, it is only calculated to demonstrate the potential of this methodology. Ignoring the uncertainties in this relationship, through comparison with the in situ sensors the inhomogeneity of the emissions is evident, with background sites lying below this assumed relationship and roadside sites lying above it, seen in Figure 4.21.
Figure 4.21: Correlation between temporally binned CityScan NO$_2$ DSCD over the length of the PEGASOS campaign with in situ monitor measured NO$_2$ concentrations at the background in situ monitor at Giardini Margherita (top panel) and the roadside monitor at Porta San Felice (bottom panel) with a 1:1 line plotted.
Comparisons with background sites, such as that seen in Figure 4.19, demonstrate that the background site is not representative of average emissions over the CityScan path length as there is little correlation between the temporal features of the two measurements. This is unsurprising as CityScan measurements will also be influenced by any emission sources in the LOS. If it is assumed that traffic is the main emission source in Bologna it would be expected that there would be correlation, perhaps with a time offset, between the CityScan measurements and the roadside in situ measurements. The exact ratio of the SCD to VMR would depend upon the rise rate, dilution rate, path length, scattering and other properties of the atmosphere. It can be concluded that in order to quantitatively determine emission from CityScan data a model is needed in order to account for all of the uncertainties in the measurement. However, CityScan data can be used to probe spatial distributions of NO$_2$ and through correlations with in situ sensors primary emission sources can be identified.

### 4.6.6 Meteorological Influence Upon the Measurements

A brief investigation has been carried out to look at any changes in the concentrations of NO$_2$ measured which are caused by variations in meteorological conditions. In terms of temperature, the campaign can be split into two periods, the beginning of the campaign (6th-15th June) where temperatures were relatively cool and the latter half (15th to the 28th June) where the temperature measured in Bologna was significantly higher. This change in temperature conditions does not appear to affect the CityScan data in a significant way, because there is no step change or gradual change in the concentrations of NO$_2$ measured between the two periods. It would be expected that an increase in temperature would result in elevated NO$_2$ concentrations as was seen in [44]. The wind direction remains relatively constant.
throughout the campaign and thus the effect of this is difficult to establish. By far the most substantial change in meteorological conditions is seen on the 13th of June when there was a very large thunderstorm in Bologna which has been seen to cause a marked effect on the CityScan data, this period will be analysed and discussed further in Chapter 3.

4.7 Conclusions

The information content which can be derived from measurements taken by CityScan when deployed for an extended length of time in a single location has been demonstrated in this Chapter. Key results include the lack of an evening rush hour visible in the CityScan data for the majority of the campaign, the explanation for this is thought to be that the boundary layer is so deep by the early evening in Bologna that the pollution will be vertically dispersed further than in the morning and thus will be seen as less of a peak in concentrations measured by CityScan than by the in situ monitors.

Explored in this Chapter is the influence of major changes in meteorological conditions on the CityScan data. It had been assumed that distinct features would be visible under specific meteorological conditions however marked changes in the spatial patterns seen in the CityScan data are not correlated with the prevailing meteorological conditions.

It has been seen that the strength of the correlation with in situ monitors is highly dependent upon the proximity of the monitor to a dominant source of pollution. Owing to the method of measurement using CityScan, whereby a concentration is measured along an integrated line of sight the influence of individual emission sources are reduced and thus CityScan represents a mixture of both the background and the emission sources within the measurement area.
A dilution factor has been calculated for average atmospheric conditions whereby CityScan would measure an approximate seven time dilution in comparison to the in situ monitor. It has been shown that background sites have a dilution factor lower than this average scenario and roadside monitors lie above it; indicating that CityScan measurements are representative of neither background or roadside measurements, with the measurement technique producing a measurement which is influenced by both background and point sources.
Chapter 5

HSI-DOAS Measurements During and Following an Active Lightning Storm

The work in this Chapter describes measurements taken during and immediately following a large storm. An attempt will be made to separate NO\textsubscript{2} produced by lightning from increased DSCDs measured as a result of clouds. The results obtained from the CityScan instrument will also be compared to an independent MAX-DOAS instrument and in situ sensors and an estimate of lightning produced NO\textsubscript{2} per strike will be calculated.

5.1 An Introduction to Lightning

Lightning is defined as a high-current electrical discharge over a path length of several kilometres. Much of the lightning formed in the atmosphere is associated with convective thunderstorms. During thunderstorms warm air rises rapidly through clouds. As the moist air rises, rain drops and ice form. The motion of the ice gener-
ates an electrical charge through friction. Several types of lightning exist including cloud to ground (CG), intercloud, intracloud and cloud to air (all grouped together as IC) [36]. The types of lightning are shown in Figure 5.1. Monitoring of lightning strikes is important for a wide range of areas including convective rainfall estimation, storm tracking, aviation hazard, forest fire forecasting, cyclone development and evolution, the physics of the global electrical circuit, magnetospheric-ionospheric interactions and solar-tropospheric studies.

![Figure 5.1: Showing lightning types and formation, image taken from [36]](image)

In the area of atmospheric science it is also important to study lightning as it is a significant natural source of NO\textsubscript{x} (LNO\textsubscript{x}). The percentage of total NO\textsubscript{x} sources attributed to lightning varies with latitude between 4 and 23% with the highest contribution in the tropics [72]. The formation of LNO\textsubscript{x} in the atmosphere is via the Zel’Dovich mechanism which is a thermally activated reaction occurring at temperatures above 1000°C; temperatures within a lightning path can reach up to 30000°C and thus the Zel’dovich reaction is made possible within a lightning path.
The Zel’Dovich reaction is shown in Equation 5.1.

\[ N_2 + O_2 \rightarrow 2NO \] (5.1)

As discussed in Chapter 1, NO\(_x\) is important in the production of ozone and hence uncertainties in the emission of NO\(_x\) through lightning causes errors in model estimations of ozone budgets. In order to reduce these uncertainties much work is now focused upon measurements of lightning, including in-situ measurements from an aircraft platform in or around storms [35] and remote sensing from space [8].

5.2 Meteorological Conditions Measured on the 13\(^{th}\) of June 2012

The meteorological conditions on the 13th of June were of particular interest because the day was dominated by a very large storm during the late morning and early afternoon over Bologna. The storm not only produced high lightning activity but also included a very heavy hail storm. The temperature, humidity, wind speed and wind direction as measured in Bologna on the 13th of June are shown in Figure 5.2.

The main storm period is clearly visible in the temperature and relative humidity traces. A spike in the relative humidity and sharp drop in temperature at approximately 14.30 marks the time at which the hail storm occurred. As the meteorological data is hourly there may be some averaging affects which may have smoothed out some of the peaks. The wind direction on the 13th is dominated by south easterlies and southerlies. With the sharpest change in wind direction occurring at the main peak of the hail storm as marked by the sudden change in humidity. The wind speed stays relatively constant and gentle throughout the day with few features which are likely to be associated with the storm.
Figure 5.2: Top panel: Temperature and humidity measurements taken in Bologna on the 13th of June, relative humidity is plotted in black and temperature in red. Bottom panel: Wind speed (red) and wind direction (blue) as measured in Bologna city centre on the 13th of June.
It is important to understand the meteorological conditions in order to give context to the measurements of NO₂ which will be discussed later in this Chapter.

5.2.1 Lightning Detection Methods

5.2.1.1 Lightning Location Network (LINET)

The LINET lighting detection network has been in continuous operation since 2006 and consists of more than 60 stations in mid-Europe. LINET has also been used in several field campaigns in Germany, Brazil, Australia and West Africa during which the network’s 3D measurement capability has been demonstrated. LINET employs the time of arrival (TOA) method which is used to locate the horizontal and vertical position of the lightning strikes, when measured with several sensors. This 3D capability allows discrimination of CG and IC lightning types and is made possible by the network operating in the very low frequency/low frequency (VLF/LF) range. It is also possible to discern the polarity of the CG lightning strike using the LINET data. The polarity of the lightning strike depends upon the charge which is transferred. Some of the numerous lightning types are shown in Figure 5.1.

