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Indoor/Outdoor Air Quality Relationship in Urban Commercial Buildings

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A thesis submitted for the degree of Doctor of Philosophy to the University of Dublin, Trinity College

March 2013

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Summary

The United Nations urban environmental unit associates up to 1 million premature deaths annually to urban air pollution (United Nations Environment Programme, 2010). Much research on indoor environments has focused on residential buildings with commercial buildings being often overlooked. This research project aimed to improve the understanding of the Indoor/Outdoor air quality relationship at urban commercial buildings in Dublin, Ireland. In order to gain the required understanding, data was required for Dublin sites, therefore monitoring was conducted. Real-time concentrations of $PM_{2.5}$ and NO_2 were recorded at 10 commercial buildings (including shops, offices and gallery spaces) all located in heavily trafficked parts of the city centre. Multiple monitoring runs were carried out at all buildings which simultaneously gathered air quality data indoors and outdoors at street levels as well as at roof level for those sites which contained mechanical ventilation units. Correction factors were then applied to the $PM_{2.5}$ data to account for the use of a light scattering nephelometer rather than gravimetric sampling and also to account for high outdoor relative humidity experienced overnight in the Irish climate.

Collected data was analysed with respect to; time series plots of the indoor and outdoor concentrations for each site, indoor/outdoor air quality ratios, lag times between outdoor fluctuations and the associated indoor fluctuations, NO/NO_2 relationships and the dosage of $PM_{2.5}$ and NO_2 to occupants of the 10 monitored buildings. Different patterns were seen for the two different pollutants and in general outdoor NO_2 concentrations were able to provide a much higher prediction for respective indoor NO_2 concentrations than the parallel outdoor $PM_{2.5}$ concentrations.

Results found that NO_2 generally showed a clear diurnal pattern in time series plots for both indoors and outdoors, with a considerably higher prediction value than $PM_{2.5}$ (average R^2=43.72 % for NO_2 versus R^2 = 3.25 % for $PM_{2.5}$). $PM_{2.5}$ was found to vary about a mean value with a large amount of noise with only a slight diurnal pattern evident between day and night outdoors but little of this diurnal pattern indoors. Indoor/Outdoor ratios of both pollutants increased significantly overnight as concentrations reduced much more outdoors than compared to indoors between 11 pm and 4 am. These increased ratios were muted slightly for non-working hours due to sharp peaks seen for NO_2 in the early morning outdoors

The influence of pollutant concentrations at the air intakes to mechanical ventilation systems showed that a great deal of consideration should be taken when choosing the location of roof top ventilation units, with one monitoring site, for example, showing that roof level concentrations of $PM_{2.5}$ were up to twice those measured at ground level. However, some other mechanically ventilated sites showed a greater influence on indoor pollutant concentrations from the air quality at ground level concentrations as opposed to the roof levels where the intakes were situated.

The combined use of the regression and recursive mass balance technique proved useful for predicting NO_2 concentrations indoors taking in account of building characteristics. This technique was able to account for mean exposure predictions that were within the 95 % CI for 2 sample T-tests at the majority of sites and also on average 52.2 % (range 20-72.2 %) of fluctuations. Higher prediction values were found for individual best fit models of the sites for NO_2. The model showed an ability to calculate the mean indoor exposure within the 95 % CI for a 2 sample t-test for $PM_{2.5}$ but not to predict the indoor fluctuations.

Finally, the forward prediction ability of trained Artificial Neural Networks using outdoor data and meteorological concentrations in order to predict indoor concentrations was also tested. This found poor ability to predict indoor $PM_{2.5}$ concentrations, but reasonable prediction ability for NO_2 provided the training period for the Artificial Neural Network included the meteorological conditions that also occurred during the forward prediction.

To the author's knowledge this research is the largest study of $PM_{2.5}$ and NO_2 conducted on commercial buildings in Dublin city centre. It found that naturally ventilated offices with a low number of air changes in older buildings showed the greatest reductions between indoors and outdoors for NO_2, while the greatest reductions in $PM_{2.5}$ were found for mechanically ventilated offices. Some buildings with mechanical ventilation systems were found to be more highly influenced by street level data than roof level intake data.

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First and foremost I offer my sincerest gratitude to my supervisor, Dr Laurence Gill, who has supported me throughout my thesis with patience and knowledge whilst allowing me the room to work in my own way. I originally approached Laurence hoping to carry out research in the waste water treatment, but he managed to sway me into the air quality field saying something along the lines of 'Air, water, sure they are all fluids, if you like one you'll like the other'. Luckily he was correct, I did like air!

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It's supposed to be hard; if it wasn't hard everyone would do it. It's the hard that makes it great!

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Abbreviations

NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen
NO	Nitrogen monoxide
$PM_{2.5}$	Particulate matter with a aerodynamic diameter less than 2.5 μm
EPA	Environmental Protection Agency
I/O	Indoor/Outdoor
RH	Relative Humidity
DCC	Dublin City Council
CI	Confidence Interval
hr	Hour
RSP	Respirable suspended particulates
ANN	Artificial Neural Network
WHO	World Health Organisation
$\mu g\ m^{-3}$	Micrograms per meter cubed
ppb	Parts per billion
DF	Degrees of Freedom

1. Introduction

1.1 Historical perspective

In Europe there is a long documented history of air pollution events. The first known regulations on air pollution were put in place after nobility protested during the reign of Edward I (1272 – 1307) about the use of "sea coal". His successor Edward II (1307 – 1327) implemented a penalty of torture to those found to pollute the air with "pestilential odour" (Stern, 1976). In 17th century London the Bills of mortality show peaks which were linked to "stinking fogs" (Brimblecombe, 1987) - these "stinking fogs" were most likely photochemical smog which occurs when the reddish brown nitrogen dioxide (NO_2) gas absorbs light and marginally reduces visibility (Haagen-Smit, 1952). NO_2 causes problems such as acidification and eutrophication via the deposition of nitrogen compounds in the ecosystem (European.Commision, 1997a). Even with increased mortality occurring alongside air pollution events, it was not until the 1930s that the general population started to make the association between the two. Previously, the increased deaths were linked with the winter temperature inversions caused by anticyclonic weather, which were the cause of the build-up in pollution concentrations due to low wind speeds and therefore an inadequate dispersion of pollution (Russell, 1926). The event which firmly began changing people's opinions occurred in the Meuse Valley, Belgium in 1930 where 10 times the normal death rate occurred with large numbers of autopsies revealing acute irritation to the respiratory tract (Firket, 1936). As well as the deaths, a large number of the population exhibited acute respiratory symptoms. In early December 1952, in London, a serious air pollution event occurred which saw 4000 deaths occur over 3 weeks. The event was due to an extended temperature inversion which saw black smoke concentrations in excess of 4000 μg m^{-3}, with an average level of about 1600 μg m^{-3} over the 4 days of the event (MOH, 1954). A large proportion of these deaths would have previously been associated with the cold weather that the inversion also brought, but surrounding towns, which did not experience the same build-up of black smoke due to a decreased density of buildings burning coal in the smaller towns, witnessed only a 15% increase in mortality compared to the 400% increase seen in London, as shown in Figure 1.1.

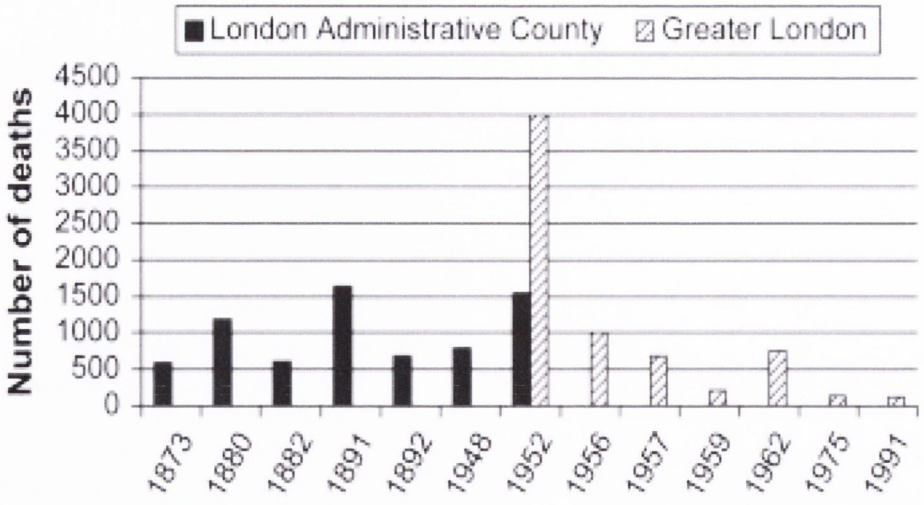

Figure 1.1 Increases in deaths due to an air pollution event in London 1952 (Brimblecombe, 1987)

Today, air quality varies across Europe, for instance PM_{10} concentrations are higher in Madrid than major cities in the UK (Birmingham) or Switzerland (Lugano) but lower than cities located in some Eastern European cities (Artíñano et al., 2004). Estimates of the European cost of health care due to air pollution derived illnesses range from €305 billion to €875 billion (European.Commission, 2005). Life expectancy varies by up to 10 year across the United States due to the varying quality of the air (Pope et al., 2009). The cost of reducing fine particulates in the United States is roughly $7,000 million per year, yet this results in $19,000 – 167,000 million per year benefit from reductions in fine particulates due to reduced mortality and improved health of the population (Dockery, 2012). Hence, improving air quality within Europe would prove financially beneficial to governments as well as the obvious benefits to populations' health.

1.2 Rationale for study

Clean unpolluted air is a basic requirement of life. Air pollution can be described as the presence of unwanted solids, liquids or gases in the air at a quantity which is high enough to cause damage to human health or the ecosystem (Seinfeld, 1985). The United Nations urban environmental unit associates up to 1 million premature deaths annually to urban air pollution (United Nations Environment Programme, 2010) and over 90% of the air pollution in developing cities has been linked with poor quality vehicles. Currently, air quality limits in Ireland only cover outdoor environments yet the quality of indoor air is an essential determinant of healthy life and a person's well-being, especially since the average person spends more than 90% of their time

indoors. Much research on indoor environments has focused on residential buildings, with commercial buildings being often overlooked. Poor indoor air quality has been tied to symptoms like headaches, fatigue, trouble concentrating, and irritation of the eyes, nose, throat and lungs all of which affect the productivity of a workforce (Heerwagen, 2000, Solomon and Balmes, 2003, Clancy et al., 2002, Dockery et al., 1993).

With people spending 40 plus hours a week in their place of work and little information available on the quality of air in Irish commercial buildings in urban areas. This study was undertaken in order to gain a greater understanding of the air quality in such places of work. The 2011 CSO statistics state that 227,429 people are at work in Dublin city centre and therefore affected by results of this research (CSO, 2011). Understanding what building characteristics influence the quality of indoor air can lead us to better choices in future with respect to building design, urban planning and on a personal level choice of workplace.

1.3 Scope, objectives and novel aspects of the project

1.3.1 Scope

Two urban air pollutants are reviewed throughout this work, these are the air pollutants specified to be of most concern in the 2008-2012 Dublin Regional Air Quality Management Plan - particulate matter of an aerodynamic diameter less than 2.5 micrometers ($PM_{2.5}$) and nitrogen dioxide (NO_2). Pollutant concentrations were collected at a selection of buildings which varied with age, ventilation method (i.e. naturally or mechanically ventilated) and type of business. The requirements for the buildings were that they were for commercial use, located in a busy urban part of Dublin City Centre and occupied with staff working an average working week. This research involved the use of two sets of monitoring equipment used in parallel, one to continuously monitor indoor air pollution in an area where staff typically worked and the second to monitor air quality out on the street or next to the ventilation intake if the building was mechanically ventilated

Following the collection of data from 10 different monitoring sites across the city centre, analyses have then been carried out in order to ascertain relationships between indoor and outdoor air quality at each site. Relationship characteristics include; lag time, reduction between indoor and outdoor and intra pollutant relationships. Finally, predictions for various building characteristics have been made in order to assess the likely impact on human health of indoor air quality in generic building types.

In addition to this, two separate prediction models have been developed in order to make indoor air quality assessments of commercial buildings in Dublin city centre. Two modelling methods have been used; one using building characteristics and another utilising meteorological data and Artificial Neural Networks (ANN). The first model was formulated on the basis that the required data inputs were easily attainable to the average commercial building occupant with no prior knowledge of air pollution. The second ANN model uses meteorological data and previously gathered indoor and outdoor air quality information at the site in order to make predictions of future indoor air quality concentrations based on outdoor conditions.

1.3.2 Aims and Objectives

This aim of this research is to investigate the relationship between the indoor and outdoor quality of two urban air pollutants, NO_2 and $PM_{2.5}$, with respect to urban commercial buildings.

The specific objectives of this project were to:

i) Monitor the air quality both indoors and outdoors of a selection of 10 commercial buildings across Dublin City Centre and across several diurnal periods during a working week. These buildings should represent the normal working environments and include; mechanically ventilated, naturally ventilated, recently constructed and older buildings.

ii) Development of a methodology for the determination of the relationship between indoor and outdoor air quality for these commercial buildings.

iii) Analysis of the results from each set of monitoring data gathered at the different sites in detail, to investigate the relationship between indoor and outdoor concentrations (including any lags), the typical dosage of occupants working in these buildings and diurnal patterns of PM and NO_2 in such an inner city environment.

iv) Synthesis of the monitoring data and analysis into understanding the mechanisms of indoor to outdoor air quality relationships for different generic building types.

i) Development of a predictive model for indoor air quality in Dublin City Centre that can be used by an average occupant of a commercial building with no prior knowledge of air quality management.

1.3.3 Novel Aspects

The novel aspects of this study include the following:

i) Monitoring of the diurnal indoor / outdoor relationship of air quality of commercial buildings in Dublin City Centre which, to the author's knowledge has not been carried out before as well as the most extensive review of $PM_{2.5}$ in Ireland.

ii) Calculation of a correction factor for use of a light scattering nephelometer in Dublin, Ireland.

iii) Development of an indoor air quality prediction model that is designed for ease of use by those with no air quality of modelling experience.

iv) Development of an Artificial Neural Network model for forward prediction of indoor concentrations of $PM_{2.5}$ and NO_2 using outdoor concentrations and meteorological data.

1.4 Format of Thesis

The chapters of the thesis are structured as follows:

- Chapter 2 outlines the background to this indoor/outdoor air quality study through a literature review. It reviews previous urban sinks and sources for both NO_2 and $PM_{2.5}$ and the parameters governing their behaviours. The chapter also examines previous studies on the relationship between indoor and outdoor concentrations in shops and offices in other cities. Finally, previous modelling techniques developed for indoor/outdoor air quality are reviewed.

- Chapter 3 deals with the monitoring procedures and equipment used in order to collect the air quality data. Details of the selected sites for this study are provided as well as the selection criteria. This section also explains the two corrections applied to $PM_{2.5}$ data.

- Chapter 4 presents the initial analysis of collected monitoring data from the 10 sites. Time series plots of the indoor and outdoor concentrations for each site, comparisons of monitored data with EPA data and best subset regressions of the data are discussed. These regressions are used to show the influence of weather factors on the indoor concentrations.

• Chapter 5 looks in more detail at the results gathered during the monitoring process. This section investigates; indoor/outdoor ratios lag times between outdoor fluctuations and the associated indoor fluctuations, NO/NO_2 relationships and the dosage of $PM_{2.5}$ and NO_2 to occupants of the 10 monitored buildings.

• Chapter 6 then moves on to detail the first modelling procedure which uses a recursive mass balance technique combined with regressions to form a prediction of indoor air quality using only outdoor air quality and a number of building characteristics which are provided by the user i.e. staff in the building. All inputs to this model are openly available to staff and therefore it is a highly useful for employees who have no previous knowledge of air quality but wish to learn about the pollutants they are exposed to and how these levels would affect their health.

• Chapter 7 discusses a second modelling approach based upon Artificial Neural Networks. Networks have been trained for each individual site for both $PM_{2.5}$ and NO_2 using outdoor pollutant concentrations in conjunction with meteorological concentrations to predict indoor concentrations. Once trained these networks can be used to predict future indoor concentrations using new outdoor concentrations and weather data.

• Chapter 8 compares the NO_2 and $PM_{2.5}$ concentration monitoring results in this study with legislative limits for comparison with health standards as well as other cities worldwide. This chapter also compares the indoor concentrations in buildings independent to their outdoor concentrations and suggests mitigation measures on how to reduce the pollutants in order to improve health standards.

• Finally, Chapter 9 presents the main findings and conclusions of this study, along with recommendations for future work in this area.

2. Literature review

2.1 Introduction

Air is considered to be polluted when concentrations of fumes, gases, particulate or odours are present in harmful amounts to humans, animals or plants. This may occur naturally, e.g. volcanoes or lightning, or be due to anthropogenic activity, e.g. burning coal or exhaust from vehicles. The United Nations Urban Environment Unit associates up to 1 million premature deaths annually to urban air pollution (United Nations Environment Program, 2010) and over 90% of the air pollution in developing cities has been linked with poor quality vehicles. Within the European Union alone roughly five million years of life are thought to be lost due to Particulate Matter with an aerodynamic diameter less than 2.5 microns ($PM_{2.5}$) every year (European Environment Agency, 2010). The aerodynamic diameter of a particle is defined as the diameter of the spherical particle with a density of 1000 kg m^{-3} that has the same settling velocity as the irregular particle. These health effects include asthma, acute bronchitis, lung cancer, damage to nasal passages and respiratory tract inflammation. Links to cancers of the bladder, kidney, stomach, oral cavity, pharynx and larynx, multiple myeloma, leukaemia, Hodgkin's disease, and non-Hodgkin's lymphoma have also been linked to urban air pollutants (Solomon and Balmes, 2003).

Outdoor air quality standards include the Clean Air for Europe or CAFE Directive which sets a limit of 25 µg m^{-3} for $PM_{2.5}$ to be achieved by 1st January 2015, and a subsequent limit of 20 µg m^{-3} to be achieved by 2020. Nitrogen Dioxide (NO_2) limits in Ireland are described in Air Quality Standards (SI 271/2002) where limits are set at an annual mean value of 21 ppb and an hourly value of 105 ppb that should not be exceeded more than 18 times per year. This study is being carried out in Dublin, a city which has a population of approximately 1.2 million (CSO, 2011) in an area of 290 km^2. A study into air pollution in 26 cities across Europe (APHEIS, 2006) noted that Dublin has comparatively low concentrations of air pollutants such as NO_2 and $PM_{2.5}$ which were within EU limits. However, a report by the Irish Environmental Protection Authority (EPA) in 2010 stated that NO_2 and particulate matter were the two pollutants of concern in Ireland. These concerns of the EPA may be due to the high respiratory and cardiovascular mortality and morbidity rates in Ireland compared to most of the rest of Europe (Ballester et al., 2008, ENHIS-1, 2002). While these illnesses are not caused by poor air quality but they may be worsened by it.