5.3 Lightning Detection on the 13th of June 2012

Lightning strikes were recorded on the 13th June 2012 in the Bologna area using LINET data; these strikes were also separated into CG and IC strikes. The lightning strikes recorded over Italy on the 13th of June for the entire day are shown on the left of Figure 5.3. Figure 5.3 shows the high frequency of lightning strikes which occurred on the afternoon of the 13th with the major part of the storm over Bologna between 11:00 and 15:00. Also shown in the right hand panel of Figure 5.3 are the strikes within the Bologna box.
Figure 5.3: Shown are: left, lightning strikes recorded over Italy for the day of the 13th of June 2012, with the colours representing time of day of the strike. Also shown on the plot is an area of interest box which is 1° by 1° centred over Bologna. Left shows the strikes with time within the Bologna box. Image courtesy of Enrico Arnone, ISAC.

In order to look more closely at the lightning strikes that occurred in the Bologna box the strike frequency has been analysed and separated into the different strike types. This is shown in Figure 5.4, with a zoomed in version on the right during the main storm period. It is clear in Figure 5.4 that the most frequent lightning strikes occurred between 12:30 and 13:30 with them mainly consisting of CG strikes and very few IC strikes.

5.4 Measurements of LNO$_x$

MAX-DOAS and CityScan measurements were recorded in Bologna throughout the 13th of June 2012. Both instruments were sited at ISAC in the north east of the city. The CityScan instrument set up is as has been previously been described in Chapter 4 and the set up of the the Bologna MAX-DOAS, TROPOGAS (TROPOspheric Gas
Figure 5.4: Lightning strikes recorded within the Bologna box on the 13th of June 2012. Showing, from top to bottom, counts of total lightning strikes, positive CG strikes, negative CG strikes and IC strikes and left to right, for the whole day and for the storm period only respectively. Image courtesy of Enrico Arnone, ISAC.

Analyzer Spectrometer), instrument is briefly discussed in Section 5.4.1. During the main part of the storm there was a heavy downpour of hail which may also effect the NO$_2$ concentrations measured.

5.4.1 TROPOGAS Instrument Description

The MAX-DOAS instrument used during the intercomparison is the TROPOGAS instrument, run by the GASCOD (Gas Analyzer Correlating Optical Differences) group [15]. TROPOGAS has been developed at ISAC-CNR with recent improvements owing to collaborations with the Geophysics Centre of Evora at the University of Evora. Several TROPOGAS instruments have been installed in permanent locations such as Monte Cimone (Italy) [41], “Mario Zucchelli” Station (Antarctica) [13], Bologna, Stara Zagora (Bulgaria) [87], Evora (Portugal) [14] and Thema (Ghana) as well as being involved in multiple field campaigns [62]. During the intercomparison
of DOAS instruments during the PEGASOS campaign the TROPOGAS instrument was sited at ISAC-CNR on a neighbouring roof to the CityScan instrument, CS1.

An exhaustive description of the instrument design and performance can be found in [15]. Figure 5.5 shows the input module (IM) which is only briefly described here. The IM includes two selectable positions for the input of external radiation allowing for two optical systems to be connected simultaneously alongside a further position for measuring internal calibration sources. Only one of these IMs was used in this work. The selected IM was coupled to the SODCAL (Scanning Optical Device Collecting Atmospheric Light) device, which is a small telescope (f/5, d=40 mm) mounted on a small alt-azimuth platform. SODCAL is therefore capable of performing measurements at various azimuth and elevation angles.

The scanning pattern used in this intercomparison study was at 1°, 2°, 4°, 8°, 16°, 30° and 90° elevation angles for all azimuth angles between 130° and 260° in 10° steps. The complete cycle takes approximately ten minutes.

5.4.2 CityScan and TROPOGAS Results

Throughout the thunderstorm on the 13th of June measurements were taken with one of the CityScan instruments (CS1) and TROPOGAS. In order to directly compare the data recorded for the two instruments, regions of interest were defined for CityScan corresponding to the TROPOGAS field of view. The region of interest was set as the viewing direction of the TROPOGAS ±1.25° both azimuthally and vertically. All CityScan data which fall within these boxes are averaged in order to give a single equivalent measurement. CityScan data for individual line of sights can then be plotted against the TROPOGAS data for that line of sight.

It is important to note that the different time resolution between measurements for each instrument will be a factor which affects the agreement between the data.
CityScan’s return time is six minutes whilst the TROPOGAS instrument has an approximate ten minute return time. The time difference between azimuth angles measured by CityScan is also smaller as there is no vertical scanning required which has to be performed by the TROPOGAS instrument. Therefore the time resolution between 10° steps is 10 seconds in comparison to 30 seconds for the TROPOGAS instrument. It is therefore expected that CityScan will be better equipped to resolve individual plumes than the TROPOGAS instrument.

Figure 5.6 shows the two NO\textsubscript{2} DSCD data sets plotted by azimuth and elevation. It is clear that there is good agreement between the data sets with a consistent offset
causing CityScan data to be always produce higher DSCDs. The offset in DSCD retrieved is caused by the difference in reference used and reference slant column amount which has then been subsequently added back into the data by the two instruments during the DOAS fitting procedure. Here, it is unnecessary to correct for this as the purpose of this work is to look at the trends recorded by the two instruments rather than the absolute values. There is generally excellent agreement between the two instruments except for when there are very short lived plumes in the field of view, in such instances either the TROPOGAS tends to underestimate the NO$_2$ concentrations or CityScan overestimates them. A clear example of this difference is seen in Figure 5.6 at approximately 10:00 for azimuth 140$^\circ$ and 11:30 for azimuth angle 180$^\circ$. The plume which is seen in Figure 5.6 at 11:30 is most distinct in the lowest elevation angles of the CityScan data and clearly progresses from south east to south hence the difference in time between the peak concentration for the two azimuth angles.
Figure 5.6: CityScan and TROPOGAS NO\textsubscript{2} DSCDs for the 13/06/12 at azimuths 140 (top), 180 (middle) and 220 (bottom). Solid lines show CityScan data and crosses and lines show TROPOGAS data. The various colours represent the different elevation angles as indicated by the legend.
Figure 5.7: CityScan and TROPOGAS NO$_2$ DSCDs for the 13/06/12 at elevations 1 (top), 4 (top-middle), 8 (bottom-middle) and 30 (bottom). Solid lines show CityScan data and crosses and lines show TROPOGAS data. The various colours represent the different azimuth angles as indicated by the legend.
In order to further understand the progression of the storm spatially, single
elevation angles have been plotted for azimuth angles $130^\circ$, $150^\circ$, $170^\circ$, $190^\circ$, $210^\circ$, $230^\circ$ and $250^\circ$ over the main storm period (between 14:00 and 15:30). This data is shown in Figure 5.7 for elevation angles $1^\circ$, $4^\circ$, $8^\circ$ and $30^\circ$, with azimuth angles from $130^\circ$ to $250^\circ$ at $20^\circ$ intervals. Figure 5.7 can be used to track the movement of the plumes measured through azimuth angles. It is clear that at lower elevation angles, the measured column amounts are consistently higher as is expected owing to a greater contribution to the column in the troposphere compared to higher elevation angles. Figure 5.7 also demonstrates the extra information which can be gained by using CityScan over traditional MAX-DOAS methods. The higher time lag between measurements from TROPOGAS causes artefacts which suggest that the plume is moving over time however when viewed alongside the CityScan data it becomes clear that this is an artefact caused by sampling. This is most obvious for elevation angle $30^\circ$ in Figure 5.7 where the peak plume concentration at 14.4 is imaged by CityScan at almost identical times whereas in the TROPOGAS data it appears to move with time. CityScan data at this time suggests that there is a large elevated plume of NO$_2$ with the highest DSCD at azimuth angle $250^\circ$ which is causing all elevation angles to show elevated DSCDs simultaneously. This observation can be validated by looking at the CityScan panorama at this time which is shown in Figure 5.8. This plume appears after the main part of the storm has passed and therefore there are questions regarding the source of the extremely high concentrations measured here. It is hypothesised that this could be caused by NO$_x$ emissions from the soil or through the melting of the hail on the ground.

The time with highest lightning activity as recorded by LINET is at approximately 13.00, this can be seen in Figure 5.4. At this time the most prominent lightning type is CG lightning. It is at this time where both DOAS instruments
Figure 5.8: CityScan Panorama of NO\textsubscript{2} DSCD at 14.4, showing a large plume centred around azimuth angle 250° (circled). Azimuth angle 0° is in the centre of the panorama at North.

measure elevated NO\textsubscript{2} concentrations in all viewing angles including the higher elevation angles which can be seen in Figure 5.9.

Figure 5.9: CityScan and TROPOGAS data for the 13/06/12 at azimuth angle 250° and elevations 0, 1, 2, 4, 8, 16, 30, 90°. Solid lines show CityScan data and cross and solid lines show the TROPOGAS data.

It appears that at this time both instruments are measuring elevated column
amounts within the clouds where lightning is occurring. There are considerable complications associated with the interpretation of this data as there is heavy cloud within the FOV. As clouds cause more scattering they also therefore increase the atmospheric path length and thus can give falsely elevated concentrations of trace gases in cloudy scenes. One method of trying to compensate for this is to look at the \( \text{O}_4 \) DSCDs; as \( \text{O}_4 \) has a relatively constant concentration in the atmosphere, changes in its concentration can be attributed cloud or increased aerosol. This concept will be considered further in the Section 5.4.2.2.

5.4.2.1 Instrumental Correlations

Correlations have been performed in order to validate the CityScan measurements and to confirm that the trends measured by both instruments are consistent. To make the two data sets comparable the CityScan data needed to be binned to the times of the TROPOGAS measurements. The threshold for this binning has been set to \( \pm 30 \) minutes in order to try to smooth some of the features which CityScan can capture that the TROPOGAS instrument doesn’t and also to ensure that there is enough valid CityScan data to be averaged. Examples of the output correlations are shown in Figures 5.10, 5.11 and 5.12.

Figures 5.10, 5.11 and 5.12 show that there is generally very good agreement between the CityScan and TROPOGAS data sets. Also obvious is the offset caused by using different references for the two instruments, which was discussed previously. This offset is different for the various elevation angles because the references used for the CityScan data set are by row in order to reduce errors caused by imaging on different rows of the detector. Thus the reference used for the 1° elevation will contain more \( \text{NO}_2 \) than that of the zenith spectrum, and therefore when a single reference slant column amount is added back in to the measurements this creates differences in the magnitude of the offset. One method to alleviate this variation in
Figure 5.10: Correlation of CityScan and TROPOGAS data over the 13/06/12 for azimuth angle 130°, colours represent the elevation angles 0, 1, 2, 4, 8, 16, 30 and 90° as shown in the legend. Displayed on the graph are best fit lines for each elevation with the corresponding correlation statistics.

The offset would be to have a different reference slant column amount for each row. However, due to time constraints this analysis will not be included here.

The results of correlations for all line of sights are summarised in Table 5.1. The 90° elevation angle results are considered to be unreliable due to the limited amount of data collected in the higher elevation angles for CityScan and thus should not be
Figure 5.11: Correlation of CityScan and TROPOGAS data over the 13/06/12 for azimuth angle 160°, colours represent the elevation angles 0, 1, 2, 4, 8, 16, 30 and 90° as shown in the legend. Displayed on the graph are best fit lines for each elevation with the corresponding correlation statistics.

The calculated gradients for this validation are, in the most, comparable to those which were calculated during the Cabauw Intercomparison Campaign of Nitrogen Dioxide Measuring Instruments (CINDI) [68]. In CINDI 22 spectrometers from 14 institutions were compared when measuring NO₂. The analysis of the data during
CINDI was treated as semi-blind, i.e. all the DOAS fits used the same settings but the analysis was performed separately and compared after the data had been analysed. The calculated NO$_2$ slant columns were then compared to a reference data set; the reference data set comprised of 30 minute averaged data from the instruments which measured most consistently during the campaign. The calculated
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### Elevation Angles

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</tr>
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</table>

Table 5.1: Correlation statistics for the comparison between CityScan and the MAX-DOAS data for the 13/06/12. displayed are R² values, gradients (c) and intercepts (m) for each line of sight of the MAX-DOAS instrument.

Slopes for all instruments were between 0.85 and 1.1. These results are marginally better than most of the CityScan vs TROPOGAS calculated gradients. However during this work the DOAS settings used to analyse CityScan and TROPOGAS data have not been synchronised and thus further errors may be introduced by this.
5.4.2.2 Imaging LNO$_2$

The main advantage of CityScan over traditional MAX-DOAS systems is the ability to build up images of NO$_2$ over a full hemisphere in a relatively short time period. The imaging capability of CityScan allows the movement and development of individual plumes to be tracked. On the 13th of June there were two main pollution events which will be discussed. Firstly, the large amount of NO$_2$ created during the storm itself and secondly the large amount of NO$_2$ which was formed at ground level several hours after the storm had passed.

![Image of CityScan and Bologna MAX-DOAS instruments NO$_2$ DSCD for the 13/06/12 at azimuth 250.](image)

Figure 5.13: CityScan and the Bologna MAX-DOAS instruments NO$_2$ DSCD for the 13/06/12 at azimuth 250. Highlighted on this plot are six main points of interest during the day which are shown as imaged data in Figure 5.14.

As can be seen in Figure 5.4, the main storm period occurred between 11:00 and 15:00 with a peak in activity at approximately 13:00. The main points of change in terms of NO$_2$ concentrations can be seen in Figures 5.13 and 5.14. There are six points which have been highlighted in Figure 5.13 and numbered one to six. The
NO₂ panorama for each of these six points is then shown in Figure 5.14.

Figure 5.14: CityScan NO₂ DSCD (x10\(^{17}\)) (left) and O₄ (x10\(^{44}\)) DSCD (right) over six minutes for the main points of activity on the date of the 13/06/12 which have been highlighted in Figure 5.13.

These six panoramas will be discussed here to demonstrate the ability of CityScan to monitor the evolution of a storm. When examining the CityScan panorama data for the 13th of June, the NO₂ DSCDs appear to be as expected until 10:30 at which point there is the start of the increase in column amount in a northern direction.
This continues to build, as does the cloud, until 13:00 where a huge spike is then seen in the NO$_2$ DSCDs. After this peak in DSCD the measured NO$_2$ DSCDs start to decrease and the plume appears to move overhead of the CityScan instrument towards the south of the city.

The DSCD of NO$_2$ continues to decrease until 14:00 where the column amount at the ground then begins to build and the boundary layer appears to deepen, with the maximum concentrations and boundary layer height seen at 15:00. This peak marks the end of the main activity after which time the NO$_2$ gradually decreases leaving the main plume of NO$_2$ in a north/north eastern direction.
It is hypothesised that at point three, occurring at 13:00 that CityScan is actually imaging NO$_2$ as it is being produced within the cloud by CG lightning strikes which were recorded within the Bologna box as demonstrated in Figures 5.3 and 5.4. The highest concentrations of NO$_2$ imaged by CityScan are seen between the west and north east which is in agreement with the lightning strike data which have been recorded between 12:00 and 13:30 by LINET. There are clear complications with the interpretation of this data due to the heavy cloud which coincides with the main part of the storm. There is likely to be increased scattering within the cloud and thus increased path lengths taken by individual photons, which in turn causes increases in the concentration of NO$_2$ observed. In order to try to remove some of this effect the NO$_2$ DSCDs were ratioed to O$_4$ DSCDs recorded at the same time. This method has previously been used in lightning studies as seen in Fraser et.al. [26], where path-enhanced NO$_2$ was separated from lightning produced NO$_2$ using this method. As discussed in Chapter 3 this ratio does not entirely remove the effect caused by increased aerosol, however it does go some way towards reducing the effect. As shown in Chapter 3 using the ratio can potentially create artefacts as a function of SAA due to the azimuthal dependence of DSCDs. However, it is assumed here that as the increase in concentrations here are extremely large the azimuthal artefacts are unlikely to be a dominant feature. Also due to the heavy cloud creating a more homogeneous sky (i.e no view of the sun) the azimuthal effects, caused by the sun location, may be minimised.