Oxides of Nitrogen (NO_x) and $PM_{2.5}$ put strain on the cardiovascular and respiratory systems, aggravating illness in those exposed, so keeping concentrations as low as possible, regardless of limit values, would benefit a population with high rates of such illnesses. Indoor health was not considered when comparing European $PM_{2.5}$ and NO_2 legislative concentrations, yet it is where the Irish population spend up to 90 % of their day (Dimitroulopoulou et al., 2001, Hancock, 2002). A European wide study known as AIRMEX reported that indoor concentrations of Volatile Organic Compounds (VOCs) and PM_{10} in two Dublin city centre offices in May 2007 were often higher than outdoor concentrations(European Commission Joint Reserach Centre, 2007). The PM_{10} results will be discussed later in section 0. Higher indoor concentrations compared to outdoors could contribute to the high respiratory and cardiovascular mortality and morbidity rates in Ireland, as discussed above.

The largest three occupation categories in Dublin (clerical/management government, professional healthcare and sales/commerce) are office-based and account for 56.4 % of work places for the Dublin population. In Ireland, no legislative limits exist for indoor air, although guidelines set out in the 2007 Code of Practice for the Safety, Health and Welfare at Work (Chemical Agents) Regulations 2001 (S.I. No. 619 of 2001) advise an 8-hour occupational exposure limit value of 3 ppm for NO_2. The conversion of ppb to µg m^{-3} is shown in Table 2.1 with conversions made at 0° Centigrade and 101.325 kPa.

Table 2.1 Conversion from µg m^{-3} to ppb

Pollutant	$\mu g\ m^{-3}$	ppm	ppb
NO	1	0.00077	0.77
NO_2	1	0.0005	0.5

The two pollutants, one particulate and one gaseous, focused on in this study are NO_x or more specifically NO_2 and $PM_{2.5}$ as these two air pollutants are of most concern to Dublin City, as stated in the 2008-2012 Dublin Regional Air Quality Management Plan. In order to help reduce exposure to these pollutants it is necessary to understand the mechanisms that allow these urban pollutants to enter and exit the buildings where the population spends most of its time. $PM_{2.5}$ and NO_2 concentrations are increased in urban areas due to the high density of vehicles and the start/stop driving patterns in cities. PM can be monitored in many size fractions (PM_1, $PM_{2.5}$, PM_7, PM_{10}) with $PM_{2.5}$ and PM_{10} being the most commonly used to measure the concentration of particles in air. Research shows that due to its smaller size $PM_{2.5}$ reaches deeper into the lungs

and has a longer residence time so is more damaging to health (Zhu et al., 2002) $PM_{2.5}$ is also a better indicator of anthropogenic (man-made) emissions than PM_{10} (DCC, 2010), which makes it a strong marker for transport emissions as well as being a highly reactive pollutant.

2.2 Pollution sources and sinks

2.2.1 Introduction

In urban environments traffic is the major factor that raises NO_x and $PM_{2.5}$ concentrations above background concentrations with industry-generated sources playing a lesser role (Lamers, 2011). Although engines used in cars and buses have become cleaner over the past number of years due to catalytic converters and improvements in engine efficiency. The increased number of cars on the road and changes in driving behaviour has resulted in increased concentrations of NO_x and $PM_{2.5}$ (O'Leary, 2010). Data from the EPA (2011) shows a steady increase over the years 2005 to 2009 of traffic-generated NO_2 in the Dublin region (Zone A), during a time period when there was a decrease in background NO_2 concentrations (see Figure 2.1). Data on traffic-generated NO_2 has not been published for 2011, but 2010 data showed a decrease from 2009 back to the 2008 concentration level. The increase in 2009 has prompted Dublin city and county councils to be contacted by the EPA to develop an air quality management plan to prevent an increasing trend in NO_2. It was noted that atmospheric conditions may have played a part in the elevated concentrations as they prevented the dissipation of pollutants outside the peak times of traffic emissions.

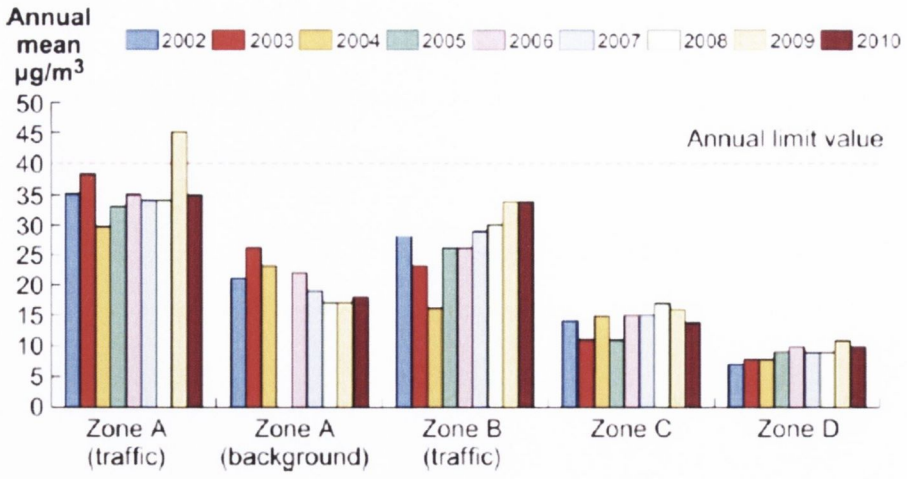

Figure 2.1 Average NO_2 Concentrations 2002 – 2010 (EPA, 2011)

Note: Zone A – Dublin conurbation, Zone B – Cork conurbation, Zone C Other cities and large towns comprising Galway, Limerick, Waterford, Clonmel, Kilkenny, Sligo, Drogheda, Wexford, Athlone, Ennis, Bray, Naas, Carlow, Tralee, Dundalk, Navan, Letterkenny, Celbridge, Newbridge, Mullingar and Balbriggan , Zone D – Rest of country

The Smarter Travel Policy for Sustainable Transport (Transport, 2011) sets out mechanisms for reductions of NO_2 concentrations from traffic. These include: electric cars, public education, green school transport, improvements in public transport infrastructure (the so-called "Transport21" policy) as well as reductions in maritime and aviation emissions.

The CAFE Directive 2008/50/EC (CEU, 2008) defines that the monitoring points for background air pollution should be "located so that their air pollution level is influenced by the integrated contribution from all sources upwind of the station". The pollution level should not be dominated by a single source unless such a situation is typical for a larger urban area. Sampling points for background concentrations in theory are representative of several square kilometres. The European Commission published a guidance document in 2002 which sets out exactly how to measure a background concentration(European Commission et al., 2002). Background concentrations should be equal over an area of 50-500 km in radius; the concentrations should be representative concentrations in rural areas with medium and long range source. As well as general background concentrations, rural stations can also be subdivided into near-city background stations (3-10 km from built up areas), regional stations (10-50 km from built up areas) and remote stations (>50 km from built-up areas and other

sources). This takes into account the higher concentration of medium range sources near cities and lack of them in remote stations (Garber et al., 2002).

Pollution sources can be long (>10 km), medium (500 m-10 km) and short (<500 m) range. Certain pollutants such as NO are highly reactive so long range sources are limited due to atmospheric oxidation which occurs over the 10 km range. Long, medium and short range sources have different levels of vertical mixing; long range sources are normally considered to be perfectly mixed while short range sources, for instance line sources such as traffic, are generally poorly mixed and depend greatly on the surrounding buildings which can shield or concentrate the pollutant on openings in the building. Long range transport has been found to be important with respect to the makeup of O_3 and particulate pollutants arriving. For example, Spanish research (Rodríguez et al., 2004) has found that mineral dust blown in from African dust events contributed up to 20-30 μg m^{-3} of PM_{10} and 10–15 μg m^{-3} in $PM_{2.5}$. At times when African dust events were not present, urban road dust became a major source of PM_{10} and to a lesser extent of $PM_{2.5}$. Easterly winds in Ireland bring air from across Europe which has high levels of pollutants. The most important short range sources are generally within 150 m and in the line of sight of major building openings i.e. ventilation intake or main door (Kukadia and Hall, 2011). O_3 concentrations affect the ability of NO to be converted to NO_2. The concentration of O_3 in Dublin has been found to be strongly linked to long range sources and studies have found that exceedances occur due to hot sunny weather combined with increases in trans-boundary sources from Europe (Environmental Protection Agency, 2008)

Reverse tracking of long range sources can be undertaken using a variety of models such as the STOCHEM and NAME, Lagrangian chemistry model, used in the UK (Collins. et al., 2006). In early August of 1998 Canadian forest fires burned over 1 x 10^6 ha of land and caused widespread haze layers across Europe, including Ireland (Forster et al., 2001). The Mace head monitoring station found increases in CO and NO_2 concentration alongside other trace gases four days after the fires started begun. The Mace head station has found 32 % and 10 % increases due to European and Northern American emissions respectively, but this particular event showed over 58 % increases in CO concentrations (Spichtinger-Rakowsky. and Forster., 2001)

Wahlin et al. (2001) examined 29 size fractions of nanoparticles (0.01 to 0.7 μm) emission rates from vehicles in order to improve street level emission models. Significant correlations between NO_x, CO and PM were found, indicating diesel and petrol-fuelled vehicles as a major source of the ultra-fine PM studied. Equally, strong

correlations were found in other research carried out in Toronto, Canada between expressways and increases in NO_2, NO_x, ultrafine particles and VOCs (Beckerman et al., 2008). Recent work involving Nanoparticles includes studying their behaviour as they are emitted from vehicles (Carpentieri et al., 2011). This work found that particles transformed in a very short time after they were emitted, and these transformations were influenced strongly by turbulence fields behind the vehicles. Although little research has been done in this field it is predicted to be a strong area of interest in the future as it is estimated that particles below 300 nm in aerodynamic diameter make up 99% of urban particles by number(Carpentieri et al., 2011). Car emissions have been found to increase nanoparticles concentration by at least two orders of magnitude relative to background concentrations (Kumar et al., 2008).

2.2.2 Nitrogen Dioxide Sources

2.2.2.1 Outdoor sources

Compounds of nitrogen are highly reactive in air and these reactions, although complex, are well documented **Figure 2.2** (Lövblad, 1997a).

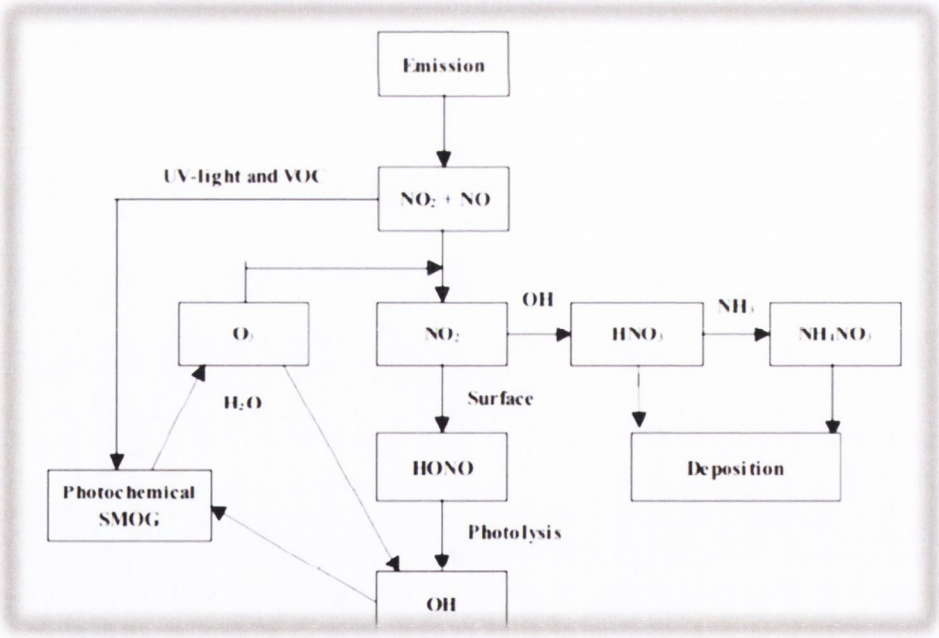

Figure 2.2 Nitrogen reactions schematic (Lövblad, 1997a)

The European Environment Agency (2000) attributes the main sources of nitrogen dioxide to the transport (55 %) energy (19 %) and industrial (14 %) sectors. In Ireland the breakdown of NO_2 sources is very similar, with transport far outweighing other sources especially in urban areas (EEA, 2000). Legislation focuses on NO_2 because of

its pronounced effects on human health compared to other nitrogen oxides. One of the main reactions (Equation 2.1) that occurs in the atmosphere is part of the cycle involving NO, NO_2 and O_3 but other interactions include NO_2 with hydroperoxy radicals (HO_2) and organic peroxy radicals (RO_2) (European Commission, 1997a)

$$NO + O_3 \rightarrow NO_2 + O_2$$ Equation 2.1

Typically, there is a non-linear relationship between NO_2 and NO concentrations, as shown in Figure 2.3 and a high correlation (0.95) has been found between the natural log of NO_2 against NO (Ekberg, 1995). O_3 availability is often a limiting factor to the conversion of NO to NO_2; therefore a point occurs where the conversion rate changes due to a lack of O_3 available. For example, in the study by Ekberg (1995) the maximum outdoor NO_2 concentrations reached 30-50 ppb when NO concentrations exceeded 100-150 ppb but after this, little increase in NO_2 was found as all the available O_3 had been utilised (Figure 2.3).

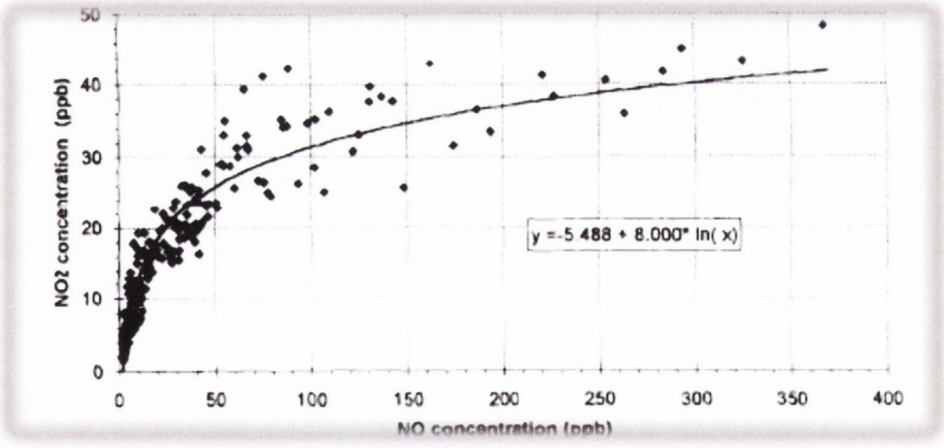

Figure 2.3 NO_2 versus NO measured in Göteborg, Sweden (Ekberg, 1995)

At 25°C the rate of oxidation of NO to NO_2 is 4.43 x 10^{-4} $ppb^{-1}s^{-1}$ (Atkinson et al., 1992), and the newly available O_2 (Equation 2.1) can then react with atmospheric O to form O_3 (Equation 2.2) which is a limiting factor in Equation 2.1 necessary for the reaction of NO to form NO_2.

$$O + O_2 + M \rightarrow O_3 + M$$ Equation 2.2

where M is a "body" of mass, primary nitrogen or oxygen molecules which absorb energy from the reaction and *hv* is ultraviolet radiation (Lövblad, 1997a). In unstable atmospheric conditions NO_2 has been linked to greater reactions with radicals in the lower boundary layer, while in stable atmospheric conditions O_3 plays a greater part in generation of NO_2. Although O_3 is a limiting factor NO_2 can also be generated by reactions between NO and O_2 as shown in

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{Equation 2.3}$$

Once in the form of NO_2 further reactions occur as seen in Figure 2.2. Some of these produce other nitrogen compounds while others complete the nitrogen cycle by reproducing NO.

$$NO_2 + h\nu \rightarrow NO + O \qquad \text{Equation 2.4}$$

But also $$O_3 + NO_2 \rightarrow NO_3 + O_2$$

The reaction rate for the NO_2 to NO_3 (Equation 2.4) is 7.78 X 10^{-7} $ppb^{-1}s^{-1}$ at 25 °C (Atkinson et al., 1992). The reaction between NO and molecular oxygen (O_2) in Equation 2.4 is a slower one than the reaction with NO and O_3 and unusually the reaction rate falls with increasing temperature i.e. during summer time (Bodenstein, 1922, P.W.Atkins, 1990).

As a result of the above reactions, levels of NO_2 have been found to have reached background concentrations within 300 m from an expressway, with NO decreasing more rapidly as it utilises available O_3 to create NO_2 (Beckerman et al., 2008). After 50 m the first NO drop off was seen and background concentrations were reached by 300 m. The NO maximum was 13 times the minimum concentration recorded with highest concentrations measured at the closest points to the expressway, as expected. It should be noted that vehicles driving at higher fuel efficiencies on major roads have a fraction of NO_2 in NO_x less than 5% by volume which increased to 12% in congested roads in central London (Carslaw and Beevers, 2005). Hence, the same volume of traffic with different driving behaviours i.e. free flow/stop and start can generate diverse concentrations of NO_2.

The vechicle fuel type also influences the proportion of NO_2 in NO_x. Research shows that diesel vehicles account for 91.8% of primary NO_2 emissions but only 63.8% of NO_x. Hence, petrol fueled vechicles emit a higher percentage of NO in NO_x compared to diesel-fueled cars, while taxis and buses were responsible for 18% and 29% respectively of primary NO_2 emissions in London (Carslaw and Beevers, 2005). The highest proportion of diesel NO_2 was found at speeds between 20-50 km h^{-1} although sharp drop offs began after 40 km h^{-1}. It should be noted that currently a speed limit of 30 km h^{-1} limit is in place in Dublin city centre placing it in the zone for highest NO_2 emissions. Other research by Jenkin (2004) has found similar percentages of NO_2 in NO_x and calculated that for diesel-fuelled vehicles $NO_2=0.996\ v^{-0.6}$ of diesel NO_X emissions by volume are generated, where v is the mean vehicle speed in km h^{-1} (valid range, 30–60 km h^{-1}). The study also agreed with Carslaw and Beevers (2005) that petrol-fuelled vehicles have a lower percentage of NO_2 with an upper limit on the NO_2/NO_x ratio of < 3%. In addition, localised roadside reductions in O_3 have been attributed to NO from exhausts utilising available O_3 to produce NO_2 (Beckerman et al., 2008). These reductions in O_3 are consistent with other work (Jo and Park, 2005, L.Hodges, 1977). Hence, an inversion of the normal behaviour that pollutants display near heavily trafficked roads would be expected for O_3 as it is utilised to create NO_2.

Previously diesel engines had lower emissions of NO, although, technology in petrol engines has increased over the years to the point where it can now match diesel engines with respect to emissions of NO per km. The introduction of catalytic converters in 1988 also caused NO emissions to drop significantly in European states. A lower tax incentive was put in place for five years after their introduction to encourage sales of new cars containing the catalytic converters in some European countries. By 1994 a third of passenger cars had catalytic converters installed and a newer three-way catalytic converter had been brought to the market. European wide reductions in NO during the 1990s were also attributed to the move from petrol to diesel engines in cars. A 27% reduction in NO occurred between 1990 and 1996 due to the introduction of catalytic converters and increased usage of diesel cars over petrol (EEA, 2000). Even with these reductions the Environment State and Outlook Report (SOER) 2010 thematic assessment (EEA, 2010b) stated that 12 EU countries expect to exceed the legally binding upper limit for NO_x emissions and only 14 countries foresee the possibility of compliance with ceiling limits for other major pollutants.

O_3 plays a major role in the NO_x cycle. O_3 concentrations have been documented as higher in urban areas increasing the availability for the conversion of NO to NO_2. Increases in O_3 concentrations in urban areas are due to interactions with nitrogen

oxides, non-methane volatile organic compounds (NMVOCs), carbon monoxide and methane, which can cause in turn, increased NO_2. In the summer of 2010 17 of the EU member states exceeded the maximum daily 8 hour mean O_3 limit of 120 μg m^{-3}. These were; Austria, Bulgaria, Cyprus, the Czech Republic, France, Germany, Greece, Hungary, Italy, Luxembourg, Malta, Poland, Portugal, Romania, the Slovak Republic, Slovenia and Spain as well as four non-EU countries within Europe namely, Croatia, the former Yugoslav Republic of Macedonia, Switzerland and Turkey. Although Ireland did not exceed the average daily 8 hour limit, a maximum 1 hour concentration of 154 μg m^{-3} was recorded and it did exceed the long term limit on 6 individual days (EEA, 2011). The exceedances occurred mostly in Mediterranean areas although more increases than previous years were noted in north Europe.

2.2.2.2 Indoor sources

In general indoor concentrations of NO_2 are lower than outdoors, unless gas cooking or heating is installed in the building (Kraenzmer, 1999). The largest source of NO_2 indoors is due to infiltration from outdoors (resulting from the sources discussed in the previous section). The influence of the outdoor concentrationson the indoor concentration increases with rising air exchange rate. Photochemical and heterogeneous reactions, detailed in Section 0 can act as sinks or sources of NO_2 indoors. Work by Drakou et al. (1998) found increased indoor concentrations of NO_2 and O_3 alongside reduced NO in a naturally ventilated building in Thessaloniki, Greece. The building contained large windows, allowing photolysis as a source of NO_2, see Section 0 for details of these reactions. Other areas in buildings however, such as ventilation systems or false ceilings contain many areas where no UV light is available. Therefore, the degradation of NO_2 to NO (Equation 2.4) is not possible and concentrations of NO_2 remain high (Drakou et al., 1998). Various building surfaces such as plastics and metals have been linked with low pollutant deposition velocities for NO_2. Such significantly reduced deposition velocities might produce indoor to outdoor (I/O) concentration ratios higher than average buildings indicating an indoor source, such as a gas cooker, even though none are present (Nazaroff et al., 1993), as was the case with the Thessaloniki building.

Extreme peaks of NO_2 indoors can be caused by gas heaters and stoves which are poorly ventilated or at times when the air exchange rate for the building is significantly reduced (Namieśnik et al., 1992). Evidence of this may be seen through the build-up of corrosive soot near the appliance, which can be exaggerated if relative humidity is high. Residential studies in the UK have found that 78% of indoor NO_2 could be

attributed to gas cookers/heating. The same work found that homes with gas cookers experienced exposures above the 1h mean concentrations of 105 ppb while this was extremely rare in buildings without gas cookers (Dimitroulopoulou et al., 2001). Another source of NO_2 in offices/shops are electrostatic equipment such as photocopiers and laser printers which are a source of NO_x (Wolkoff et al., 1997)

Finally, although not a direct source of NO_2, air purifiers such as electrostatic precipitators, negative ion generators and ozone generators can all produce O_3 increasing its availability to react with NO and produce NO_2 (Bernstein et al., 2008).

2.2.3 NO_2 sinks

Due to highly reactive nature of NO_2 it is in a constant state of change and therefore can be degraded through several mechanisms some of which have been mentioned above but are discussed in more detail below.

2.2.3.1 Photolysis

Ultra violet (UV) light (wavelength 300-400 nm) is necessary for degradation of NO_2 to NO. Indoors there are two components which may cause photolysis: artificial lighting and natural sunlight entering through windows or skylights (Nazaroff and Cass, 1986). The amount of photolysis due to artificial lighting can be calculated using the hours the lights are turned on and the photon flux specified in each band, depending on the lighting type. In a conventionally lit building, reactions may occur indoors during the day by reactions normally associated with night-time chemistry outdoors, for example the oxidation of NO_2 to NO_3 which is photolytically unstable in the presence of sunlight and therefore NO_3 in ducting or suspended false ceilings concentrations of this nitrate radical increase (Pitts, 1984). A commercial building in the United States (Burbank, California) measured the generation of 2 ppb h^{-1} of NO_3 due to high O_3 and NO_2 concentrations (Weschler, 2004).

For sunlight, the outdoor UV changes seasonally and daily and therefore this must be measured and a visible attenuation factor applied to calculate the outdoor UV influence on the indoors. For instance skylights are estimated to transfer a photon flux equal to 0.7% of the visible light and 0.15% of the ultraviolet light falling on the roof of the building outdoors.

The University of Dundee undertook a study on the level of UV emitted by the three main types of energy saving light bulb; compact fluorescent lamps (CFLs; both double and single enveloped), energy-efficient halogen lamps and light emitting diodes (LEDs)

(Fenton et al., 2012). The work found that LED lights emitted the lowest UV concentrations and that the concentration of UV emitted by CFLs varied greatly. These variances were not only between brands and wattage, but within individual boxes of the energy saving bulbs. Halogen lamps and CFLs were found to emit UVA light even with double enveloping of the bulbs.

For glass walled buildings indoor concentrations of several key species, including 0_3, 0_2, Nitric acid ($HN0_3$) and polyacrylonitrile (PAN) are significantly over the base case values and in fact are seen to exceed the outdoor levels. This combined with the reactions due to certain lighting types can greatly affect the chemical makeup of the indoor air as photolysis rates increase (Equation 2.5). PAN for example, has been known to extend the life of NO_x by approximately 1 day. PAN can be removed by thermal degradation, 1hr 295 K or months at 250 K (Colls, 2002).

$$CH_3C(O)OO + NO_2 + M \rightarrow PAN + M \qquad \text{Equation 2.5}$$

2.2.3.2 Heterogeneous reactions

Heterogeneous reactions on the surface of walls, floor and ceilings of buildings can increase the indoor NO concentrations while reducing NO_2. The surface area of a room will always be considerably more than the surface area of the airborne particles contained within it and buildings with ventilation ducting will have further areas for these reactions to occur. These reactions whereby NO_2 is converted to NO have been generalized according to Equation 2.6 (Yamanaka, 1984, Spicer et al., 1989b, Weschler and Shields, 1997),

$$\frac{dc}{dt} = -v\left(\frac{A}{V}\right)C \qquad \text{Equation 2.6}$$

where A/V is the superficial surface to volume ratio of the room (Nazaroff and Cass, 1986) and v is the velocity of the air movement. A previous study has found that without accounting for any heterogeneous reactions occurring on surfaces, NO was under-predicted while NO_2 was over-predicted indoors owing to the sinks and sources documented in Table 2.2 (Nazaroff and Cass, 1986). The same study also found that HNO, $HN0_3$, $HN0_4$, NO_3, and N_2O were also produced at substantial net rates by chemical reaction indoors.

Table 2.2 Sinks and sources of Nitrogen Oxides (Nazaroff and Cass, 1986)

		Base case		NO_2 source		Glass-walled building	
		Source	Sink	Source	Sink	Source	Sink
NO	Ventilation	17.6	15	17.6	36.2	17.6	16.6
	Chemical reaction	1.6	5.7	3.4	24.1	129	131
	Emission	0	0	38	0	0	0
	Wall loss	0	0	0	0	0	0
NO_2	Ventilation	69	58	69	99	69	67
	Chemical reaction	172	172	154	136	418	418
	Emission	0	0	38	0	0	0
	Wall loss	0	12	0	19	0	1

The increased temperatures and solar radiation during summer, combined with an increased HNO_2 provides the correct conditions to utilise the OH radicals and increase NO_2 concentrations. Within the nitrogen cycle NO_2 (Equation 2.7, Equation 2.8 and Equation 2.9);

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$ Equation 2.7

$$2NO_2 + H_2O \rightarrow HONO + H^+ + HNO_3^-$$ Equation 2.8

$$NO_2 + HONO \rightarrow NO_3^- + NO + H^+$$ Equation 2.9

As a consequence of this up to 15% of NO_2 may be converted to NO on indoor surfaces. Materials which are known to induce higher reaction rates are; Masonite, ceiling tiles, plywood, oak panelling, plasterboard, bricks, carpet (polyester, wool and acrylic).

Ammonia nitrate (NH_3) will also react with NO_2 (Equation 2.10) in order to form NH_4NO_3 particulates which can be deposited on indoor surfaces;

$$NO_2 + NH_3 \rightarrow NH_4NO_3$$ Equation 2.10

Finally, a reaction with sodium chloride producing nitrosyl chloride can occur (Equation 2.11) on certain surfaces but due to the slow speed of the reaction it is less significant than the previous reactions (Wan et al., 1996).

$$2NO_2 + NaCl_5 \rightarrow CLNO + NaNO_3$$ Equation 2.11

2.2.4 Particulate matter sources

Particulate matter (PM) consists of sulphates, inorganic ions, nitrates, sodium, calcium magnesium, potassium, organic/elemental carbon, water bound particles, crushed material and heavy metals (WHO, 2006b). Concentrations of particulate matter are expressed in two ways, mass per unit volume (μg m^{-3}) or the aerodynamic diameter that the particle is less than (μm). The first describes a concentration while the latter helps indicate possible sources and the lifespan of the particle. There are several size fractions commonly used to describe particulate matter: PM_1 (particulate matter with an aerodynamic diameter less than 1 micrometer), $PM_{2.5}$, PM_{10} and TSP (total suspended particles). Particles with an aerodynamic diameter less than 2.5 μm are often called the "fine" particles and are anthropogenic pollutants while larger "coarse" particles are considered to be from natural sources. Larger particles in the coarse range tend to settle faster. PM_{10} is the size fraction monitored by the EPA for many years although recently, $PM_{2.5}$ has been monitored. Currently Dublin and the rest of Ireland has been shown to have concentrations that are consistently below the $PM_{2.5}$ requirements as set out by the CAFE Directive, although 2011 was only the third year that measurements were collected (EPA, 2011).

Sources of urban PM include combustion of solid fuels, vehicle emissions and road dust created by friction between tyres and the road, with the vehicle exhausts being the largest urban generator of $PM_{2.5}$ and PM_{10} (Rodríguez et al., 2004, Artíñano et al., 2004) and urban roadside $PM_{2.5}$ concentrations have been shown to be six times that of rural ones in Ireland (Yin et al., 2005).

2.2.4.1 Outdoor sources for particulate matter

The exact make up of PM varies globally although Irish and UK constituents have been shown to be similar, with Irish PM containing a higher fraction of sea salt due to its proximity to the sea (Harrison et al., 2001). Due to its more anthropogenic nature $PM_{2.5}$ is made up of different road dust components compared to PM_{10}, which has been linked to vehicle exhaust (NO^{3-}, NH^{4+}, Pb, OC^{+}, EC, Cu, Zn, Cl and K), road dust (Ca, Ti, Fe, P, K, Cr, V and Mn) and brake lining particles (Cu, Zn and minor amounts of Cr) (Sternbeck et al., 2002, Schaap et al., 2002). Rodriguez (2004) found that components such as Ca, P and Ti were present in the PM_{10} road dust but not in the $PM_{2.5}$ size fraction. $PM_{2.5}$ concentrations measured in 2001-2002 at the heavily trafficked College Street in the centre of Dublin by Yin et al. (2005) found that elemental carbon (23-33%) and ammonium sulphate/nitrate (17-29%) were the major components of $PM_{2.5}$. The rest of the contributions were from sea salt, calcium, potassium, magnesium and methane sulphuric acids (MSA). The percentage contribution by various components changes depending on weather, season, long range transport of pollutants and proximity to sources with increases of the crustal contribution occurring over the spring and summer months and increases of non-mineral carbon during the winter (Artíñano et al., 2004). As the source of particulate matter changes between winter and summer, this can often be seen in a change in the ratio between $PM_{2.5}$:PM_{10}. Some literature suggests that in winter 80% of PM_{10} is due to $PM_{2.5}$ and the concentrations strongly correlate with fluctuations in NO_x, whereas during the summer the re-suspended soils and dusts influence PM_{10} to a greater extent and the contribution of $PM_{2.5}$ decreases to about 50% (Harrison et al., 1997), with other studies suggesting an average of 54% ±14% (Lall et al., 2004). Ultimately the contribution of the smaller size fractions depends on metrological and geographical factors and hence a variance in reported data is expected. In an Irish study conducted by Yin et al., (2005), the makeup of $PM_{2.5}$ differed between the heavily trafficked Dublin site and more rural sites which found $PM_{2.5}$ which had a lot less elemental carbon and more sea salt, sulphate, nitrate and ammonium. The more heavily trafficked College Street had mean elemental carbon concentrations of 6.54-7.81μg m^{-3} while the other Dublin monitoring site (Coleraine Street), which had lower traffic concentrations, had average values of 2.31-3.79 μg m^{-3}. The proportion of elemental carbon drops even more away from urban areas showing that elemental carbon is a source which is generated by vehicle exhaust emissions or other combustion sources prominent in cities. Little variation occurred seasonally for elemental carbon compared to other components of the $PM_{2.5}$ such as sulphate, ammonium and nitrate with lowest concentrations occurring during the summer and

highest in the spring (Yin et al., 2005). However, these three had significantly less variation with respect to the location of the sample indicating that they are less dependent on anthropogenic sources and more on background concentrations. The organic contribution to $PM_{2.5}$ varied from 27% in winter to 37% in summer at urban sites, the increase being attributed to the generation of secondary organic compounds. The contribution of organic compounds dropped significantly in rural areas due to lower traffic concentrations, 18% in winter and 25% in summer. A study in Hong Kong (Cheng et al., 2010) found organic carbonaceous (OC) material and elemental carbon (EC) contributed up of 70% of $PM_{2.5}$ for urban roadside sites sources. The OC/EC ratio of 0.8 ±0.1 suggests a high proportion of vehicle exhaust derived materials, with the contribution dropping to 48% if ambient urban sites were considered. If the organic and elemental carbon are combined for the Irish study during a summer period, this results in a 53% organic contribution to the $PM_{2.5}$ for Dublin. It should also be noted that non sea salt calcium can be used as a marker for resuspended road dust if it is present in the same ratio as seen in gypsum ($CaSO_4$ $2H_2O$), which is a common component in Irish roads (Yin et al., 2005).

The increasing percentrage of diesel engines is also affecting the make-up of $PM_{2.5}$, as diesel engines have been shown to emit higher concentrations of many pollutants tested (except for V, Sb and Ba) when compared with petrol (gasoline) engines (European Commission, 1997b, Cheng et al., 2010). Diesel engines in central California were found to produce 40% of secondary nitrate, compared to 20% in petrol engines fitted with a catalytic converter (Ying et al., 2009). $PM_{2.5}$ has been found to vary widely in urban areas with sharp gradients in concentrations. In Ireland the total number of licensed vehicles on 31st December 2008 was 2,416,387 with 39.19% of these operated on diesel, 60.28% on petrol alone, 0.22% on petrol and electricity and 0.30% on petrol and ethanol (Department of Transport, 2010). Trends show a shift away from petrol fuelled cars with a decrease from 82% in 2008 (Broderick and Marnane, 2002). Efforts have been made to reduce particulate generation due to transport (Rudell et al., 1996, Fino et al., 2003) by attempting to reduce diesel exhaust emissions by placing a particle trap over the exhaust. However, emission concentration reductions as a direct result of the trap were not great enough to decrease bronchoconstriction (the constriction of the airways in the lungs).

2.2.4.2 Indoor sources

In the absence of pronounced indoor sources the majority of the indoor concentrations of PM can be attributed to the infiltration of outdoor sources, especally for particles less than 1μm in aerodynamic diameter (Goyal and Khare, 2011). Buildings with a HVAC (heating, ventilation and air conditioning) system in place have been found to have relatively small particles passing through the system, generally in the range of 0.1-1 μm (Tung et al., 1999). Particles finer than 0.1 μm are removed by diffusion while particles larger than 1 μm are removed via inertial impaction and interception mechanisms.

Those particles that are generated indoors tend to be coarser partlicles (i.e. above $PM_{2.5}$) with human activity the main contributing factor. For example, a common source of indoor particulates in residential buildings is cigarette smoke (Guerin, 1987), although the Irish 2003 ban on smoking in work places means cigarette smoke will not influence the commercial buildings in this thesis work. Research on the effect of removing smoking indoors in Irish pubs found 93% (23 vs. 340 m g m $^{-3}$) reductions on $PM_{2.5}$ concentrations (Connolly et al., 2009) Similarly fireplaces, burning candles and cooking will not have the same influence in this thesis study on commercial buildings as has been predicted in other studies on residential premises (Koponen et al., 2001).

One indoor source which is common in commercial buildings is the resuspension of particles which have deposited on surfaces. Resuspension of particles depends on the type of indoor activities as well as the manner in which the activity is carried out, i.e. dry dusting versus damp dusting of a bookcase. The resuspension of particles can be described in two forms; the resuspension factor, R, surface concentration removal rate or as the resuspension rate, λ_{res}, which is the ratio of mass of particles resuspended from a unit area of a surface in unit time to the particle loading per unit area of that surface. Residential studies in the UK have found R increases two fold during the day compared to the night which can be attributed to human movement within the house (Zhang et al., 2008, Rosati et al., 2008). The larger the particle the easier it is to resuspend with particles of 10 to 25 μm resuspending easily by movement of people around a room. For particulates in the size range of 1-5 μm, cleaning, especially vaccuming, has been found to significantly increase concentrations to 3.5 times that of an unoccupied room (Thatcher and Layton, 1995).