The NO$_2$/O$_4$ ratio has been calculated for the entire day and is shown in Figure 5.15 with the ratio at the top, NO$_2$ DSCD in the middle and O$_4$ DSCD at the bottom for north, south, east and west at both 10° and 50° elevation angles. Through examination of Figure 5.15 it can be seen that the enhancement in NO$_2$ at 13:00 within the cloud (50° elevation) is mainly attributable to path enhancement within
Figure 5.15: CityScan NO$_2$/O$_4$ ratio (top) NO$_2$ DSCD (middle) and O$_4$ DSCD (x10$^{40}$) (bottom) or North (black), South (green), East (blue) and West (red) at both 10° (solid line) and 50° (dashed line) elevation angles over the main storm period on the 13/06/12.

the cloud whilst it is clear that the high NO$_2$ concentrations at the lower elevation angles (10° elevation) are likely to be caused by actual NO$_2$ enhancements. At this time the main lightning sources were cloud to ground strikes and so it is likely that this enhancement is a direct result of those lightning strikes that are not within the cloud.
At 15:00 the highest concentrations of NO\textsubscript{2} are seen for the entire campaign, it is clear in both the panorama and ratio summary for this time that these high concentrations are mainly observed at the lower elevation angles; as the main storm activity has passed by this time it is unlikely that these concentrations are a direct result of lightning in the Bologna area. There are several possible explanations for these unusually high levels. Firstly, this could be related to the melting of hail and the changes that causes in soil moisture. Schindlbacher and Zechmeister-Boltnstern [71] have shown that NO\textsubscript{x} emissions from soil are inhibited by a water-saturated soil and thus it is possible that the NO\textsubscript{x} emissions from the soil could have been suppressed during the main part of the storm and then as the hail melts and evaporation from the soil occurs the NO\textsubscript{x} emissions begin again. At this time it is also the peak of the %RH for that date which is in agreement with this explanation.

A second potential reason for this very large increase in NO\textsubscript{2} could be downwind NO\textsubscript{2} from storms which are occurring outside of the immediate measurement area. Throughout the 13th June there was high storm activity in the areas surrounding Bologna and it is possible that CityScan is measuring the downwind NO\textsubscript{2} from these. It is likely that these upwind storms are also responsible for the high ground level concentrations of NO\textsubscript{2} seen at approximately 16:00 also. A third possible explanation is that the rainfall has washed a significant amount of aerosol from the atmosphere, thus causing increased visibility and therefore an increased measured SCD.

5.5 Comparison with in situ Monitors

CityScan data has been compared to the in situ monitor data to investigate how wide-spread the elevated NO\textsubscript{2} generated during and after the storm was. The comparison has been performed using the same method outlined in Chapter 4. The comparison between CityScan data and in situ monitors for those monitors closest
to CityScan (Porta San Felice, Via Chiarni and villa Torchi) is relatively good, with all three monitors showing the daily maximum at approximately the same time as the CityScan DSCDs peak concentration. The comparisons can be seen in Figure 5.16. The best agreement is found between CityScan and Porta San Felice, which is also the monitor which is closest in proximity to the CityScan deployment location. Interestingly, the three monitors, whilst being the closest to CityScan, are all in opposite viewing directions from CityScan and thus this confirms that the effects of the storm were widespread azimuthally. It is important to note that the gaps in data from the in situ monitors (VC and VT) are caused by concentrations dropping below the detection limit of the system.

For reference, the comparison with the other three in situ monitors (SL, SM and GM) is shown in Figure 5.17.
Figure 5.16: CityScan NO₂ DSCDs (black) vs in situ monitors (blue) with PSF in the top panel, VC in the middle panel and VT in the bottom panel.
Figure 5.17: CityScan NO$_2$ DSCDs (black) vs in situ monitors (blue) with SL in the top panel, GM in the middle panel and SM in the bottom panel.
5.6 Summary

This chapter has made clear that the potential uses of CityScan do not end with air pollution monitoring. Here CityScan’s ability to monitor and image the progression of a large naturally occurring source of NO\textsubscript{2} has been demonstrated. This method could prove invaluable in studies of lightning NO\textsubscript{2} as it can provide not only information on the emissions that can be directly attributed to the storm but can also give indications of dynamical processes affecting NO\textsubscript{2}. There have also been demonstrated some potential areas of interest for further research such as looking at soil emissions of NO\textsubscript{2}.

It has also been demonstrated that the CityScan measurements are comparable to a well characterised MAX-DOAS set-up. When the instruments are compared the gradient value is generally between 0.7 and 1. As this comparison was performed relatively crudely in terms of comparison of data analysis set-ups this is an excellent result. As discussed in this chapter there is a consistent offset caused by the differences in the reference which was used in the DOAS fit. However due to the differences between instruments this is challenging to correct for and outside the scope of this work. A comparison with the in situ monitors also confirms that the increased NO\textsubscript{2} measured by CityScan after the storm had passed was relatively widespread.
Chapter 6

HSI-DOAS Measurements During the ClearfLo Campaign - Preliminary Results

6.1 Introduction to the Campaign

The Clean Air for London (ClearfLo) campaign was a large collaborative NERC (Natural Environment Research Council) funded project involving several UK and international partners. The overarching aims of the campaign were to set up air pollution monitoring sites alongside meteorological measurements to investigate boundary layer pollution across London. These measurements were to be made at street level and elevated sites and complemented by modelling in order to improve knowledge of London’s urban atmosphere.

The ClearfLo project ran from January 2010 for three years with two intensive operational periods (IOPs) in 2012. The first IOP ran from the 9th of January to the 12th February and the second IOP2 from the 20th July to 23rd August. During these IOP’s, a main measurement site was established in North Kensington (lat...
51.521°, lon -0.214°) where the majority of participating instrumentation was based for the measurement period. This site was based alongside a long term London Air Quality Network (LAQN) monitoring site which is classified as urban background (UB). Results from the summer campaign are presented in this thesis.

ClearfLo has six overarching aims \[64\], these are:

- Establish an infrastructure to measure meteorology, gaseous composition and particulate loading of London’s urban atmosphere at both street level and elevated sites.

- Develop a climatology of London’s urban atmosphere in order to determine the relationships between surface meteorology, gaseous composition and particulates at a rural location, a city background site (away from local traffic sources) and a city street site (close to local traffic sources) through the full range of seasonal cycles.

- Determine the meteorological processes that control the heat content, mixing properties and depth of London’s urban boundary layer, especially the nighttime boundary layer, and place them in the mesoscale context, including the prevalence of sea breezes.

- Determine the chemical processes that control the loading of $O_3$ and $NO_2$ in London’s urban atmosphere, particularly the role of biogenic emissions and the role of nitrates in night-time chemistry, and place the urban concentrations into the synoptic context.

- Determine the chemical and physical processes that control the size and number distribution of particulate matter in London’s urban atmosphere, and identify their chemical sources, and place the urban characteristics into the synoptic context of the background.
Evaluate the strengths and weaknesses of a current air quality model.

As part of the ClearfLo campaign CityScan instruments were installed in London for both IOPs.

6.1.1 CityScan Deployment Locations

As discussion of all of the measurements taken during the ClearfLo campaign is beyond the scope of this work only the measurement sites which were locations for the instruments whose data are used in this work will be discussed here.

During IOP1 two CityScan instruments were installed in London. CS1 was installed in North Kensington atop Trellick tower (lat 51.523°, lon -0.206°) and the second on Dartrey Tower (lat 51.482°, lon -0.178°) in Chelsea. For IOP2 a third CityScan instrument was installed in Soho upon Kemp House (lat 51.513°, lon -0.135°). The locations of all three of these deployment sites are shown in Figure 6.1. It should be noted that during IOP2 CS1 was deployed on Kemp House, CS2 on Trellick tower and CS3 on Dartrey Tower.

Trellick Tower is a 32 storey tower in North Kensington which provides largely uninterrupted views of West London and some views over central London. Dartrey Tower is a 16 storey building in Chelsea where the field of view provides clear lines of sight to the north and East and give an unobstructed view of Trellick Tower. The third tower is Kemp House, a 20 storey building located in the centre of Soho, with clear views over much of central London and of both other CityScan deployment locations. The locations for the CityScan installations were identified using a 3D model data set of London, in order to select sites which would provide the best viewpoints of London.

Examples of the 3D panoramas which were created for each building are shown for Trellick Tower in Figures 6.2 and 6.3 with Figure 6.2 showing the view from
Figure 6.1: The locations of the three CityScan deployment sites during the ClearLo IOPs

Trellick in several directions and Figure 6.3 highlighting the areas of the city which would be obstructed by structures on the roof of Trellick Tower. This form of analysis provided knowledge of the obstructions which would be in the FOV of each instrument and allowed potential deployment sites to be assessed remotely. The views from Trellick shown in Figure 6.2 demonstrate that the FOV for an instrument deployed here would be unobstructed by other buildings and the LOS to the main site in North Kensington was clear. However, the roof structure itself contained several features which would block sections of the azimuthal rotation. Both of these findings could be taken into account when assessing the potential deployment location. Ultimately, the decision was made that the position on the roof itself could be optimised to minimise the impact of the roof structures but that the FOV which Trellick provided could not be improved upon with other alternative buildings.

The installations on each tower are shown in Figure 6.4.
Figure 6.2: The view from Trellick Tower in three directions; view one in a NEE direction, view two SE and view 3 towards the main campaign site at North Kensington.
Figure 6.3: A birds-eye view of London showing the areas of the city which will be obscured from the CityScan FOV (in black) by structures on the roof of Trellick Tower.

Figure 6.4: The installations of the three CityScan instruments during the ClearfLo IOPs, from left to right Kemp House, Dartrey Tower and Trellick Tower.
<table>
<thead>
<tr>
<th>Air Pollutant</th>
<th>Monitoring Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>UV Absorption</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>Chemiluminescence</td>
</tr>
<tr>
<td>SO₂</td>
<td>UV Fluorescence</td>
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<tr>
<td>CO</td>
<td>IR Absorption</td>
</tr>
<tr>
<td>PM₁₀ and PM₂·₅</td>
<td>Tapered Element Oscillating Microbalance (TEOM)</td>
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<tr>
<td></td>
<td>Beta Attenuation Monitor</td>
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<td></td>
<td>Gravimetric Monitor</td>
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<td></td>
<td>Filter Dynamics Measurements System (FDMS)</td>
</tr>
</tbody>
</table>

Table 6.1: Standard LAQN Measurement Techniques for each measured species.

### 6.2 London Air Quality Network

The LAQN is an extensive network of in-situ monitors across Greater London with over 100 sites monitoring NOₓ and many also measuring PM₁₀, CO and O₃[2]. LAQN is operated and managed by the Environmental Research Group (ERG) at Kings College London. The techniques used to monitor the different species are shown in Table 6.1

The LAQN monitors within the network are classified as either kerbside, roadside, suburban, urban background or industrial depending upon their situation (the definitions of each classification can be found in the AEA Energy and Environment Report concerning Diffusion Tubes for Ambient NO₂ Monitoring: Practical Guidance [76]). Briefly here, kerbside monitors should be within 1 m of the kerb, roadside between 1 m and 5 m of the kerb and mounted ideally on a lamp post on the pavement, urban background sites must be located more than 20 m from a busy road, 10 m from a main road and 5 m from where vehicles may be stopped and idling.
6.2.1 Representativity of point measurements

The representativity of individual monitoring site measurements over large spatial scales very much depends upon the position of the instrument, ie whether the instrument is at a roadside, if the surrounding area is homogeneous (in terms of topology), whether the instrument is directly influenced by specific emission sources. The main influence on roadside monitors will often be the neighbouring road and therefore they are unlikely to be representative of a wider spatial area than that directly near to them. On the other hand urban background sites are usually positioned in an area where there is thought to be little influence from local sources and therefore they are more likely to represent the urban background concentrations on a wider scale. It is for this reason that LAQN data used in this work will be from urban background sites as these are most likely to show the large scale air quality trends which CityScan instruments are able to measure.

Three urban background instruments which were located within the CityScan measurement area were selected for the initial comparisons with CityScan measurements. Those are Bloomsbury in Camden (lat 51.522°, lon -0.126°), Horseferry Rd in Westminster (lat 51.495°, lon -0.214°) and North Kensington (lat 51.521°, lon -0.133°) in the Kensington and Chelsea borough. These three monitoring sites are shown in Figure 6.5 alongside the three CityScan instrument locations.

6.3 Background to the Campaign Period

During the summer IOP of the ClearfLo project the London Olympic Games were held; this makes this a period of both scientific and political interest. Throughout the IOP, CityScan instruments were operated in London with almost continuous data streams.
The London Olympic games took place between the 27th of July and 12th of August 2012. In order to minimise the impact of the Olympic Games in terms of air quality and disruption to London residents, several changes to the London’s transport network were made. Such modifications provide an opportunity to examine the impact of the Games on air quality. It is hoped that the measurements taken during ClearfLo will be able to contribute to understanding of the effectiveness of these modifications to the transport network.

Meteorological data were recorded at the main North Kensington site however owing to the location of the weather station in relation to the surrounding buildings the weather station was shielded from winds from the North and East. As such, the wind data recorded at this site will not be presented here.

The most striking feature in the meteorological data for the summer ClearfLo campaign is a period of unusually high temperatures in excess of 27°C in the first
week of the campaign, between the 24th and 27th of July with temperatures reaching over 32°C on the 26th of July. A plot of the temperature measurements taken at the North Kensington site can be seen in Figure 6.6; the heatwave can be identified between the 24th and 27th of July.

Figure 6.6: Temperature recorded at North Kensington during the ClearfLo summer campaign.

6.4 Instrument Performance During the ClearfLo Campaign

In order to assess any possible degradation to CS1 which may have occurred between the PEGASOS and ClearfLo campaigns (and the one thousand mile journey which took place between the two) the ILS and spectral shift were recalculated us-
ing ClearfLo data. The ILS and spectral shift were calculated using the method described in Sections 2.4.1 and 2.4.2. The output from the analysis is shown in Figures 6.7 and 6.8.

Figure 6.7: The ILS of CS1 during the ClearfLo campaign calculated at six discreet points within the QDOAS fitting window.

When compared with Figures 2.28 and 2.31 it can be seen that there is some degradation in the ILS in the ClearfLo data. However, the overall variability in the ILS over the CCD remains relatively constant, with the exception of increased variability in window five. It can also be seen that there is significant degradation in the FWHM of the ILS in the top eight rows of the detector. The comparison
of the spectral shift between the campaigns shows that transit of the instrument caused increased variance in the spectral shift, again this is especially marked in window five. Possible explanations for the degradation in ILS and spectral shift include movement of the optics during transit between the two campaigns and also differences in operating temperature during the campaigns.

As with the PEGASOS campaign owing to wear and tear on the spectrometer shutter, the data collected during the campaign, after the first few days, in the lower viewing geometries, indicate incomplete shutter operation and therefore no
scattered-sunlight measurements are recorded in the low elevation angles. The data were most usable in the first six days of operation.

### 6.5 Panoramic Data from CS1

Data has been collected for CS1 from the 20th of July to the 24th of August with some breaks in the data owing to instrument failures. Figure 6.9 shows the radial plot summary of data collected by CS1 in July 2012. The summary shown in Figure 6.9 demonstrates that the data quality degrades from the 26th of July onwards, with more gaps in data visible in the radial plots.

Panoramic data from the 21st of July will be discussed here as it shows large scale features which were not seen in the PEGASOS data set. There are two time periods of interest on the 21st, the first between 12:00 and 15:30 and the second between 17:00 and 18:00. Panoramas of NO$_2$ and O$_4$ DSCDs are shown for both time periods in Figures 6.10 and 6.11. Both figures show the development and movement of what appears to be a large NO$_2$ plume. In both cases this plume appears to originate over the city centre, West of the instrument and passes directly over the instrument.