High usage of photocopiers and printers in offices will also cause spikes in $PM_{2.5}$ concentrations as seen by Saraga (2011) during an non-smoking office study. Peak concentrations were recorded which correlated with days of high usage of such equipment.

2.2.5 $PM_{2.5}$ sinks

Unlike NO_x, the $PM_{2.5}$ main sink is not due to chemical reactions but due to settling out of the air and the agglomeration of particles. Several types of removal of PM occur such as thermophoresis, gravitational and Brownian. In addition, many factors affect the rate of settling such as the type and area of furnishings in the room, air flows and if the room is carpeted or not.

In a well-mixed room with constant environmental factors the rate of settling will be exponential over time and the concentration at time T (C_t) can be expressed as a function of the initial concentration (C_0) and time,

$$C_t = C_0 \, e^{-\lambda t} \qquad \text{Equation 2.12}$$

where λ is the decay constant is characterised by the air exchange rate, which is an indication of dilution and deposition rate of particles (Thatcher et al., 2002). The deposition rate or velocity of particles can be described as:

$$v_d = \lambda_d \frac{V}{A} \qquad \text{Equation 2.13}$$

where λ_d is the deposition rate constant, V is the room volume and A is the total surface area. Use of the deposition velocity instead of the deposition rate is useful as it factors in the size of the room which affects deposition. Deposition rates of $PM_{2.5}$ have been estimated by Sinclair (1990) as 6×10^{-5} to 5×10^{-3} for commercial buildings using mechanical ventilation systems although Tung (1999) found higher rates of 3.7×10^{-2} for office buildings which had their mechanical systems shut off.

For particles 0.1 μm and below, diffusion effects are the major depositional force, as the gravitational and thermophoresis forces increase as particles increase in size (Tung et al., 1999). Thermophoresis forces are due to temperature gradients, and with a difference of more than 1 K between the wall and air the thermophoresis force on a particle increases in importance with respect to the gravitational force. Tung (1999) found that such forces have the most influence on PM_{10} deposition in a office containing HVAC. Therefore, as larger particles tend to settle due to gravitation forces, an increase in surface areas of furniture in the room will not significantly increase deposition to the same rate as it would if particles were of a smaller size fraction. This is especially true for vertical and downward facing surfaces where submicron particles

deposit easily, particularly if textured furnishings are present. Thatcher et al. (2002) noted that carpets can significantly alter the air flow patterns of the room by increasing the roughness of the surface compared to other floor types. As the airspeed in the room increases it was found that the mass transfer also increased thereby significantly increasing deposition rates, as was found from other research (Byrne et al., 1995).

2.3 Air quality

2.3.1 Air quality legislation history

The European Environmental Agency (2005) states that 200 million working days a year are lost and up to 6.4% of child deaths are attributable to air pollution related illness with higher figures in some of the newer European Union member states. As well as human health, air pollutants cause damage to the ecosystem and food sources. Acid rain and smog formation were the first aspects of air pollution that were tackled by the European environmental regulations. However, in general, subsequent policies aimed at reducing air pollutant concentrations across Europe have seemed less effective due to increasing vehicle numbers which have tended to mute the beneficial impacts of good work done.

Currently in Ireland no legislative limits exist for indoor air, although guidelines are set out in the 2010 Code of Practice for the Safety, Health and Welfare at Work (Chemical Agents) Regulations 2001 (S.I. No. 619 of 2001) (HSA, 2007). These guidelines set out an 8 hour occupational exposure limit of 3000 ppb and a 15 minute exposure of 5000 ppb for nitrogen dioxide (NO_2). No particulate matter size fraction guidelines are mentioned although "dust" is classed as either respirable or inhalable with limits of 4000 µg m^{-3} and 10000 µg m^{-3} respectively. Outdoor air quality standards include the CAFE or Clean Air for Europe Directive (European Parliament, 2008) as mentioned previously, which sets a limit of 25 mg m^{-3} for $PM_{2.5}$. NO_2 limits in Ireland are described in Air Quality Standards (SI 271/2002) where limits are set at an annual mean limit of 40 µg m^{-3} and an hourly limit value of 200 µg m^{-3} (EEA, 2000).

Summary of the history of air pollution legislation in Ireland

1878: First legislation Public Health Act (Publin Health (Ireland) Act, 1878) on air pollution was introduced in Ireland after the Industrial Revolution increased pollution concentrations.

1979: UNECE Convention on Long Range Transboundary Air Pollution (UNECE, 1994)(CLRTAP) was set up to address air pollution issues in a scientific and political manner. The convention's signatories have yearly meetings, implement protocols and share knowledge among themselves and the rest of the world.

1988: The first protocol of the CLRTAP was brought into force which included a protocol target to stabilise nitrogen oxide emissions to 1987 levels by 1994 (UNECE, 1988). This considered air pollution for the first time as an international issue rather than a national one. 51 of the 56 UNECE states have signed up to the treaty, which was brought into force in 1983 and since then 8 protocols have been added to it.

1993: Several other initiatives have been put in place since, including six European Action Programs (EAPs). The fifth EAP (European Commision, 1993), which aimed for a 30% reduction on concentrations by 2000 with respect to 1990 levels, was not achieved by the European Union. The plan lasted from 1993-2000.

1987: The Air Pollution Act of 1987 (S.I. No. 201/1987) (Air Pollution Act, 1987) gave local authorities the primary responsibility for monitoring air quality, including the nature, extent and effects of emissions. They were also given the power to enforce the Act and District Courts can set out the following punishment for a summary conviction: a fine not exceeding €1,270 (as well as a fine not exceeding €127 for every day on which the offence is continued) or imprisonment for any term not exceeding six months. If the infringement is severe both a fine and imprisonment may be given. For a conviction or indictment in the District Court a higher fine which cannot exceed €12,700 (as well as a fine not exceeding €1,270 for every day on which the offence is continued) or imprisonment for any term not exceeding two years. If these are not complied with the local authority has the option to go to the High Court in order to get an injunction (Citizens Information, 2010).

In 1987 WHO published their first guidelines on the health impacts of air pollution. These have since been updated in 1997 and 2005 to have first a European and then a worldwide scope, as well as revising recommended limits for several pollutants.

1990: A special zone was set up for the areas governed by Dublin city, Fingal and Dun Laoghaire/Rathdown councils which banned the marketing, sale and distribution of bituminous fuel (Air Pollution Act (Marketing Sale and Distribution of Fuels), 1990). This was hoped to improve the health of the Dublin area population as well as reduce smog in the city during the winter.

1994: The second sulphur protocol was put in place. This was the first time emission targets dependent on the ecosystem's sensitivity of the area were implemented (UNECE, 1994).

1995: Cork followed in the Dublin regions' footsteps and set up a special control area for the marketing, sale and distribution of bituminous fuel.

1996: *Air Quality Air Framework* Directive (European Commision, 1996) set out updated limit values for protection of human, ecosystem and vegetation health. This included methods to monitor, access and manage ambient air quality.

1998-2000: 10 other areas enforced the ban on marketing, sale and distribution of bituminous fuel: Arklow, Drogheda, Dundalk, Limerick, Wexford, Celbridge, Galway, Leixlip, Naas and Waterford. These were declared special control areas and included in the fuel ban.

1999: The Directive (99/30/EC) relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead was put in place (European Commision, 1999). Also S.I.33/1999(Environmental Protection Agency Act, 1999) was enacted in Ireland, this is known as the Ambient Air Quality Assessment and Management Regulations

2001: Directive (2001/81/EC) on *National Emission Ceilings* (NECD) by the European Commission (European Parliament, 2001). This covered the same pollutants as CLRTAP (nitrogen and sulphur oxides and VOCs) plus ammonia. This Directive used critical limit values which had a maximum number of allowable exceedances as well as the ecosystems' sensitivity approach. These limits have not yet been adopted although similar laxer national European state ones have been (as of 1 December 1999) in conjunction with the CLRTAP(European Commission, 2006). According to Artíñano (2004) 80% of the $PM_{2.5}$ monitors located in Madrid stations would exceed daily limits set at the time of 50 $\mu g\ m^{-3}$. 80% of the European population were experiencing PM_{10} concentrations above recommended standards according to the European Environmental agency, second assessment (European Environmental Agency, 1998)

2002: S.I. 271 of 2002 (Environmental Protection Agency, 2002), known as the Air Quality Standards Regulations of 2002, gave effect to 1996/62/EC, 2000/69/EC and 1999/30/EC within Irish law. It put in place limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter, lead, benzene and carbon monoxide in ambient air. In 2002 the third daughter Directive (2002/3/EC) on *O_3 in Ambient Air* was published and, was transposed into Irish law via S.I. 53 of 2004.

The sixth and newest EAP for 2002 – 2012 hopes to attain, 'levels of air quality that do not give rise to significant negative impacts on, and risks to human health and the environment'. This will be done through regularly changing targeted reductions in air pollutant concentrations throughout member states, including new legislated targets such as those set out in the clean air for Europe program (CAFE).

2004: The fourth daughter Directive (2004/107/EC) was published, containing limit concentrations for cadmium, nickel, arsenic, mercury and polycyclic aromatic hydrocarbons. Also S.I. 53 of 2004 transposed the third daughter Directive on O_3 into Irish law. Currently there are no plans in place to develop a new EAP to replace the 6th EAP when it ends in 2012.

2008: The *Clean Air for Europe (CAFE)* Directive (2008/50/EC) replaced the first 3 air framework Directives putting in place stricter limit concentrations. It also brought in limit values for finer particulates $PM_{2.5}$.

2009: The fourth daughter Directive was transposed into Irish law via S.I. 58 of 2009.

2011: Two acts were passed in 2011. The first was an amendment to the Air Pollution Act 1987 (S.I. No. 270/2011) which set out limits on the marketing, sales and distribution of fuels. The second was the Air Quality Standards Regulations 2011 (S.I. No. 180/2011) which transposes the Directive on *Ambient Air Quality and Cleaner Air* for Europe (CAFE) into Irish law.

Even if the CAFE limits are reached by 2020, analysis done by the 6th EAP suggests that significant negative implications on human and ecosystem health will still be visible. The 6th EAP strategy aims (if implemented) to save €42 billion across Europe in reduced sick days, increased labour productivity and health care costs. It has been estimated that the implementation of the strategy itself would cost in the region of €7.1billion or 0.05% of EU 25 GDP in 2020. Although these targets have not yet been reached it is said that to achieve the current reductions on 1990 levels that have so far been realised by industry and improved technology, Europeans would have to

collectively reduce the amount they drive by 90% to reach 2005 concentrations (EEA, 2005).

The latest EPA report on ambient air quality in Ireland suggests that Irish $PM_{2.5}$ concentrations are low with an expected Average Exposure Indicator (AEI) in the range 8.5 to13 μg m^{-3}. However, such an AEI will put Ireland in a category for reductions of $PM_{2.5}$ by 10% in 2020 to comply with EU regulations. In order to achieve this, the EPA suggests an integrated approach across a number of sectors including transport and residential emissions (EPA, 2011).

Current limits in Ireland are set out in terms of annual mean concentrations and also one hour limits which may be exceeded up to a set number of times per calendar year and are present to account for spikes in concentrations, as shown in **Table 2.3**.

Table 2.3 Current limit values in Ireland

Pollutant	**Limit Value Objective**	**Averaging Period**	**Limit Value**	**Limit Value**	**Basis of Application of the Limit Value**	**Limit Value Attainment Date**
			μgm^{-3}	ppb		
NO_2	Protection of human health	1 hour	200	105	Not to be exceeded more than 18 times in a calendar year	01-Jan-10
NO_2	Protection of human health	Calendar year	40	21	Annual mean	01-Jan-10
NO_x (NO + NO_2)	Protection of ecosystems	Calendar year	30	16	Annual mean	19-Jul-01
PM_{10}	Protection of human health	24 hours	50		Not to be exceeded more than 35 times in a Calendar year	01-Jan-05
PM_{10}	Protection of human health	Calendar year	40		Annual mean	01-Jan-05
Pollutant	Limit Value Objective	Averaging Period	Limit Value	Limit Value	Basis of Application of the Limit Value	Limit Value Attainment Date
$PM_{2.5}$ Stage 1	Protection of human health	Calendar year	25		Annual mean	01-Jan-15
$PM_{2.5}$ Stage 2	Protection of human health	Calendar year	20		Annual mean	01-Jan-20

2.4 Patterns in Air Quality

2.4.1 Seasonal

PM_{10} and NO_x vary with seasonal patterns although in urban areas this trend is muted due to traffic related pollutant concentrations influencing the natural cycle (Artíñano et al., 2004). NO_x reduces in spring/summer time due to photochemical interactions with UV light and O_3, both of which increase in these seasons. Inversely in the winter months when there are fewer daylight hours, NO_x maxima can be seen. In addition to the reductions in daylight hours, increases of NO_x during the winter are due to fluctuations in atmospheric pressure, wind direction and speed, as well as other meteorological seasonal changes (Hatzianastassiou et al., 2007). NO concentrations contribute a greater percentage to NO_x compared to NO_2, hence even with the winter decreases of NO_2 and O_3 due to decreasing photochemical reactions, NO_x concentrations can increase (Hatzianastassiou et al., 2007). Hence, the greatest peaks for NO_2 are generally found to occur when temperatures are high, winds are weak and intense solar irradiation is present.

A year's worth of PM_{10} and NO_x data collected by Harrison (1997) at various sites in Birmingham city found that minimum concentrations of particulates often occurred during times of high precipitation. Comparisons of winter and summer concentrations showed a high significance between site correlations for hourly, daily and seasonal mean data. For example, in winter months $PM_{2.5}$ made up 80% of PM_{10}, while in summer months $PM_{2.5}$ only accounted for 50% of PM_{10}. This was accredited to the presence of resuspended surface dust and soil particles. In the winter months the PM_{10} strongly correlated with vehicle exhausts emissions, secondary ammonium salts and resuspended surface dusts.

Irish research on $PM_{2.5}$ in urban Cork found no correlation with wind direction and particulate concentrations but did find that peaks in $PM_{2.5}$ occurred on dry days with less than 1 mm rainfall (Byrd et al., 2010). This may or may not be linked as a considerable number of the particulate measurements were taken under such dry conditions. However, the study found lower average concentrations on sunny days was linked to lower traffic volumes. A second Cork based study found increasing $PM_{2.5}$ concentrations in winter compared to summer (Kourtchev et al., 2011). This work did find bias to higher concentrations when wind originated from specific directions, namely

from industrial or more urban areas bringing high levels of vehicular emissions with them.

As well as seasonal patterns due to the weather, humans can promote the seasonal trends on air pollution. For example, an English study found decreased NO_2 concentrations over the Christmas and New Year period due to the shutting down of local industry, schools and offices, reducing gas fuelled heating system demands (Hargreaves et al., 2000). The same work also found increased concentrations of NO_2 in June to September which was linked to higher road traffic in the area.

Seasonally can therefore be expected to be higher NO_2 concentrations during the summer, especially on still sunny days but higher NO_x in winter due to increased NO. For $PM_{2.5}$ the makeup varies seasonally, with rain "washing out" the air and thereby decreasing concentrations increased traffic levels and variations raising concentrations.

2.4.2 Daily

As well as a seasonal cycle, pollutants generally follow a 24 hour diurnal cycle which also varies between weekday and weekends, with weekends showing 47% decreases of $N0_x$ concentrations compared to weekdays (Morawska et al., 2002). The week day cycle of both NO_2 and $PM_{2.5}$ have strong peaks corresponding to the morning rush hour; the evening traffic rush hour does not always display the same strength of a peak, as shown in Figure 2.4 (Morawska et al., 2002). Dublin based studies of non methane hydrocarbons outdoors found similar patterns, with high morning peaks, troughs at lunchtime and less pronounced evening peaks (O'Donoghue et al., 2007). A lunch time increase has also been recorded in some studies as show in Figure 2.4 which shows a sharp weekday morning spike and smaller lunchtime one (Morawska et al., 2002). The same pattern is not visible on the second time series in Figure 2.4 as this represents weekend concentrations. Local short range, time dependent pollutants e.g. a factory which discharges a large volume of pollutant corresponding to production will also influence a daily cycle of pollutants.

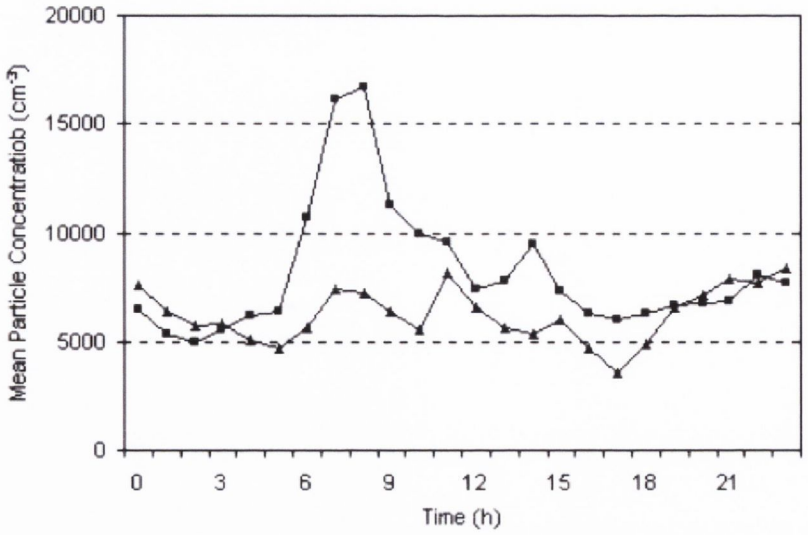

Figure 2.4 Daily diurnal concentrations (Morawska et al., 2002)

While anthropogenic pollutants play a key role in the daily cycle, natural changes such as temperature and available UV light also affect the cycle. O_3 is formed during daylight hours but is destroyed during the night. This gives a diurnal flux in O_3 concentrations which increase throughout the day while O_3 is being generated and reduce during the night while it is broken down. This pattern subsequently influences NO_2 concentrations as varying amounts of O_3 are available to oxidise NO to form NO_2. Ultraviolet radiation can break the NO_2 bond to form NO plus O which then couples with readily available O_2 to reform O_3 (Equation 2.15). This cycle can be interfered with by oxidisation compounds such as VOCs, RO_2 and HO_2.0

$$NO_2 + hv \rightarrow NO + O \qquad \text{Equation 2.14}$$

$$O + O_2 + M \rightarrow M + O_3 \qquad \text{Equation 2.15}$$

At daybreak, the sunlight causes a rapid reaction causing gaseous HONO to form NO and OH, which in turn can increase the O_3 concentrations.

As well as sunlight, wind can affect the diurnal cycle of air pollutants. Dispersion of the generated pollutants is greater during periods of high wind speeds. In Dublin, cyclists experienced higher concentrations of the VOC, ethylene during times of still wind conditions (O'Donoghue et al., 2007). The increased VOC concentrations were also linked to colder weather conditions. These affect the efficiency of vehicles in the city, as

their catalytic converters do not work to optimum efficiency, therefore generating higher emissions which in turn are not dispersed due to lack of wind.

2.4.3 Indoor Cycles

The indoor cycle of air pollutant concentrations is frequently highly linked to the outdoor cycle although fluctuations outdoors may be lagged and/or smoothed due to deposition and chemical reaction of pollutants as they enter the building (Kukadia and Palmer, 1998, Ekberg, 1995). Ekberg (1995) found clear correlations for several pollutants including NO_2, NO, CO and particulate PAHs, as well as linear relationships with their primary combustion products between outdoors and the inside of an office in Göteborg, Sweden. The research concluded that pollutant peaks in indoor office environments will be found at times when traffic densities are at their maximum on nearby roads for three mechanically ventilated and one naturally ventilated buildings. The higher the air changes per hour and lower the filtering ability of the building the more correlated indoor and outdoor concentration changes will be. Indoor concentrations in a commercial building were found to follow the outdoor peaks from 7-9 am and outdoor lows from 1-4 am for $PM_{2.5}$, the major difference being a lower standard deviation indoors. Measurements within a HVAC filtration system of return and supply air showed very little difference (ratio = 0.98) between the two concentrations indicating the filters did little to reduce $PM_{2.5}$ concentrations in the air, see Figure 2.5.

Lags of ten minutes to one hour have been found in buildings for both particulates and gaseous pollutants in studies in a variety of cities across Europe (Hussein et al., 2005, Chaloulakou et al., 2003, Morawska et al., 2001, Diapouli et al., 2008). In Espoo, Finland's second largest city, lag times from 10 minutes up to 45 minutes were found for naturally ventilated homes when PM was monitored (Hussein et al., 2005). The work found unstable I/O ratios which were attributed to the fluctuation of the natural ventilation. Longer lag times of up to an hour were measured in Athens, with the indoor pollutant concentration patterns following the outdoor levels for $PM_{2.5}$ and gaseous pollutants such as CO in two separate research studies (Diapouli et al., 2008, Chaloulakou et al., 2003). Both studies were carried out under naturally ventilated conditions, the first in a private home and the second in an office.

Cooking will increase ultrafine particles sharply indoors but due to the nature of commercial buildings cooking is normally not as prevalent a source as for residential buildings. Increases in particulates and NO_2 have been found in naturally ventilated offices from 9 am, as shown in Fig. 6 below. This pattern did not occur on days when

staff were not in work (Dimitroulopoulou et al., 2008), as the doors would be opened less frequently thereby decreasing the number of air changes per hour compared to when the building was open during the day. Section 2.8 will deal with the issue of ventilation practices and their differing influences of outdoor air on indoor air. Indoor concentrations can also be affected by fuel usage such as gas heating systems or cooking. During the winter, heating systems are in use for longer periods and can heighten sources of indoor pollutants; gas heating in particular will increase NO_2 and $PM_{2.5}$ concentrations (Kornartit et al., 2010). Use of an electrical aerosol analyser (EAA) by Koponen et al.(2001) found that in relatively airtight residences, human activity dominated the production of particulates in the air.

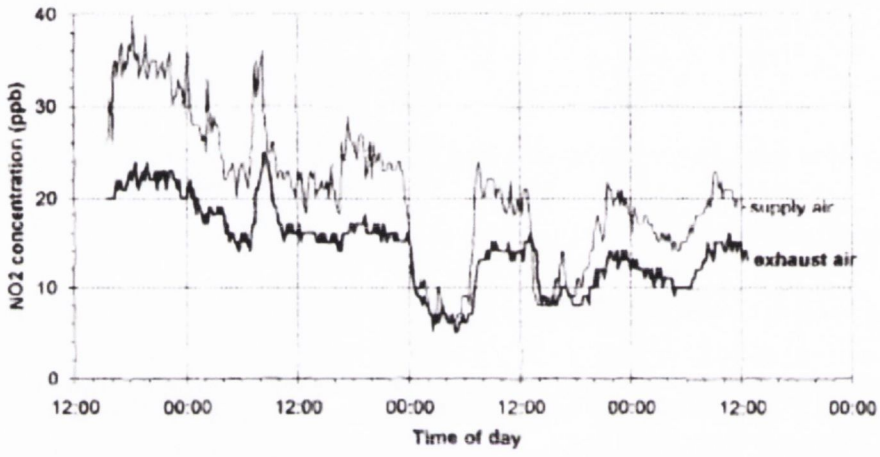

Figure 2.5 Supply and exhaust air NO2 concentrations(Ekberg, 1995)

In buildings with mechanical ventilation the number of air changes per hour or ACH are reduced out of work hours in order to conserve power. Koponen et al. (2001) monitored an office in Helsinki where the ventilation was running from 6am until 11pm on working days. During these hours the ACH was 3.7 compared to 0.3 outside of these times. The same feature was also noted by Kukadia and Palmer (1998) where the ACH for their studied building varied from 1.2 during working hours to 0.4 out of working hours. The change in ventilation rates in the Helsinki office resulted in a change in lag times from less than 10 minutes when the ventilation system was switched on to 20 minutes when the ventilation was off.

During an air pollution event in London in 1992 an investigation was carried out on the indoor effect of the outdoor event field (Field et al., 1992). Various pollutants' behaviour differed, NO and CO showed very close relationships between indoor and outdoor, NO_2 infiltration rates were below these and VOCs infiltration actually decreased.

Phillips et al. (1993) found that indoor thermal and humidity conditions followed outdoor ones, although with a smaller range. Temperature peaks corresponded with relative

humidity lows which occurred in the mid afternoon. The author noted that a kettle left boiling indoors showed the most significant effect on relative humidity, which had a maximum value of 50% indoors across four buildings apart from this event; the max relative humidity measured outdoors was 97%. A change in wind direction may also affect the indoor concentrations, for example if a fixed short range outdoor source, such as an extraction vent from another business, is downwind of the intake for the building in question during prevailing wind conditions. This may cause indoor concentrations to rise during specific wind conditions but not during prevailing ones as seen in a mechanically ventilated building study by Kukadia and Palmer (1998) during which exceptionally high levels of CO_2, NO_2, NO and SO_2 were recorded for two periods. The author attributed this to cross contamination from an exhaust which was only an influence during specific wind directions.

The Irish climate is known as temperate maritime, with average temperatures of 9°C and average annual rainfall of 800 mm in the Dublin area. On average April is considered the driest month of the year and January/ December are the wettest. The prevailing winds in Ireland are south westerly with an annual mean of 4 to 7 ms^{-1} (Met.Eireann, 2006). The quality of the air varies depending on the origin of the wind; if the wind is coming from the west i.e. from the Atlantic it is moisture laden but relatively clean. On the other hand winds from the east are lower in moisture but are much more polluted after travelling across industrial and urban areas of Europe.

Weather conditions can affect the concentrations of air pollutants, for instance precipitation has been linked with "washing out "of rain leading to reduced particulate concentration. This washing out can be further influenced by reducing temperatures which cause an increasing condensation ratio onto particulates (Jamriska et al., 2008, Harrison et al., 1996). The opposite occurs when an inversion occurs, which causes the build-up of pollutants as they are unable to escape the urban canopy layer. Inversion conditions are described as dry, clear and still days or nights with cooler air remaining trapped close to the ground as a warmer layer moves above it. Inversion events have been linked to several air pollution crises such as London in 1991 where 160 were killed or Pozo Rico in Mexico in 1950 where 6000 were left ill and 60 were killed. Inversely, hot sunny weather causes the production of photochemical smog due to the availability of UV light and reactions among O_3, nitrogen oxides and VOCs (DCC, 2010). Chan (2002) found that solar irradiation as well as humidity and temperature increased the I/O ratio for $PM_{2.5}$, while pressure and wind speed were found to have little effect on the I/O ratio.

Wind dictates the direction and dilution of air flow and when it is not present high concentrations of pollutants can build up downwind of major sources. During these

periods of low wind speed the movement of vehicles within street canyons will create a certain amount of movement of air (Qin and Kot, 1993). Wind speeds affect various particulates differently, the higher the wind speed the greater the resuspension of coarse particulates (Harrison et al., 1997). Conversely, resuspension of elemental carbon which has its main source from road traffic reduces with increasing wind speeds. For fine size fractions such as $PM_{2.5}$ calm wind conditions are associated with highest concentrations during the winter, although these can also be linked to higher traffic concentrations (DeGaetano and Doherty, 2004).

Temperature affects reaction rates of gaseous pollutants and therefore alters the interactions occurring (Ying et al., 2009). Nitrogen oxide is particularly affected by the diurnal temperature changes on an annual and daily basis. A modelling study carried out in late 2000 by Aw and Kleenman (2003) studied the effect of temperature on nitrate formation. Researchers reduced input temperatures by 2°C while holding the relative humidity constant. It was found that the 24h average concentrations of nitrate uniformly reduced by 1–2 $\mu g\ m^{-3}$ due to this drop in temperature. This reduction occurred due to the decreased reaction rates with decreasing temperature.

Relative humidity has little effect, compared to wind, on gaseous pollutants such as NO_x but does affect particulates to a greater extent. In general relative humidity and temperature have an inverse relationship. High relative humidity can increase concentrations of particles generated during the combustion process by affecting the air/fuel ratio. The higher moisture content leads to less O_2 in the air therefore affecting the ratio and in turn reducing energy efficiency of the engine and increasing emissions (Jamriska et al., 2008).

2.5 Vertical distribution in cities

Difference in concentrations between ground and upper floors in busy roadside buildings have been found with evidence that $PM_{2.5}$ decreases significantly until a height of 19 m, at which point it is 73 % of the maximum ground level concentration (Wu et al., 2002). This result reiterates the 80% drop in concentrations at 20m found by Väkevä(1999). After this point the decrease in $PM_{2.5}$ concentration for every extra meter in height decreases. At 8m the concentration of $PM_{2.5}$ was 87% of the maximum ground level (Wu et al., 2002). At 60m it has been found that PM are only 25 % of street level concentrations (Bauman et al., 1982). NO_x concentrations on the other hand halved by a height of 25 m (Qin and Kot, 1993). In a naturally ventilated office which was monitored on two separate floors increases in particulates and NO_2 were found from

9am, except for Sunday when staff were not in work (Dimitroulopoulou et al., 2008). Monitoring occurred on the first and third floor with slightly lower concentrations on the third floor due to lower outdoor concentrations infiltrating into the building at increased vertical distance from the road.

A study in Singapore (Kalaiarasan et al., 2009) focused on typical multi-storey public housing buildings within 30m of major highways and their occupant's exposure to $PM_{2.5}$. The buildings selected for the study consisted of two typical public housing buildings, both naturally ventilated residential apartment blocks, of point block configuration (22 storey) and slab block configuration (16 storey). Concentrations were taken at various heights and the analysis took account of age-specific breathing rates and body weights for different age categories. It was found that mid and lower level floors have between 1.34 and 1.81 increased risk of contracting a respiratory disease compared to the upper floors in a point block design. Those living in the slab block had up to 1.62 increased risk compared to the upper floors. The study concluded that a good façade design could further mitigate the penetration of the ambient fine traffic-generated particulate matter indoors.

2.6 Indoor/Outdoor air quality in the workplace

2.6.1 Introduction

Up to 75% of daily NO_2 exposure occurs during working hours, therefore it is important to monitor this within the working environment in an effort to reduce air pollutants, (Lee et al., 2000). In Dublin the EPA has a number of ambient monitoring stations but previous work in other cities has found that ambient outdoor measurements can prove to be a poor predictor of personal work day exposure (r=0.34) with the higher personal exposures often due to increased indoor concentration of the measured pollutant (Kousa et al., 2001). The EXPOLIS study of personal exposures in various urban centres around Europe focused on the working public. Kousa (2002) found median correlations of r= 0.79 (in Amsterdam) and r=0.76 (in Helsinki) between personal and outdoor $PM_{2.5}$ concentrations. However, more varied correlations were found by Kousa (2001) in Prague (0.39) and Basel (0.91), concluding that while ambient fixed site monitors may not always be a good predictor of workday exposure, in some cases such as in the Basel study they are. Mosqueron et al.(2002) only found a correlation of r=0.05 when comparing urban background concentrations with in-office concentrations for NO_2 and $PM_{2.5}$ in Paris. Certain workplaces have recorded particularly high concentrations, for instance bus garages (2.8 mg m^{-3}), ice hockey rinks (7.5 mg m^{-3})

and in one case concentrations of 470 mg m^{-3} over 4 minutes were documented by astronauts as they returned to earth (Colbeck, 1998).

To the author's knowledge no study on the relationship between indoor and outdoor air pollution has been carried out for commercial Irish buildings although studies in the UK, which has a similar climate and building practices can be reviewed. A sample of 385 naturally ventilated buildings in the UK found infiltration rates of 0.63 and mean air changes per hour of 0.29 (AIVC, 1994). Another UK study of non residential buildings found Indoor/Outdoor ratios (I/O) for PM of up to 1.4 (Lai et al., 2004) and ratios up to 0.54 for NO_2 at roadside shops (Colbeck, 1998). Within these studies previous authors based in the UK have noted the lack of data on I/O in commercial buildings (Colbeck, 1998). Previous research on commercial buildings in Hong Kong found that outdoor air pollutants on heavily trafficked streets had a very strong influence on indoor air concentrations (Liao et al., 1991). Shops located on ground floors with doors left open to allow customers to enter freely were found to have statistically similar indoor and outdoor concentrations, whereas offices, which were generally located on the upper floors of buildings and fitted with central air conditioning systems which contained particulate filters, were found to have lower concentrations of NO_2, carbon monoxide (CO) and PM (Liao et al., 1991). As well as the filters, reductions were also attributed to the fact that the air inlets were located farther from traffic sources. Naturally ventilated offices in the UK were found to have up to 80% of outdoor concentrations for gaseous pollutants such as CO and NO_2 but on certain occasions greatly exceeded outdoor concentrations due to unvented gas appliances (Phillips et al., 1993). The study also showed that indoor pollution trends followed outdoor trends with some time delays. Another study of London offices showed strong agreement between indoor concentrations and outdoor concentrations (Field et al., 1992) but again with a short time lag. Correlations between indoor and outdoor concentrations across Europe seem to vary greatly. For instance, in Athens, Greece correlations of r=0.74 were measured between indoor and outdoor CO time series data (Chaloulakou et al., 2003) compared to the previous study referred to for $PM_{2.5}$ in Prague (r=0.39) and Basel (r= 0.91) (Kousa et al., 2001). The differences may be due to a number of reasons including different building styles, air tightness and occupant behaviour. Even within particular countries, ventilation rates and therefore the influence of outdoor pollutants, vary. For instance, in mechanically ventilated buildings studied in Sweden, NO_2 reductions of 5-10 ppb were found in three out of four buildings with one building found to have higher concentrations of NO_2 indoors (Ekberg, 1995).

2.6.2 Office studies

There have been several studies on the I/O relationships in commercial buildings, as well as the major EXPOLIS study with which combined many researchers across Europe (Bae et al., 2004, Baek et al., 1997, Phillips et al., 1993, Kousa et al., 2001, Mosqueron et al., 2002, Kingham et al., 2000). Nevertheless, as mentioned in the introduction to this section, no studies have been carried out in Dublin on I/O relationships. While pollutant concentrations may vary greatly in other cities compared to Dublin, the methodology to carry out a similar study would not. For instance in previous studies of office buildings, heights of monitoring between 1 to 1.5 m, have been used in order to sample from the breathing zone of the buildings' occupants. Parameters such as ventilation type, traffic density, smokers present and number of occupants have also been noted as important (Liao et al., 1991). Positive correlations (r=0.74) were seen for CO between inside an office in Athens and outdoor concentrations on heavily trafficked streets (Chaloulakou et al., 2003). These high correlations infer that as outdoor concentrations rise due to increased traffic, so do indoor workplace concentrations. Important information can be gleaned from non-Irish studies, for instance, truck related traffic was found to increase levels of NO_2 and $PM_{2.5}$ indoors in the Netherlands (Janssen et al., 2001). Other studies that have investigated the link between outdoor sources of VOCs and indoor concentrations also cited motor vehicles as the most probable source of the outdoor VOCs (Baek et al., 1997).

PM_{10} I/O ratios were found to increase when fans were turned on compared to background ventilation states in London based studies. These increases were from 0.60 to 0.69 and 0.64 to 0.67. The same study found that cross ventilation rather than single sided ventilation increased $PM_{2.5}$ concentrations from 0.71 to 0.73 (Ní Riain et al., 2003). Lai et al. (2004) found much higher ratios of 1.4 showing a clear indoor source for the measured $PM_{2.5}$. The presence of such sources is often seen in residential studies due to cooking, fires etc, but Kingham (2000) also recorded above 1 values for the I/O ratio in an office. As well as direct sources other variables may cause increases in indoor concentrations for a commercial type building. For instance, a O_3 generator in the ducting of an office building in Sweden facilitated chemical reactions (such as that given in Equation 2.1) and increased NO_2 concentrations within the building resulting in an I/O ratio of 1.9 (Ekberg, 1995).

For NO_2, indoor residential studies often find I/O above 1 due to the greater presence of indoor sources such as gas cookers. These are less prevalent in offices and therefore I/O ratios would be expected to be below 1. Kukadia and Palmer (1998)

found slightly higher I/O for naturally ventilated buildings at 0.9 compared to the 0.8 recorded for mechanically ventilated offices in Birmingham, UK. A similar result of 0.73 for 24 hour averaged I/O ratios in a naturally ventilated office was found in Goteborg, Sweden when reviewing NO_2 (Ekberg, 1995). The effect of the ratio being below 1 was reductions of 5-10 ppb in NO_2 between indoor and outdoor. The reduced I/O ratios for mechanically ventilated buildings was also published by Liao et al. (1991) where it was considered to be due to the height of the offices which were located at medium to high levels. The pollutants were found to mostly come from vehicular emissions, although some industrial derived pollutants were also found.

Research from Phillips et al.(1993) indicates that indoor concentrations in naturally ventilated offices may often be greater than associated outdoor concentrations. The study also noted that indoor pollution trends followed outdoor trends with some time delays as agreed in other literature (Field et al., 1992). Central London studies have determined that in non-ventilated office spaces, indoor concentrations of $PM_{2.5}$ are dependent on wind direction and generally have 20-30% lower I/O ratio than mechanically ventilated office spaces (Ní Riain et al., 2003). Again, these results were in agreement with studies carried out by Raunemaa (1989).