Unfortunately, the interpretation of this data is made more complicated as the 21st of July is a cloudy day, which can be seen in the webcam images shown behind the DSCD data. Enhancements in the O$_4$ DSCDs during both these periods in-cloud show the effect of path length increase on the retrieved DSCD. In order to try to separate increases in NO$_2$ concentration from path length enhancement caused by cloud the NO$_2$/O$_4$ ratio plots are examined.

Radial summary plots have been produced for NO$_2$, O$_4$ and NO$_2$/O$_4$ for the 20th to the 25th of July for investigation of path length enhancements. The O$_4$ radial plots stay relatively constant throughout the time period discussed whilst both NO$_2$ and the NO$_2$/O$_4$ ratios show large variability with viewing direction and time of day.
Therefore, it is concluded that the measured changes in NO$_2$ DSCDs seen during this period are likely caused by variability in the emission sources rather than path...
length enhancement owing to clouds; the radial plots for the 21st, 23rd and 25th of July are shown in Figure 6.12. Examination of 6.12 shows that the O₄ DSCDs remain relatively constant over the time period in comparison to the NO₂ and ratio plots. Whereas the NO₂/O₄ ratio plot, especially on the 23rd of July, contains similar spatial features to the NO₂ radial plot. Further work needs to be conducted to reinforce the following hypothesis, however, the results shown here point towards changes in emissions being responsible for changes in NO₂ DSCD measured in the two time periods considered.

As can be seen in Figure 6.12 the ratio radial plots for the 21st and 25th of July both contain very high values which are off the colour scale which is used under normal conditions and as such the spatial variability of the ratio cannot be easily interpreted. Therefore, the NO₂/O₄ ratios for these two days were recalculated and plotted on a different colour scale, the results of this are seen in Figure 6.13. The NO₂/O₄ ratio plots for the 21st and 25th of July in Figure 6.13 now show clear structure in space and time which correlates very well with the NO₂ radial plots, this structure is not seen in the O₄ radial plot in Figure 6.12. It is likely that the variability seen in the NO₂/O₄ ratio and NO₂ plots is caused by changes in emissions on these days rather than path length enhancement caused by clouds in the FOV owing to the lack of increase in O₄ DSCDs at the same time. This hypothesis is only true for the lowest part of the panorama when performing this analysis as the radial plots only show the 5° viewing angle.

To establish whether the enhancements in NO₂ seen between the 21st and 25th in the elevated FOVs are due to emissions or path enhancement, radial plots for NO₂, O₄ and NO₂/O₄ DSCDs have been generated for the 40° viewing angle, which will be more representative of measurements taken in the higher part of the FOV. The radial plots for this time period are seen in Figure 6.14.
Figure 6.14 indicates that enhancements in the NO\textsubscript{2} DSCD are caused by both path length enhancements and emissions, both of the effects can be seen in the radial plots. Clear examples of where path enhancement is the likely cause of increased NO\textsubscript{2} concentrations are seen on the morning of the 23rd July, in an Easterly direction and in all directions for all days in the morning. During the early morning the light path through the atmosphere at this viewing angle is very long owing to the high SZA. This effect is less marked in the 5° radial plots shown in Figure 6.12 as the stratospheric column is smaller compared to the tropospheric column at the lower elevation angles however it is still visible. On the afternoon of the 21st at the elevated angle shown in Figure 6.14 the higher concentrations of NO\textsubscript{2} measured are mirrored in the O\textsubscript{4} radial plot and thus it is likely that the apparent increase in NO\textsubscript{2} which has been observed and discussed earlier in this section is partly due to path enhancement in the clouds which are present at this time.

On the 25th there is an example of where an increase in NO\textsubscript{2} DSCD is likely caused by increased emissions, in the afternoon in the southern half of the hemisphere which can be seen in Figure 6.14. The elevated NO\textsubscript{2} DSCD measured at this time is not replicated in the O\textsubscript{4} measurements and thus it is likely that it is caused by emissions.

The investigation into the cause of elevated NO\textsubscript{2} DSCD has lead to several conclusions. It has been shown that on the 21st of July that increased NO\textsubscript{2} DSCD in the lowest viewing angles is dominated by heightened emissions whilst at higher elevation angles, in a cloudy scene, the path enhancement produces DSCD which are high not due to emissions but because of an increase in path length caused by additional scattering in cloud. It has been shown that it is possible to untangle path enhancement effects from emissions on a case-by-case basis. However, to do this automatically would require considerable algorithm development and further analysis.
which were not possible to perform within the time constraints of this thesis.

6.6 Comparison with in situ Monitors

As with the PEGASOS analysis, CityScan time series have been created in the ROI around the chosen in situ monitors. The ROI is ±5° around the LOS to the in situ monitor azimuthally and an average of the bottom 15° vertically. In this case BL0 (ROI, 31.75-41.75°), WM0 (ROI, 167.87-177.87°) and KC1 (ROI, 272.85-282.85°). As data quality deteriorates after the 25th of July, comparisons between the two instrumental methods will initially focus only on data from the 20th to the 25th July. Summary plots of the comparison for the three in situ monitors and CityScan are shown in Figure 6.15.

The agreement between all of the in situ monitors and the CityScan ROIs is on the whole quite poor, however, on the 25th of July some agreement is shown for all monitors and also there is some level of correlation on the 24th between BL0 and the CityScan ROI around it. To examine these days more closely daily plots have been created and are shown for the 25th of July in Figure 6.16. Figure 6.16 shows a good level of agreement between the two measurement techniques with all in situ monitors and CityScan capturing the morning and evening rush hours. There is a clear time offset between the measurements demonstrated in Figure 6.16 with the in situ monitors consistently measuring peak NO\textsubscript{2} concentrations before CityScan does. This is likely to have been caused by the time taken for the pollution to rise into the FOV of CityScan from ground level. Interestingly this offset is not consistent for all three monitors with the temporal offsets being approximately 30 minutes for BL0, one hour for KC1 and 3.5 hours for WM0. The difference in time offsets could be attributed to many factors including, street canyon dynamics, wind direction and speed and position of the monitor relative to the nearest road source. As the peak
NO$_2$ concentration is seen in the WM0 monitor measurements sometime before the other monitors and CityScan it suggests that the main area of high pollution is likely to be south of CS1 in the area nearest to WM0 in the early morning and then it is being blown across the city in a southerly direction as the morning progresses.

On the 24th of July there is also some agreement between the CityScan ROI and BL0 but little correlation with the other two in situ monitors, a daily time series for BL0 on the 24th July is presented in Figure 6.17 Again for this day and ROI the morning and evening rush hours are apparent in both the CityScan and in situ monitor data. In order to establish why there is significantly better agreement between CityScan and BL0 in comparison to the other monitors the NO$_2$ radial plot of the day has been investigated.

The radial plot in Figure 6.18 establishes that the area of the highest NO$_2$ concentration on the 24th of July is north east of CS1, which is also in the direction of BL0, whilst in other azimuthal directions the NO$_2$ concentrations remain relatively low. The fact that there is better agreement in the direction of the area of highest pollution suggests that CityScan DSCDs, in situations where there are not large areas of pollution, measures a so called diluted background which is less susceptible to ground level emission sources than even urban background sensors owing to the heights of the CityScan measurements. Whereas in high pollution events, the emissions are so high that there is still a significant concentration of NO$_2$ by the time it rises above the rooftops as significant amounts of NO$_2$ haven’t been removed through chemical reaction pathways or dilution.

**6.6.1 Plume Positioning Using Multiple Instruments**

When measurements have been collected from several instruments it should be possible to pin-point the area with the largest NO$_2$ concentrations. This would be
especially true if there was a situation where three CityScan instruments running concurrently and viewing the same area. During the ClearfLo campaign there are days where all three CityScan instruments were collecting data at the same time. However, owing to time constraints the data from all three could not be analysed and presented in this work. Even so it has been possible to produce a very preliminary data set from CS2, based on Trellick Tower, for the 25th of July. Combining the measurements for CS1 and CS2 for this day provides potential to make a first attempt at a very basic 2D tomographic method. In the morning of the 25th of July the radial plot of NO$_2$ DSCDs from CS1 shows high concentrations in all azimuth directions whilst CS2 shows the peak concentrations in the southern half of its measurement hemisphere. Even this very limited information provides evidence that the area of highest pollution on that morning was South of Trellick tower. After 12:00 on the 25th of July the area of peak concentrations of NO$_2$ from both instruments is more constrained which allows a smaller area to be identified as that where peak concentrations of NO$_2$ are likely to be positioned.

The data shown in Figure 6.19 are the daily NO$_2$ DSCD radial plots for both instruments CS1 and CS2 positioned over a map of London. Marked on the map are the FOVs from each instrument which measure the peak NO$_2$ concentrations, the areas where the two instruments FOVs overlap is the area with the highest probability of having the highest concentrations of NO$_2$ on this day at this time. The area which is highlighted on this day is over central London.

It is evident from this study that if more than two instruments worth of data was available that triangulation of a plume should be possible.
6.7 High Pollution Events

The most prominent feature in the July time series for all ROIs is the very high NO$_2$ concentration during the heatwave period, that occurred between the 24th and 27th of July with this being seen most strongly in the BL0 and KC1 ROIs. The time series for all three instruments are shown in Figure 6.20.

Interestingly, the concentrations measured at the in situ monitor at WM0 and the ROI around it specified for the CityScan data are considerably lower during this period in comparison to the other two monitors, with maximum concentrations recorded by the in situ monitors being $<90 \, \mu g \, m^{-3}$ in comparison with KC1 where values over $160 \, \mu g \, m^{-3}$ were recorded. WM0 having the lowest concentrations measured during this period is unexpected because the monitor at WM0 is more centrally placed than KC1; however WM0 is also in the congestion charging zone which may be contributing to the reduction in NO$_2$ observed. Another potential contributing factor could be the meteorological conditions over this time period which may reduce the influence of emission sources under specific conditions. For example if there was a specific wind direction which could bring in clean air over the monitor instead of the monitor being downwind of the city centre.

6.8 Summary

The potential range of information that can be derived from CityScan data collected during ClearfLo has been demonstrated. Examination of panoramic data and the relationship between NO$_2$ DSCD and path length enhancement has been performed and untangled for some specific scenarios using NO$_2$ /O$_4$ ratios. Furthermore this effect has been studied at several elevation angles, showing that in the lowest elevation angles NO$_2$ DSCDs are dominated by emissions whilst at higher elevation
angles path enhancement often plays the major role.

Comparisons with in situ monitors have shown that during high pollution episodes agreement is improved between CityScan and the in situ monitors. Finally an attempt has been made to demonstrate the tomographic potential of this measurement technique when two or more instruments are measuring concurrently.
Figure 6.10: NO$_2$ DSCD (x10$^{17}$) (left column) and O$_4$ DSCD (x10$^{14}$) (right column) panoramas collected by CS1 on the 21st July 2012 between 12:06 and 15:23. All units are mol cm$^{-2}$, with the scales on the NO$_2$ and O$_4$ being x10$^{17}$ and x10$^{14}$ respectively.
Figure 6.11: NO₂ DSCD (x10^{17}) (left column) and O₄ DSCD (x10^{44}) (right column) panoramas collected by CS1 on the 21st July 2012 between 17:00 and 18:00. All units are mol cm^{-2}, with the scales on the NO₂ and O₄ being x10^{17} and x10^{44} respectively.
Figure 6.12: NO$_2$ DSCD ($\times 10^{17}$) radial plots (left column), O$_3$ DSCD ($\times 10^{14}$) radial plots (middle column) and NO$_2$/O$_4$ DSCD radial plots (right column) measured by CS1 on the 21st (top row), 23rd (middle row) and 25th July 2012 (bottom row). Colour bars for each radial are shown on the bottom row. All units are mol cm$^{-2}$. 
Figure 6.13: NO$_2$ DSCD radial plots (left column) and NO$_2$/O$_4$ DSCD radial plots (right column) measured by CS1 on the 21st (top row) and 25th July 2012 (bottom row). NO$_2$/O$_4$ DSCD radial plots now scaled to 4.5x10$^{13}$. All units are mol cm$^{-2}$.
Figure 6.14: NO$_2$ DSCD ($x10^{17}$) radial plots (left column), O$_4$ DSCD ($x10^{14}$) radial plots (middle column) and NO$_2$/O$_4$ DSCD radial plots (right column) measured by CS1 on the 21st (top row), 23rd (middle row) and 25th July 2012 (bottom row) for the 40° viewing angle. Colour bars for each radial are shown on the bottom row. All units are mol cm$^{-2}$.
Figure 6.15: Time series for the 20th to the 25th of July of CityScan (CS1) NO\textsubscript{2} DSCD ROIs (plotted in black) in the direction of BL0 (top), KC1 (middle) and WM0 (bottom) with in situ data for that location over plotted.
Figure 6.16: Time series for the 25th of July of CityScan (CS1) NO₂ DSCD ROIs (plotted in black) in the direction of BL0 (top), KC1 (middle) and WM0 (bottom) with in situ data for that location over plotted in blue for each day.
Figure 6.17: Time series for the 24th of July of CityScan (CS1) NO$_2$ DSCD ROI (plotted in black) in the direction of BL0 with BL0 in situ data over plotted in blue.
Figure 6.18: NO$_2$ DSCD radial plot for the 24th of July from CS1.
Figure 6.19: NO$_2$ DSCD radial plots for the 25th of July from instruments CS1 (Trellick Tower) and CS2 (Kemp House), marked on the map are the FOVs which measure highest concentrations of NO$_2$ in the afternoon from both instruments.
Figure 6.20: July time series of CityScan NO₂ DSCD ROIs (plotted in black) in the direction of BL0 (top), KC1 (middle) and WM0 (bottom) with in situ data for that location over plotted.
Chapter 7

Conclusions

7.1 Summary of Instrument Design, Build and Performance

A key motivation for this work was to offer a solution which could improve knowledge of the spatial variability of NO\textsubscript{2} within an urban environment, whilst also demonstrating a new technique which has the potential for development as a satellite payload. As has been outlined in the introductory chapters of this work, NO\textsubscript{2} is an important air pollutant that can have debilitating effects on human health. Regulations to control NO\textsubscript{2} struggle to reduce concentrations to a level which is deemed acceptable by EU standards therefore better understanding of the main sources of emissions within urban environments and the transport and chemistry which subsequently takes place is needed in order to allow more targeted regulatory control. CityScan has the potential to offer improved understanding of the emissions within a city and identify fugitive sources.

Much of this work was focused on the design and build of three CityScan instruments. Many of the original goals were achieved, however there were some
challenges. During the design stage of this work the main challenges were the design of a reliable shutter given very tight space constraints as has been shown in this work this was not entirely successful. Another challenge was managing the data download and storage. CityScan produces huge data volumes 24 hours a day and is often deployed in remote locations. The solution employed to deal with this was the addition of large external hard drives to the system and the use of two computers, one for spectrometer control and data collection and the second being dedicated to file management and the environmental control. This method whilst not allowing near-real time collection of data, which would be most useful if this instruments were used operationally, did allow the instruments to operate for extended periods of time un-manned. When CityScan is deployed in locations with a fast, wired internet connection however near-real time data collection becomes more feasible.

A further design criteria was to develop an instrument that was transportable and weather-proof ensuring that it could be used in a variety of locations including some more remote ones. On the whole this was met; the instrument, although heavier and bulkier than one would ideally choose, can be separated into three parts which can then be moved with two operators into many locations.

In terms of the spectrometer performance and thus data quality, the data collected was more than adequate to demonstrate the potential of the instrument. It has been shown that CityScan can produce data which allows spatial variability of NO₂ within an urban environment to be identified; this would be much improved with data being used from two or more instruments. Furthermore, the instrument has shown potential for use with other large-scale phenomena which effect the composition of the atmosphere such as thunderstorms. This development extends the potential uses of CityScan further.