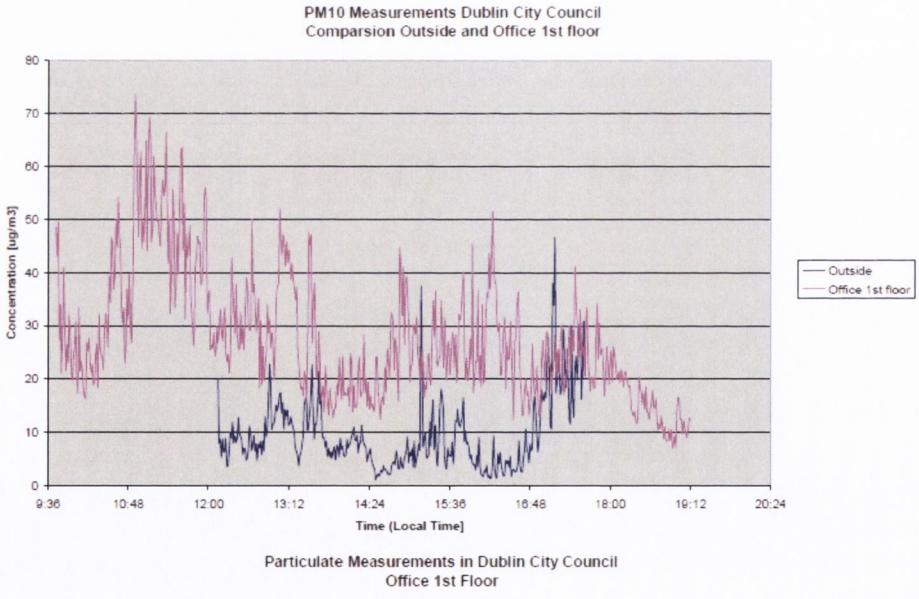

Figure 2.6 AIRMEX study PM_{10} Dublin city Council office

The project *AIRMEX* by European Commission Joint Research Centre (2007) carried out monitoring of 2 commercial buildings in Dublin. One was a City Council office along the quays of the river Liffey and the second a library located along Pearse Street. In the Dublin City Council offices, a mechanically ventilated building in Dublin city centre, the

indoor concentrations of PM_{10} found were consistently higher than outdoors as can be seen in Figure 2.6. Monitoring was carried out in a large office located on the first floor of the building and windows were kept closed throughout monitoring, outdoor monitoring took place on the first floor balcony overlooking the street (European Commission Joint Reserach Centre, 2008). The heating system was operating as the outdoor ambient temperature was 6 to 12 °C and average relative humidity was 75 %. Indoor concentrations in the office building were in the range of 10 to 70 $\mu g\ m^{-3}$ for PM_{10}, with morning data producing higher peaks than concentrations in the afternoon and evening. $PM_{2.5}$ concentrations were much lower with concentrations of 5-7 $\mu g\ m^{-3}$ indoors and 8 - 10 $\mu g\ m^{-3}$ at the first floor balcony. This study also considered a library building, where samplers were placed on the ground floor, which found outdoor $PM_{2.5}$ concentrations in the region of 18 - 20 $\mu g\ m^{-3}$ for the date of monitoring (26/2/08) with lower indoor concentrations of 8 - 11 $\mu g\ m^{-3}$.

2.6.3 Shop studies

Vehicular emissions are considered to be an "overwhelming influence" on the indoor air of shops with open fronts (Liao et al., 1991) Street canyons in urban centres can channel pollutants causing increased concentrations, and if businesses located along these streets leave doors open to allow the free passage of customers in and out of their shops, this facilitates the route of pollutants into their workplace.

Passive diffusion tubes were used by Valerio et al. (1997) to monitor carbon monoxide (CO) concentrations in 38 shops in Genoa, Italy giving average concentrations over a 8 hour exposure time. The study found that only in five businesses (two small shops, two bars and a delicatessen), were indoor CO concentrations significantly higher than outdoor values, attributed to heavy smokers in tree of the five businesses with no reason given for the final two. A high proportion of the remaining sites showed no statistically significant difference between mean indoor and outdoor CO concentrations. CO concentrations in 10 shops without smokers were linearly correlated ($r = 0.99$; $p < 0.0001$) with the nearest outdoor measurements, with two of the shops having forced ventilation. Indoor concentrations in these buildings were on average 16-30% lower than outdoor in non-smoking buildings. However, the same study noted that no statisically significant correlations were detected between concentrations indoors and the weather, traffic densities and height of buildings. It was found that indoor maxima exceeded outdoor maxima for CO.

A study of shops in Colchester, England found I/O ratios (averaged over a 24 hour period) of 0.34 to 0.54 with indoor concentrations in the studied roadside shops averaging 25 μg m^{-1} for NO_2 (Colbeck, 1998). These ratios are much lower than the data from Hong Kong which saw I/O ratios of 0.82 for shops (Liao et al., 1991). The same study by Liao (1991) found considerably lower I/O ratios (0.19) for offices, citing doors left open in shops which allowed outdoor air in and the height of office blocks as reasons for the lower ratios. Differences of I/O ratios for various shop studies may be due to hours of operation, indoor sources and infiltration. It should be noted that in both studies by Colbeck (1998) and Liao (1991) passive diffusion tubes were used which averaged concentrations over a one week period. Therefore, any peaks and troughs could not be attributed to particular outdoor events nor could the average over a working day be calculated. Gernerally, shops are open during the highest outdoor air pollution concentrations, and so with the influx of customers comes an increased number of air changes per hour. Therefore, the I/O may be skewed when averaged over a 24 hour period rather than just calculated across the working hours of the business which were found to be only 32% of the day.

2.6.4 Residential studies

Although this research focusses on commercial buildings, valuable information can be found by reviewing the more extensive studies on the residential sector.

Dockery and Spengler (1981) proposed in a major study that the four most influential factors on how outdoor air infiltrates into a residential building are: heating systems, air conditioning, kitchen ventilation and storm windows. This study was carried out over 68 homes in America where (unlike Ireland) storm windows and residential air conditioning are more popular. Results showed that the type of heating system may affect the flow of air into the building as well as create a possible source for particulates and NO_2. It was found that buildings which use ventilation systems are better sealed throughout the year, as the ventilation system is relied on to supply fresh air, while the inhabitants of naturally ventilated buildings tend to open windows and doors in order to allow new air into the building. This air, unlike that which goes through a filter within the ventilation system in mechanically ventilated buildings, passes into the building through open doors unfiltered. Ultimately, the study found that air conditioning best characterised the infiltration of particles out of the four variables. These findings have been agreed upon by several other studies including Abt (2000) who demonstrated the importance of indoor sources and ventilation rates. While increased ventilation reduced indoor generated sources, it was also a mechanism for increasing outdoor related sources.

Activities which occur in both work-places and home such as indoor work and cleaning were found to increase $PM_{(0.7-10)}$ by 0.25 $\mu g^3 cm^{-3} min^{-1}$ and 0.25 $\mu g^3 cm^{-3} min^{-1}$ respectively (Abt et al., 2000). This size range of particulates displayed lower penetration efficiencies (0.12 to 0.53) than the smaller size ranges such as $PM_{(0.0-0.5)}$ as a result of greater gravity settling deposition. The efficiency of penetration is the fraction of PM removed due to physical deposition or chemical transformation and has units of $h^{-}1$. Other studies have found that the fine particulates such as $PM_{2.5}$ are less affected by the air exchange rates than larger size fractions, as they have higher penetration efficiencies compared to larger particles (Diapouli et al., 2008).

Finally, a residential study in the UK by Coward (1996) showed a much higher I/O ratio for NO_2 in residential sites compared to results in other literature on shop and office studies. This work investigated buildings with no indoor sources yet measured very high ratios between 0.70 to 0.99 for central urban sites indicating that much of the outdoor concentration infiltrated the homes.

2.7 Health effects

2.7.1 Introduction

The quality of air is rarely, if ever, considered when choosing a place of work, yet poor air quality will significantly affect the quality of health enjoyed by the employees. The average human inhales 20,000 litres of air daily or 14 litres per minute increasing to 50 litres per minute under intense physical exercise (European Environmental Agency and Organization, 1999). Over the past two decades strong evidence has been gathered showing links between fine particulate matter and respiratory / cardiovascular illnesses (Dockery et al., 1993, Delfino et al., 2005, Mehta et al., 2008, Molinelli et al., 2006, Thatcher et al., 2002, Thacker, 2006). These illnesses include asthma, acute bronchitis, lung cancer, damage to nasal passages and respiratory tract inflammation. Respiratory illness is the third most reported illness in the state after cardiovascular and musculoskeletal diseases. In Europe, Ireland has particularly high rates of respiratory illness such as asthma and bronchitis, 1 in 7 children and 1 in 20 adults are affected with asthma alone according to the Asthma Society of Ireland. A study of the 274,000 asthma suffers in Ireland found that 73% of them felt some way limited in everyday activities due to their asthma while 55% were woken up at night due to their asthma. The loss of working hours, estimated at 3 days per adult due to asthma is estimated to cost the Irish economy €16.6 million (DCC, 2010). Ireland ranks second out of 16 countries studies by the European Community Respiratory Health Survey,

with 8% of its population suffering with chronic bronchitis; the average of the 16 countries was only 2.6%.

It should be noted that these rates would be higher if not for a 1990 ban on bituminous coal in the Dublin area, as discussed earlier, which is thought to be responsible for saving 359 deaths per year, (116 respiratory and 243 cardiovascular) as a consequence of the improved air quality (Clancy et al., 2002).

2.7.2 Health effects of Oxides of Nitrogen

Asthma, coughing and reduced pulmonary function are heightened by the exposure to diesel exhaust fumes which are a major source of NO_x as well as respiratory problems. Links to cancers of the lungs, bladder, kidney, stomach, oral cavity, pharynx, and larynx, multiple myeloma, leukaemia, Hodgkin's disease, and non-Hodgkin's lymphoma have also all been made to these fumes (Solomon and Balmes, 2003). Even at low concentrations, biochemical reactions to NO_x are known to cause respiratory illness including altered respiratory mechanisms, chronic lung disease due to premature ageing, and general respiratory illness (Lipfert, 1994). Statistically, significant increases in hospital admissions have been recorded with increased periods of NO_2 in Athens (Pantazopoulou et al., 1995), which agrees with a calculated 0.5% increase expected for every 10 $\mu g\ m^{-3}$ increase in NO_2 concentrations (European Commission, 1997a)

O_3 is undeniably linked with the NO_x cycle (as shown earlier), with its release and utilisation occurring frequently, but research also shows links with particulate concentrations. Parkhurst et al. (1999) found correlations as high as 0.74 between daily average $PM_{2.5}$ concentrations and 1 hour maximum O_3 levels. O_3 has been linked by the European Commission in 1999 (EEA, 2000) to serious health effects including inflammatory responses and impaired lung function. This is backed up by (Frischer et al., 1997) who found that children's lung function can reduce with repeated exposure to O_3.

2.7.3 Health effects of Particulate Matter

Individual particles vary widely in composition and toxicology and evidence suggests that even short term changes in ambient particulate concentrations can affect mortality especially in countries such as Ireland which has high cardiovascular mortality (Nevalainen and Pekkanen, 1998, Lipfert, 1994). Exposure to unhealthy concentrations of fine particulate matter has been connected to increased respiratory / cardiovascular illnesses by many research groups including (Dockery et al., 1993, Delfino et al., 2005,

Mehta et al., 2008, Molinelli et al., 2006, Thacker, 2006). As the air particles decrease in aerodynamic diameter they can penetrate deeper into human lungs and these small particles have longer residence time (Mauderly and Chow, 2008, Delfino et al., 2005). Particulates may be primary or secondary; primary particles are directly from sources such as vehicles or road dust, while secondary particles are due to oxidation of primary gases, such as NO and sulphur (European Commission, 1999c). Efforts which have been made to reduce particulate matter emissions from vehicles have worked but the European Commission has published records stating that PM_{10} emissions will be above limit values, designed for the protection of human health, for most urban areas in EEA member countries(European Commission, 1999c). Even though these limits are not being met by all EEA members, recent legislation on limits for PM, TSP and black smoke levels are due to further decrease in many areas of Europe in line with the CAFE Directive (EEA, 2000).

For those living near highly trafficked roads there is an increased risk of stroke and cardio-respiratory illnesses. The American Cancer Society has linked exposure of $PM_{2.5}$ to increased incidents of cardio-pulmonary mortality and lung cancer. The study carried out over 16 years concluded that every 10 μg m^{-3} of $PM_{2.5}$ was associated with approximately a 4%, 6%, and 8% increased risk of mortality, cardiopulmonary mortality and lung cancer mortality (Pope Iii et al., 2002). A Welsh and English research project (Maheswaran and Elliott, 2003) noted a 7% and 4% increase in stroke mortality in men and woman respectively living within 200 m of a main road compared to those living more than 1 km away. Hoek et al.(2002) also found an increased mortality rate due to particulate matter for those living near busy roads.

Diesel related $PM_{2.5}$ and PM_{10} can cause the development of pulmonary inflammation through pro-inflammatory cytokine induction which in turn causes increases in respiratory diseases (Veranth et al., 2004). Cytokines are important within the body as they are cell signalling protein molecules necessary for intercellular communication (Gilman et al., 2001). Interleukin 1 (IL-1), interleukin 6 (IL-6), tumour necrosis factor-alpha (TNF-α), were recognised to be some of the main cytokines related to inflammation in lung injuries (Van Eeden et al., 2001, EEA, 2010a). A study of 77 different street vendors in Bangkok, Thailand found that 35% of these vendors worked within 100 m of the busy road section and a further 44% within 500 m (Kongtip et al., 2006). These vendors were found to be at increased risk symptoms of poor health such as dizziness, upper respiratory illness, eye irritation and headaches.

2.8 Ventilation systems

The purpose of most modern ventilation systems is to provide thermal comfort combined with acceptable indoor air quality. The main inhibiting factors to this are humidity, temperature, biological pollutants, gaseous pollutants, particulate pollutants and the movement of air (Graudenz et al., 2005). Mechanical ventilation in buildings provides the needed air exchanges in large office blocks which would be difficult using natural ventilation alone. Further, they have also been found to increase the prevalence of sick building syndrome and diseases such as legionnaires as well as consuming vast quantities of energy in order to run (Sidheswaran et al., 2012).

Ventilation practices vary from building to building although there are two generic categories; *natural*, where openings in the building structure allows air to flow and provide new air into the building or *mechanical*, where air is forced in and out of a building through an air handling unit. Mechanical systems often include heat recovery systems, chillers and filters in order to clean the air. There are several types of mechanically ventilated systems including conventional HVAC systems, dedicated outdoor air systems (DOAS), independent control of temperature and humidity systems (ICTHS) and cooling ceiling and displacement ventilation systems (CC/DV).

If the quality of the various types of air shown in Figure 2.7 is known then the ventilation effectiveness (e_v) can be described as the relationship between supply, indoor and extract air, and can be calculated by Equation 2.16 (European Standard, 2006).

Type of Air	Definition
Outdoor air	Air entering the system or opening from outdoors beflore any air treatment
Supply air	Airflow entering the treated room, or air entering the system after any treatment
Indoor air	Air in the treated room
Extract Air	The airflow leaving the treated room
Recirculation Air	Extract air or part of it that is returned to the air treatment system
Infiltration	Leakage of air into building through leakage paths in elements of structure separating it form the outdoor air
Exfiltration	Leakae of air out of the building through leakage paths in elements of structure separating it form the outdoor air

Figure 2.7 Types of air in mechanically ventilated buildings (European Standard, 2006)

The breathing zone is the area which occupants of commercial buildings take air in, i.e. the area above 0.5 and below 2 m.

$$e_v = \frac{C_{eta} - C_{sup}}{C_{ida} - C_{sup}} \qquad \text{Equation 2.16}$$

C_{eta} = Concentration of pollutant in the extract air

C_{ida} = Concentration of pollutant in indoor air in the breathing zone

C_{sup} = Concentration of pollutant in the supply air

Conventional ventilation systems draw air in from outdoors and supply it to the building; this is usually done from roof level. Before air is dehumidified and heated/cooled it must first be filtered which removes particles from the air which reduce the indoor air quality but also may cause damage to the ventilation system itself. BS EN 1822-1 rates filters on a range of 1-17 according to their ability to trap pollutants whilst BS EN ISO 14644-1 covers high efficiency HEPA filters. For many new buildings using large commercial HVAC systems, panel and bag filters are put in place to filter supply air while only panel

filters are used for return air. If the filter is ineffective, maintenance issues will occur due to a build-up of particles in the duct work. Maintenance issues also occur when O_3 and acid gases react within the ducting and cause corrosion to the system. Another filter type, active carbon, is more effective at removing gaseous pollutants such as NO_2 but is rarely used due to its technical difficulty to set up and higher costs. However, buildings such as airports will often use active carbon filters in order to remove kerosene odours (Kukadia and Hall, 2011).

After filtration the air must be heated, cooled or dehumidified in order to meet indoor air quality standards. In the summer, supply air may need its temperature reduced, whereby a refrigerant is passed through a heat exchange coil in a gaseous state in order for it to lose its heat and return to a liquid state. This is then passed through a second coil, the evaporating coil, where the refrigerant draws the heat from the passing warm supply air, cooling it as it enters the building. Some systems offer a reverse valve so the one coil system can heat the air during the winter and cool it during the summer. In a country like Ireland this air usually requires heating throughout the year. A building management system (BMS) can control the level to which the building is heated or cooled to through a central computerised system. Relative humidity is generally kept below 60 % in summer or 40 % in winter using an evaporator which removes moisture from air by running it through a system of coils which are below the dew point temperature, this causes the moisture in the air to condense on the evaporator coils rather than travel through the system into the building (European Standard, 2006). Absorption dehumidifiers may also be used where moisture is removed from the air via a sorbent material.

Absorption dehumidifiers also control odours and the relative humidity of the air keeping it below 60% which is important for occupants' comfort in the buildings. Large buildings may have several parallel ventilation systems which draw in outdoor air and mix it with recirculated air from indoors. The outdoor and recirculated air is mixed and enters the various rooms in the building via vents near window ledges, along the ceiling or walls. The location of the air intake for the ventilation unit is important for the quality of the indoor air; placement near air exhausts, sewers or rubbish bins deteriorates the quality of indoor air (Turiel et al., 1983, Morawska et al., 2009). Relocation of poorly placed ventilation intakes can give up to 55% improvements on the quality of the air brought into the system (Morawska et al., 2009). The forced ventilation guarantees a pre-programmed air exchange rate and depending on system capabilities may control the intake air temperature and humidity. Part L of the Building Regulations (Department of the Environment, 2011) states that the standard acceptable air permeability is up to

10 $m^3(hr.m^2)^{-1}$ at 50 Pa for new buildings. In order to assess this, air tightness measurements were conducted on a naturally ventilated office block in the UK by Dimitroulopoulou (2008) using a PFT tracer. It found that when extract vents were open the permeability was 16.2 m^3 $(hr.m^2)^{-1}$ and when they were shut the permeability reduced to 14.7 m^3 $(hr.m^2)^{-1}$. No details were given for the age or condition of the building but 20 years of BRE results have shown that "leaky" buildings such as these are common.

DOAS systems are a newer concept and have become popular due to their ability to combat against airborne viruses such as avian flu and Sars (Mumma, 2001). For this system air is taken in and chilled to no more than 7°C. If air is above this temperature it is cooled by water in a sensible heat removing terminal device (SHRTD) which is below 4°C until it reaches the required temperature, see Figure 2.8. The SHRTD contains a fan coil unit (FCU), cooling ceiling (CC) and unitary air conditioner. Moisture in the air is removed by a solid dehumidifier in a desiccant wheel. A DOAS system is automated to ensure temperatures are always at the required levels. The DOAS system has no return air, which is why it is thought to be a good system with respect to the spread of infections.

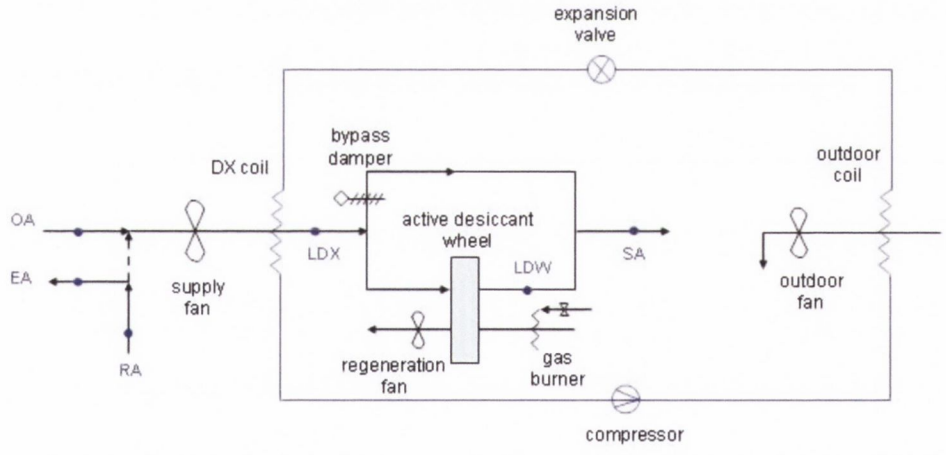

Figure 2.8 Schematic of DOAS ventilation system

ICTHS use separate temperature and humidity controls in order to reduce the issue of high energy consumption, mildew affecting the indoor air quality and low evaporating temperatures of the supply air. This type of ventilation system uses a liquid desiccant system and a grid system for heating and cooling, (see Figure 2.9). The system uses various combinations of the available grid at different times of the year, for instance during the summer the heating grid valve (B) is turned off. During the summer the

system uses a dehumidifier and during the winter a humidifier is utilised in order to get the optimum indoor air quality. Again this system uses chilled water in order to reduce the temperature of the supply air. In this system the water is usually at 15-18ºC which removes the latent load and some of the sensible load, while the remaining sensible load is removed once the air is inside the building. [Note, the sensible load is in reference to the dry bulb temperature of the building while the latent load refers to the wet bulb temperature which is affected by humidity]. Due to the use of heat removal via water this system is also known to reduce the energy consumption compared to conventional air conditioning systems by up to 75 % (Liu et al., 2006).

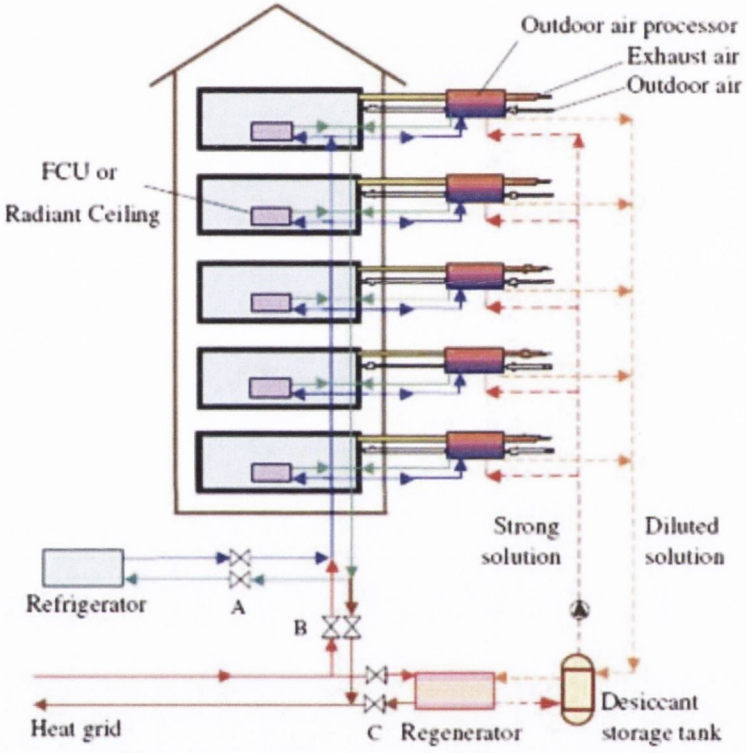

Figure 2.9 Schematic of ICTHS (Liu et al., 2006)

Displacement ventilation (DV) systems have been used in the past to improve indoor air quality via the reduction of pollutants and a further development in this ventilation system is the CC/DV system. This development removes the cooling issues which were present in DV systems in order to provide thermal comfort using the CC (cooling ceiling) system which performs well with respect to cooling but has had issues with the removal of pollutants. If the temperature gradient between the supply air and air already in the room is too great, then an increase in velocity due to the downward airflow motion caused by negative buoyancy force from the CC ventilation will occur. This velocity increase reduces the comfort of the building occupants and therefore is to be avoided (Loveday et al., 2002). Alamadrai (1998) found that a downward convection

near the walls of the room, which are cooler than the air within the room, can cause the movement of air pollutants from above the occupant zone (i.e. up to 1.5 m, the height at which people generally breathe) into this breathing zone causing higher exposures to pollutants as shown in Figure 2.10.

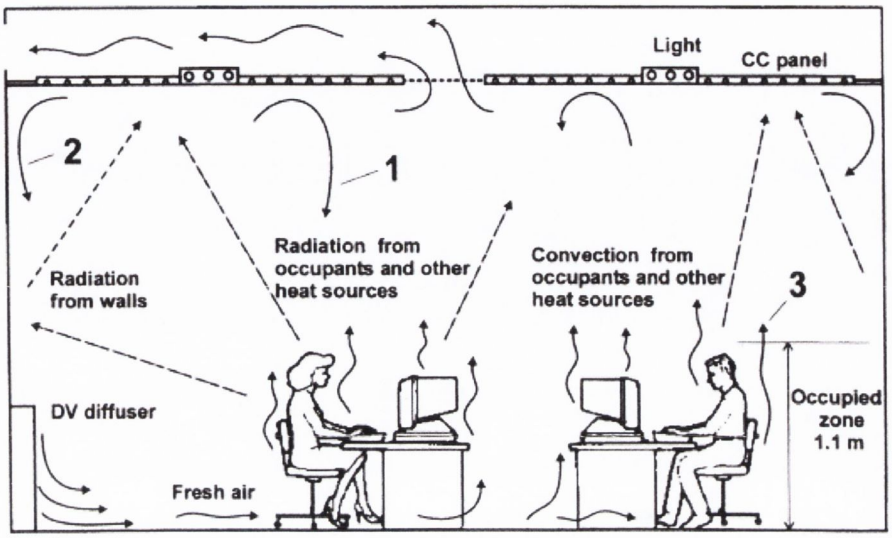

Figure 2.10 CC/DV system

Several studies have been carried out on the Indoor / Outdoor relationships within residential properties with respect to different ventilation systems. For example, Morawska et al. (2001) found a positive relationship between indoor and outdoor concentrations for air exchange rates above 0.5 h^{-1}. Monitoring conducted in mechanically ventilated shops in the late 1980s found low outdoor to indoor exchange rates (0.3-2 h^{-1}) yet internal recirculation rates were found to be much higher at 8 h^{-1} due to convection currents (Nazaroff and Cass, 1986). These results match Fadeyi's (2009) findings where similar recirculation rates of 7 and 14 h^{-1} were found alongside ventilation rates of 1 and 2 h^{-1} in an office environment. In residential studies, energy efficient buildings were thought to have ventilation rates of 0.1 – 1 h^{-1} while energy wasting buildings had above 1.2 changes h^{-1} (Moschandreas and Zabransky Jr, 1982). More recent work has found filtration rates of 56% for poorly designed systems; with upgrades these systems can reach filtration efficiencies of up to 82% for $PM_{2.5}$ (Morawska et al., 2009).

Naturally ventilated buildings are generally considered to have higher air pollutant concentrations due to the location of air inlets being through windows and doors on lower floors and often directly onto traffic bearing streets. Dimitroulopoulou et al. (2001) found that naturally ventilated offices showed higher concentrations of NO_2 compared

to mechanically ventilated spaces although with very similar patterns and a consistent 2 ppb when UK field data was utilised.

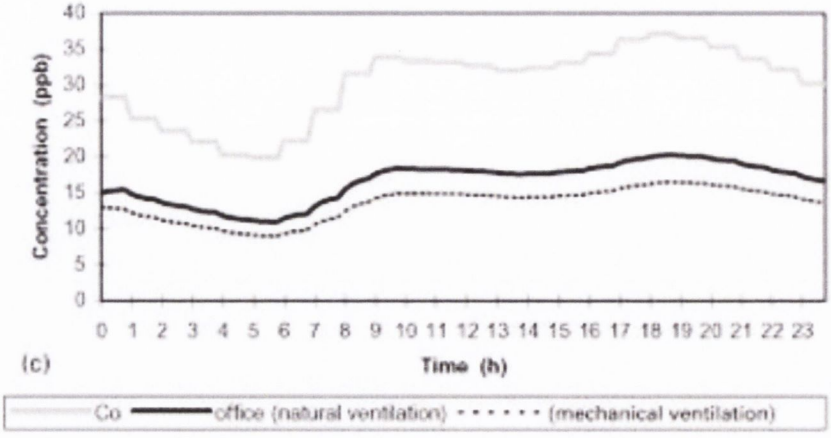

Figure 2.11 Natural versus mechanically ventilated office (Dimitroulopoulou et al., 2001)

In comparison, well designed mechanically ventilated buildings use intakes away from the street and at the highest point of the building. Naturally ventilated buildings may employ cross ventilation, where two or more openings are located on different sides of the building wall or single sided ventilation where two or more openings are present on the same side of the building Niachou et al. (2008). A study of a naturally and mechanically ventilated building by Kukadia and Palmer (1998) found that while mean CO levels in the naturally ventilated building were twice that of the mechanically ventilated building, concentrations of CO_2, NO, NO_2 and SO_2 were similar in both buildings. High variability has been found for the number of air changes per hour for naturally ventilated buildings due to the variance in the natural pressures which cause the air changes (Niachou et al., 2008). One of the few studies which did not take direct measurements for air changes per hour was carried out by Dockery and Spengler (1981). This study characterized ventilation by four variables; storm windows, heating systems, kitchen ventilation and air conditioning, and showed that air conditioning was the only variable which significantly affected the infiltration of particulates into a building. A reduction in the infiltration 0.67 to 0.45 h^{-1} was seen when full air conditioning was present within a building. It was felt that air conditioned homes were built to be more tightly sealed compared to naturally ventilated homes which had designed in vents and open windows more often.

Finally, natural filtration of air entering the building has been shown to occur at lower levels due to tree foliage or other natural boundaries being present and acting as a

barrier to low level pollutants (Kalaiarasan et al., 2009, McNabola, 2010, Gallagher et al., 2011).

2.9 Modelling indoor and outdoor air pollution relationship

Various parameters can be used in order to develop a model which predicts indoor concentrations of particulate and gaseous air pollution using outdoor concentrations; these use the knowledge of building parameters, weather variables and pollutant behaviours. Various modelling strategies have been discussed in literature; these include mass balance models, Gaussian plume models, neural networks and finite element models. Complex computational fluid dynamic (CFD) modelling can be used if detailed knowledge of the building and surrounding environment are known and to date has focused either on indoor or outdoor modelling rather than the combination of the two due to the large numbers of uncontrollable variables which must be considered. Hence, they are currently not recommended for regulatory models in this area until further work has been carried out (J.T. Milner, 2004) and so are not discussed in further detail here.

Gaussian plume models can be used to calculate building facade exposures to outdoor sources of air pollution such as traffic and building exhausts by calculating the rate that the plume spreads from each source (Lushi and Stockie, 2010, Cheung and Melbourne, 2000). Again these models have problems in complex urban environments due to the large number of complex dispersion effects from surrounding buildings etc. They are designed for calculating the concentration of pollutants that will come in contact with a building facade rather than enter the building. The OSPM model is a popularly used Gaussian model which can account for the concentration of pollutants on the building facade using direct sources i.e. cars, wind speeds and building geometry as shown in Figure 2.12 (Berkowicz, 1997).

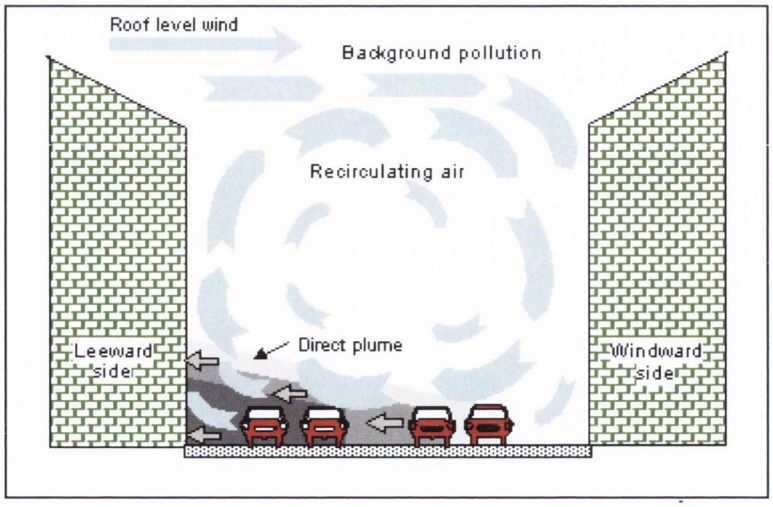

Figure 2.12 Street canyon model (Berkowicz, 1997)

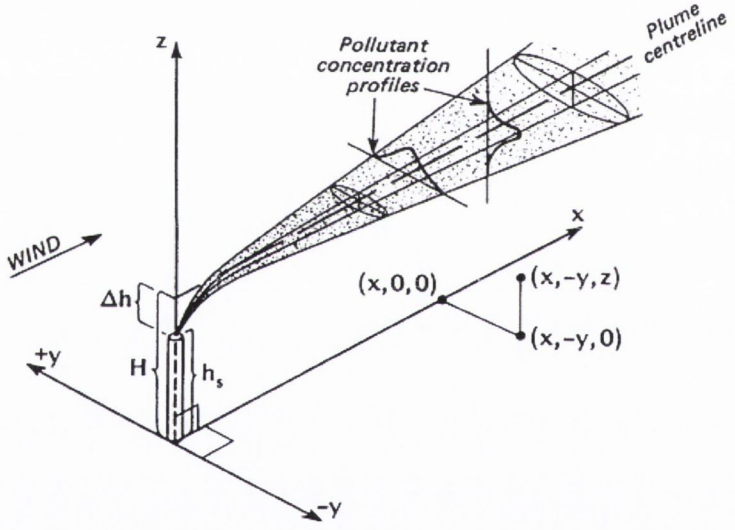

Figure 2.13 Gaussian Plume

Within the urban environment transport is the main source of pollutants to create the plume. Tall buildings combined with wind can create vortices along the street canyon trapping pollutants and creating pockets of very high concentrations, (Figure 2.12) and plumes spread away from the source i.e. vehicle tailpipe as shown in

Figure 2.13. Concentrations generated from transport have direct unmixed components as well as diffuse ones and the impact on the building should be calculated at peak and

general traffic conditions using Equation 2.17 and Equation 2.18 (Kukadia and Hall, 2011);

$$C_{Dir} = C_b + \frac{Q_l}{(U_H + U_T)[(X_1^2 + Z_1^2)^{0.5} + h_0]^2} \quad \text{Equation 2.17}$$

$$C_{Dif} = C_b + \left(\frac{Q_l}{(U_H + U_T)W}\right)\left(\frac{H - z}{H}\right) \quad \text{Equation 2.18}$$

where:

C_{Dir} = Direct plume concentration at building face

C_{Dif} = Diffuse plume concentration at building face

C_b = Background concentration

Q_l = Line source discharge (i.e. traffic) (g s^{-1} m^{-1})

U_H = The windspeed at roof top height m s^{-1}

U_t = Velocity of traffic induced turbulence

X_1 and Z_1 = Horizontal and vertical distances from line source (m)

H_o = Initial dilution of the traffic line source, taken at 2 m

H = Average height of buildings in street canyon

W = the street width

While Gaussian plumes are not directly used for indoor/outdoor relationships, they can be used to calculate the correct location for air intakes in order to reduce pollutant infiltration to the building. Many Gaussian plume models are calculated numerically or by use of wind tunnels. Within wind tunnels scaled models of the building or street can be made with complete control of parameters such as wind speed, wind direction and temperature. The issue with such models is that they are site specific and generated in highly controlled environments which may not account for all real world interactions. Green et al. (2001) used wind tunnel plume experiments at a scale of 1:100 to calculate the dispersion of traffic pollutants in urban areas and from this calculate the best location of air intakes to avoid contamination indoors. This work found that

concentrations on the back facade of the building can be 50 % lower than those on the side facing the road. The study also found that minimal reductions were found between intakes located at ground level and at the first floor but if intakes are at roof level (in this case 8 m) significant reductions of pollutant concentrations can be seen. These reductions were not affected by wind direction. The work by Green et al. (2001) recommended use of a ventilation strategy which adjusted with respect to indoor and outdoor pollutant concentrations in order, i.e. if concentrations were high outdoors ventilation should be decreased but if concentrations were higher indoors then ventilation should be increased. Other work on Gaussian Plume modelling in wind tunnels found that the density of buildings affected the region size in which pollutant sources affect a building with lateral spread of the plume increasing with an increase in density of buildings (Mfula et al., 2005).

Many of the numerical modelling studies discussed in this literature review use mass balance techniques in order to determine the relationship between indoor and outdoor concentrations (Chaloulakou and Mavroidis, 2002, Dimitroulopoulou et al., 2001, Dockery and Spengler, 1981). Most studies have focused on residential properties with far less research being reported on commercial buildings especially in the case of shops, possibly due to the difficulty of acquiring suitable sites. Mass balance models review at three main aspects of how indoor concentrations fluctuate; air exchange rates, indoor sources and pollutant decay rates. Pollutant concentrations may vary slightly throughout a room but for modelling purposes it is often assumed that the room is perfectly mixed and concentrations are equal throughout.