Data has been collected from three instruments deployed in up to three locations.
Data from the best characterised instrument CS1 have been analysed and characterised in this work and have shown to meet many of the original design criteria; including, the FOV, spectral resolution and spectral range. In order to improve the ILS, which would result in a reduction in uncertainties in the spectral retrieval of absorbers’ slant columns, the entire optical system would need to be better aligned. Currently an iterative method has been used to optimise the alignment by eye however this is rather crude. A better quality entrance slit would also be needed to improve ILS, with a consistent slit width which is made to specification.

Improvement in temperature stability and reduction of overall temperature inside the spectrometer could also cause significant improvement in the noise on the detector and thus improve the signal to noise. To allow temperatures below 0°C, which would improve the noise on the detector dramatically, the seal on the spectrometer would need to be improved so that it could remain purged to prevent ice or water condensation forming on the optical elements and the detector.

Error analysis has been performed to assess the reliability of the data and has shown that the percentage error on the DSCD of NO₂ retrieved is between 5 and 30% for scenarios with very different NO₂ concentrations. Furthermore, comparison of the CityScan data to a well-characterised DOAS instrument running alongside has shown results with gradient values between 0.7 and 1 with R² values rarely lower than 0.7. This is an extremely promising result as the comparison was performed very crudely.

### 7.2 Summary of Modelling Work

Through a modelling study it has been shown that CityScan data cannot be fully understood without some knowledge of radiative transfer effects. CityScan’s biggest strength and also one of the largest complicating factors is its hemispherical viewing
geometry. Changes in both SAA and SZA dramatically change the retrieved SCD when there are constant atmospheric conditions and thus CityScan’s rotating FOV is constantly changing the effective SAA and therefore the SCD retrieved.

It has been shown that it will be possible to identify distinct plumes within the CityScan FOV whilst large, diffuse plumes which surround CityScan in all directions will be more difficult to analyse quantitatively.

In the future it would be valuable to perform further RTM studies, including varying the boundary layer height and aerosol composition (these factors have currently been overlooked). Development of a function which could be used to correct retrieved DSCDs for changes in the viewing geometry of CityScan would also offer a significant improvement to the CityScan analysis. This could be in the form of a look up table for various atmospheric scenarios.

### 7.3 Future Developments

The element of the CityScan instruments which has been most problematic is the shutter in the spectrometer. As the only moving part within the spectrometer it has been shown to limit the instrument’s usability to less than two weeks. In order to improve the length of this working period the shutter needs to either be improved or removed. With the space constraints around the shutter improving its design is extremely difficult and thus the most attractive solution is to remove it. The preferred method of solving this problem would be to employ a frame-transfer CCD in place of the current CCD. This frame transfer CCD would need to be twice the size of the current detector in order to maintain the large FOV currently used by CityScan. This would be prohibitively expensive and therefore the solution which will be employed is to reduce the FOV by half and to then use half of the CCD to collect the photons and the other half for frame transfer. This solution has now
been implemented and is undergoing testing in Leicester. An example of some of the data with the improved, frame transfer version of CityScan is shown in Figure 7.1.

![Image of data collected in Leicester on 25th of August 2013 using a frame-transfer CCD]

Figure 7.1: Data collected in Leicester on the 25th of August 2013 using a frame-transfer CCD, shown in the panels are NO$_2$ DSCD (top panel and then left hand-side top to bottom, webcam images, RMS, ratio of pixel intensity and O$_3$ and right hand-side panel top to bottom O$_4$, H$_2$O, pixel 100 intensity and glyoxal.

The data displayed in Figure 7.1 shows the improvement in terms of noise and striping that can be achieved by using the frame-transfer CCD. It does also highlight the loss of data spatially which occurs using this method. The RMS values are seen to be lower using this detector as well generally staying below $5 \times 10^{-3}$. A
further interesting point is that the DSCD for water look like they may contain some significant data content, this is an improvement over previous data collected using CityScan. This method shows great potential for providing higher quality, more reliable data over a smaller spatial area.

Substantial improvements in interpretation of the CityScan data could be made if several instruments were installed and their data analysed concurrently. This step forward would also unlock the potential for developing a tomographic retrieval and therefore being able to map NO$_2$ within a city in 3D. Implementation of a tomographic retrieval would make the identification of individual emission sources possible and hence be most useful for monitoring individual sources within a complex urban environment.

Deployment of CityScan in environments, other than urban, may also demonstrate the full potential of this instrument. If CityScan were deployed at point sources it would be much simpler to monitor the emission and transport of the source. If a tomographic retrieval were developed and used with several instruments at a point source this would offer unprecedented detail on the movement of plumes and could be used to develop dispersion models further. CityScan also has other potential uses at harbours or airports as individual ships or planes could easily be separated from the main area of high pollution usually associated with these locations. Ideal candidates for CityScan deployment would be Heathrow airport and Port Talbot harbour. Both sites are a complex mixture of emission sources with background concentrations of NO$_2$ elevated owing to road sources and then individual emitters on top. Heathrow is an especially interesting test case as it is surrounded on two sides by motorways and also has large car parks which are a significant source of air pollution. In order to be capable of untangling the individual emissions from planes, installation of I-DOAS instruments such as CityScan, around
the runway, would offer an excellent solution.

Developing a UV version of the CityScan spectrometer would allow retrieval of other trace gases of interest such as SO$_2$ which would make CityScan suitable for use at volcanic sites. In order to make a UV version of CityScan several alterations would need to be made including:

- Changing the CCD for a UV sensitive version.
- Ensuring all optical elements are UV transmissive.
- Altering the optical layout in order to align for UV optics (personal correspondence with Dan Lobb, SSTL)

It has been shown that some volcanoes may also cause increased concentrations of NO$_2$ [57] and thus it may also be of interest to deploy the visible versions alongside any UV ones. The production of NO$_2$ by volcanoes is not wholly understood as it is not a primary volcanic emission. However, it is likely that NO$_2$ is produced through the thermally controlled Zel’dovich reaction which has been discussed in Chapter 5. This reaction could originate in the atmosphere or potentially from magmatic N$_2$ at the surface of lava lakes which would generate NO that could be oxidised in-plume to NO$_2$.

An example of measured NO$_2$ at the Mt. Erebus volcano in Antarctica is shown in Figure 7.2 which has been recorded using a simple 2-telescope UV spectrometer mounted on a rotating platform so that the plume could be scanned as it rose. Shown in Figure 7.2 are the results of 100 co-added spectra captured at an 80 ms time interval. Each cycle in the data represents alternating scans back-and-forth across the vertically rising plume.

A UV version of CityScan would also make it possible to monitor biogenic coastal emissions through the retrieval of DSCDs of BrO and OIO. These species are of in-
Figure 7.2: Time-series of SO$_2$ and NO$_2$ at Mt. Erebus, Antarctica on the 11th of December 2001. Each cycle in the data represents alternating scans back-and-forth across the vertically rising plume. Data were collected at 80 ms resolution and then 100 consecutive spectra were co-added.

Other future work would be to use CityScan data as a satellite validation tool. The footprint of several overlapping instruments is comparable to that of a satellite instrument such as OMI and therefore CityScan offers a significant improvement in satellite validation as this is regularly performed with a point source measurement or a remote sensing instrument with a smaller FOV than CityScan [42].

7.4 Final Conclusions

The CityScan instruments which have been developed and tested through this work have proven to be a new and valuable tool in air quality monitoring. Providing concentrations of NO$_2$ at higher spatial resolution and over a larger spatial areas than have been achieved before. The data, although not fully optimised, has demon-
strated the potential of this instrument as an air quality monitoring tool. Also apparent from this work are the many other situations where CityScan could prove to be invaluable such as at point source emissions. The development of UV version would extend these applications further. This could prove to be a huge step forward in plume detection and monitoring and in identifying fugitive emission sources.
Bibliography


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trometer system for atmospheric differential optical absorption spectroscopy. 