The simplest models use regressions of indoor and outdoor data in order to predict future behaviour of indoor data using outdoor concentrations. Many models have utilised this alone but also within more complicated models in order to predict specific parameters such as infiltration factors (F_{inf}) and the source within a building (Bennett and Koutrakis, 2006, Allen et al., 2003, Chen and Zhao, 2011). For instance Hoek et al.(2002) used this type of modelling to attain values for $PM_{2.5}$ sources of 2.6, 10.8, 4.7 and 3.3 $\mu g\ m^{-3}$ for Helsinki, Athens, Amsterdam and Birmingham respectively when carrying out research on indoor-outdoor relationships of particulates across Europe. The values found for the infiltration of $PM_{2.5}$ were 0.51, 0.30, 0.38 and 0.37 for Helsinki, Athens, Amsterdam and Birmingham respectively. The equation used to find these parameters is shown in Equation 2.19.

$$C_i = f_{inf} C_o + C_{ig} = \frac{Pa\, C_o}{a + k} + \frac{S}{(a + k)V} \qquad \text{Equation 2.19}$$

Where;

C_i= Concentration of particles indoors ($\mu g\ m^{-1}$)

C_o = Concentration of particles outdoors ($\mu g\ m^{-1}$)

C_{ig} = Concentration of indoor source ($\mu g\ m^{-1}$)

P = (1- f_{inf}) = Penetration factor

f_{inf} = Fraction of pollutant filtered in the entering air

k = Rate of decay, settling, and removal (h^{-1})

a = Air changes per hour (ach) (h^{-1})

V = Volume of building (m^3)

S= interior source rate

Dockery and Spengler (1981) published a paper in 1981 detailing the relationship between indoor and outdoor respirable particles and sulphates. Their research used a conservation of mass model, finding infiltration rates of outdoor particles indoors up to 70%. The study involved 68 residential monitoring sites used to collect data and parameters for the model. The model assumed uniform mixing within a building and that the volume of air entering the building is balanced by the volume leaving. The work stated that the indoor concentration can be calculated using Equation 2.20 .

$$\bar{C}_i = \frac{Pa}{(a+k)}\bar{C}_o + \frac{1}{V(a+k)}S \qquad \text{Equation 2.20}$$

Where:

$\bar{C}_i$ = Concentration of particles indoors ($\mu g\ m^{-1}$)

$\bar{C}_o$ = Concentration of particles outdoors ($\mu g\ m^{-1}$)

P = (1- f_{inf}) = Penetration factor

f_{inf} = Fraction of pollutant filtered in the entering air

k = Rate of decay, settling, and removal (h^{-1})

a = Air changes per hour (ach) (h^{-1})

V = Volume of building (m^3)

S = Interior source ($\mu g\ h^{-1}$)

The study used rates of 1.5 air changes per hour (ach) and a rate of sedimentation of respirable particulates of 0.5 h^{-1} in the well mixed room. The pollutant decay was due to physical and chemical reactions including settling, oxidation, filtration and absorption; decay rates were assumed to be constant. Linear regression was then used to estimate the unknown parameters f_{inf} and S using Equation 2.21

$$\bar{C}_i = P\bar{C}_o + (aV)S \qquad \text{Equation 2.21}$$

Long et al. (2001) used a physical statistical model to predict the infiltration rate of PM in nine non-smoking homes in Boston. This model used the ratio of indoor to outdoor pollutants to calculate the infiltration factor, F_{inf}; this can be seen in Equation 2.22;

$$\frac{C_i}{C_o} = \frac{Pa}{a+k} = F_{inf} \qquad \text{Equation 2.22}$$

F_{inf} was calculated using nightly average concentrations when sources are less prevalent and the effect of lag times between indoor and outdoor is constant. The night time hours were concluded to be 1 am to 6 am although they varied slightly between the nine residential houses monitored. In order to test for the usefulness of the estimates gained using this ratio, a regression of C_o/C was used to estimate the standard errors for p and k based on the covariance of the slope(k/p) and intercept(1/p). The estimates of p and k were used for the model if the slope and intercept were significant at $\alpha = 0.005$ level. The model found summer night-time data values of p=0.2 and k = 0.55 h^{-1} and winter night-time data values of p=0.61 and k = 0.37 h^{-1} with average annual values p=0.72 and k = 0.45 h^{-1} for particles up to $PM_{2.5}$.

While the previous two models focused on $PM_{2.5}$ Sexton (1983) examined NO_2 across 6 cities in the United States. This study again had little knowledge of the magnitude of variables such as F_{inf} or a and did not calculate them using pressure tests. The steady state equilibrium equation used to estimate the indoor concentration of NO_2 is shown in Equation 2.23. In order to calculate the source and F_{inf} the same regression method

used by Hoek (2002) found substantial spatial and temporal variation in the short term, but longer term averaging periods provided acceptable approximations of s and F_{inf}. Annual averages were used to find an approximated infiltration value of 0.6.

$$C_{in} = \frac{S + aC_{out}}{a + k} = \frac{S}{a + k} + \frac{aC_{out}}{a + k} \qquad \text{Equation 2.23}$$

The physical model developed by Dimitroulopoulou (2001) named INTAIR was a simple dynamic compartment model using 1 hour averages which assumed steady state conditions in a particular micro-environment could be calculated by Equation 2.24;

$$\frac{C_i}{C_o} = \frac{af_{inf}}{V_d\left(\frac{\mathrm{A}}{\mathrm{V}}\right) + \mathrm{a}} \qquad \text{Equation 2.24}$$

Where V_d = Deposition velocity and all other factors are as discussed previously.

This equation was taken from Equation 2.25 by assuming a steady state interaction between the two compartments and was originally developed by Roed and Goddard (1990):

$$\frac{dC_i}{d_t} = -V_d C\left(\frac{\mathrm{A}}{\mathrm{V}}\right) C_i + \mathrm{a}fC_o - \mathrm{a}C_i + \mathrm{a}(C_j - C_i) + \frac{\mathrm{S}}{\mathrm{V}} \qquad \text{Equation 2.25}$$

(Dimitroulopoulou et al., 2001)

Where:

C_i = Indoor concentration in compartment i

C_j = Indoor concentration in compartment j

Several works have followed on from these techniques implementing an indoor air quality model which used mass balance techniques. For example, the following equations Equation 2.26 to Equation 2.30 are taken from Goyal and Khare (2011) who utilised it for $PM_{2.5}$ but a similar technique has been used by (Chaloulakou and Mavroidis, 2002) for CO and (Hayes, 1991) for O_3 which will be discussed later in this section;

$$C_{n+1} = D_1 C_n + D_2 \frac{(C_{o\,n} + C_{o\,n+1})}{2} + D_3 \left(\frac{\frac{S_n}{V} + \frac{S_{n+1}}{V}}{2} \right)$$ Equation 2.26

$$D_1 = \frac{2 - b_1}{2 + b_1}$$ Equation 2.27

$$D_2 = \frac{2kT\mathrm{a}}{2 + b_1}$$ Equation 2.28

$$D_3 = \frac{2T}{2 + b_1}$$ Equation 2.29

$$b_1 = k\mathrm{Ta} + (R_c\, D \frac{A}{V})$$ Equation 2.30

Hayes(1991) used similar recursive mass balance techniques but implemented them for gaseous pollutants in mechanically ventilated buildings for multi-compartmental and the simplified single compartment case environments, like an office building. This work accounts for infiltration air changes a_f, air supplied via the buildings ventilation system or makeup air a_m and return/recirculated air. T is time in units of hours. A schematic of the model can be seen in Figure 2.14. All units are air changes per hour or h^{-1}. The model also accounts for a source within the building. This model does not assume perfect mixing and includes a mixing term 'K' to account for mixing between time steps within the building. For offices K=1 can be assumed which represents uniform mixing, but the range for other buildings is 0.33 – 1. The same equation as used by Goyal and Khare (2011) was utilised with some amendments to the b_1 and D_2 variables. These changes are listed in Equation 2.31 and Equation 2.32 which were used to account for the addition of a ventilation system's air changes as well as the infiltration air. The study used typical ventilation values of 7.71 ach for non-energy efficient buildings (2.64 of this from make-up air and 5.07 from recirculation) and 10 ach for energy efficient buildings (1 of this from make-up air and 9 ach from recirculation). The study found that

an office in which a ventilation system with filters supplies 100 % of the air to the room had a I/O ratio of 0.82, which was seen in other buildings studied by Sabersky et al. (1973). For naturally ventilated buildings the study used the following ach; 1 closed windows. 2.4 partly open windows, 6.4 open windows, 18.9 all windows and large door areas open.

$$b_1 = KT(a_m + a_f + a_r(1 - E_r)) + (k\frac{A}{V}) \qquad \text{Equation 2.31}$$

$$D_2 = \frac{2KT(a_m + a_f E_f)}{2 + b_1} \qquad \text{Equation 2.32}$$

Where:

E_f = Efficiency of the make-up air filter

E_r = Efficiency of the return air filter

a_m = air exchange rate from natural infiltration

a_f = air exchange rate due to mechanical ventilation

a_r = air exchange rate due to return air

T = time (hrs)

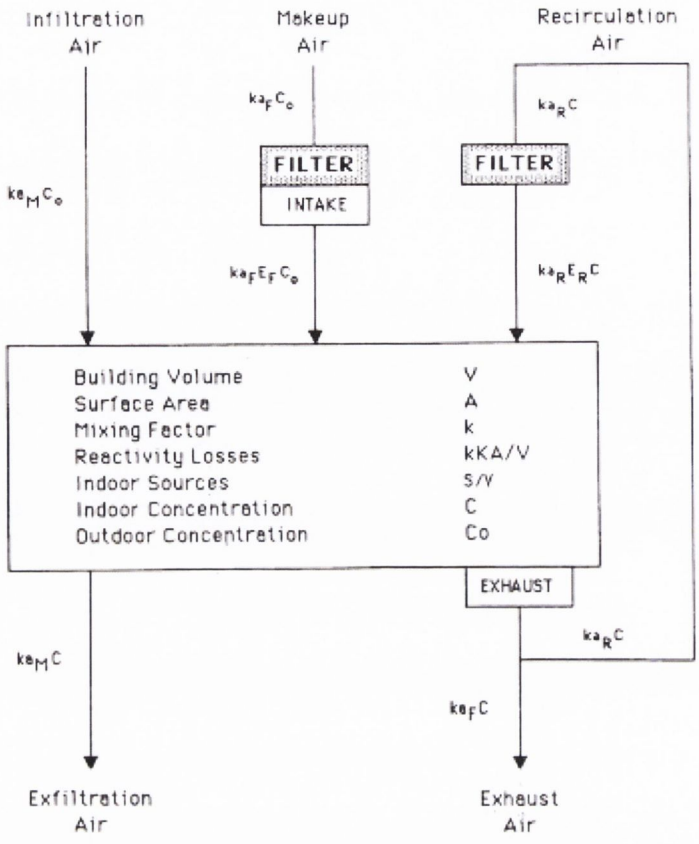

Figure 2.14 Schematic of indoor air quality model (Hayes, 1991)

Ten years after the publication of Hayes (1991) study, Chaloulakou and Mavroidis (2002) used a similar model for predicting indoor air concentrations of CO in a public school. The same equations were used as for Hayes et.al (1991) but an additional calculation for K was also included in Equation 2.33. A lower mixing range of between 0.01 – 0.38 was used for this research, which found weekday figures to be on the higher range of this scale and recommended that mean values of K be used if high variations in the value are found. Chaloulakou and Mavroidis (2002) used ach of 1.2 in winter, 1.5 in summer (windows open) and 0.8 for mechanically ventilated offices, with 0.9 m^{-1} the A/V value utilised for this school based study.

$$K = \left| \frac{\log C_{i\,(n+1)} - \log C_{i\,(n)}}{T} \right|$$

Equation 2.33

Ozkaynak et al. (1982) then developed a single compartmental reactive chemistry model for forward predicting the rate change in the indoor air concentrations and

fluctuations in NO_2, as shown in Equation 2.34. The author used chemical production and loss terms derived from known reactions, with a steady state assumption for O_3.

$$\frac{dC_{ii}^{l}}{dt} = p_i^l - l_i^l + (c_{io}^l - c_{ii}^l)R - k_{hi}C_{ii}^l + s_i^l$$

Equation 2.34

Where:

c_{io}^l = Concentration of the ith species outdoors at time step l

c_{ii}^l= Concentration of the ith species indoors at time step l

R = Infiltration/exfiltration rate

k_{hi} = Heterogeneous rate constant for series i

s_i^l= Source of species I at time step L indoors

p_i^l = Chemical production of species I at time step l

l_i^l = Chemical loss of species I at time step l

The concentration at the next time step is given in Equation 2.35;

$$C_i^{l+1} = C_i^l + \tau\frac{dC_i^l}{dt}$$

Equation 2.35

Where τ is the time interval.

The time rate change of NO_2 was calculated using Equation 2.36

$$\frac{d(NO_2)}{dt} = k_2[O_3][NO] - J_1[NO_2] + a([NO_2^o] - [NO_2]) - k_{h2}NO_2 + QNO_2$$

Equation 2.36

Where:

K_{h2} = Heterogeneous rate constant for NO_2

K_2 = 25.2 ppm^{-1} min^{-1} or 0.013 $\mu g\ m^{-2}$

a = Ventilation rate

Q_{NO2} = The NO_2 emission rates

J_1 = Photolysis rates

The work detailed k_{h2} for NO_2 ranging from 0.5 to 0.1 $h^{-1}$and photolysis rates for NO_2 ranging from 0.003 to 0.017 min^{-1} found through monitoring. The final two sets of parameters used for simulations of the model were k_{h2}=0.0124 and J_1= 0 or k_{h2}=0.00474 and J_1= 0.00304. Using a photolysis value of 0 will remove the effect of reactive O_2 species from chemistry whereby O_2 will only be present therefore via infiltration. In this first simulation the heterogeneous loss rate was higher than for the second set of parameters meaning the reduction of NO_2 was higher. The second simulation used a higher photolysis rate with lower heterogeneous reactions, see Figure 2.15. The reason for two simulations was due to the difficultly of separating how NO_2 reduces from the two separate reactions.

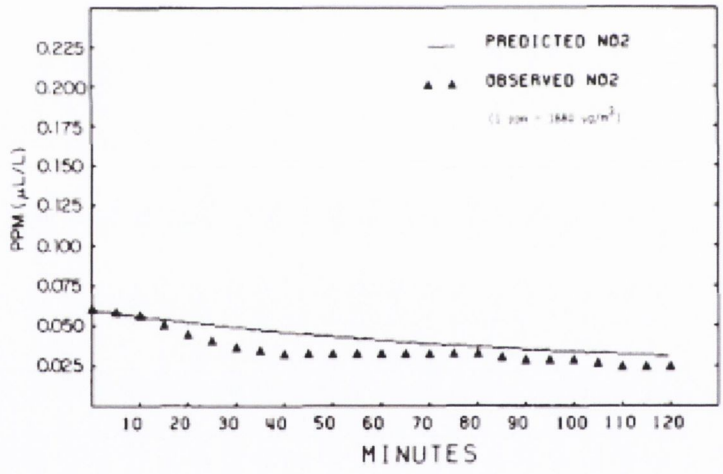

Figure 2.15 Predicted versus observed NO_2 (Özkaynak et al., 1982)

Another method for estimating particle penetration via recursive mass balance model was a non-linear regression of air exchange rate, particle decay and particle infiltration (Allen et al., 2003). This work assumes a well-mixed room and constant air exchange values with 1 hour average values for concentrations of PM taken. This model is designed for use with PM data collected using instrumentation based upon the light scattering method. This model states that the indoor concentration ϕ is equal to the total particle loss rate and has units of h^{-1}.

$$(b_{sp})_t^{in} = (b_{sp})_t^{out} a_1 + a_2 (b_{sp})_{t-1}^{in} + s_t^{in}$$ Equation 2.37

$(b_{sp})_t^{in}$ is the average indoor light scattering coefficient and $(b_{sp})_t^{out}$ is the traction of average outdoor light scattering coefficient, s_t^{in} is the light scattering contribution to from indoor sources

$$a_1 = f_{inf} \{1 - exp[-\Phi t]\}$$ Equation 2.38

a_1 is the fate of the outdoor particles once indoors, F_{inf} is the particle infiltration efficiency

$$\Phi = a + k$$ Equation 2.39

ϕ is equal to the total particle loss rate and has units of h^{-1}, a is the air exchange rate while k is the particle removal rate due to diffusion or sedimentation.

$$a_2 = [exp[-\Phi t]]$$ Equation 2.40

This work found a Pearson's r = 0.31 for the correlation between indoor and outdoor light scattering data when using hourly concentrations although this rose to r=0.62 for 24 hour data. While the use of 24 hour data increases the correlation it also removes one of the strongest reasons for using light scattering data collection for PM as the real time element of the data is removed. For night-time hourly non-source periods the r value is 0.77. Use of a non-linear regression to find F_{inf} found that the average value was 0.65 ± 0.21 which agreed with other work which found values between 0.5 and 0.86 in non-air conditioned homes in America, as shown in Figure 2.16.

location	season	no. of residences	particle size/tracer	mean F_{inf}	ref
Riverside, CA	fall	178	$PM_{2.5}$	0.7[a]	11
Uniontown, PA	summer	24	sulfate	AC = 0.69[b] non-AC = 0.86[b]	21
Virginia & Connecticut	summer	58	sulfate	0.74[b]	22
Boston, MA	spring–summer & fall–winter	9	$PM_{2.5}$	0.74[b]	24
Boston, MA	summer & winter	4	PM: 0.7–1 μm	0.53[a]	20
			PM: 1–2 μm	0.50[a]	
Birmingham, AL	summer & winter	10	$PM_{2.5}$	0.66[a]	23
Six cities	all seasons	68	$PM_{3.5}$	0.70[a]	19
			sulfates	0.75[a]	
Seattle, WA	all seasons	44	light scattering	0.65[a]	this work
		10	sulfur	0.60[b]	

[a] Modeled. [b] Measured.

Figure 2.16 Summary of Published Mean Infiltration Efficiencies (Allen et al., 2003)

f_{inf} increased on days when the windows were open compared to days they were closed, with increases in the air exchange rate also seen. The highest air exchange

rate recorded 4.63 h^{-1} when windows were open, while average ach of 0.46 ± 0.26 h^{-1} if the influence of one highly leveraging event was removed which increased the average ach to 0.54 ± 0.60 h^{-1}.

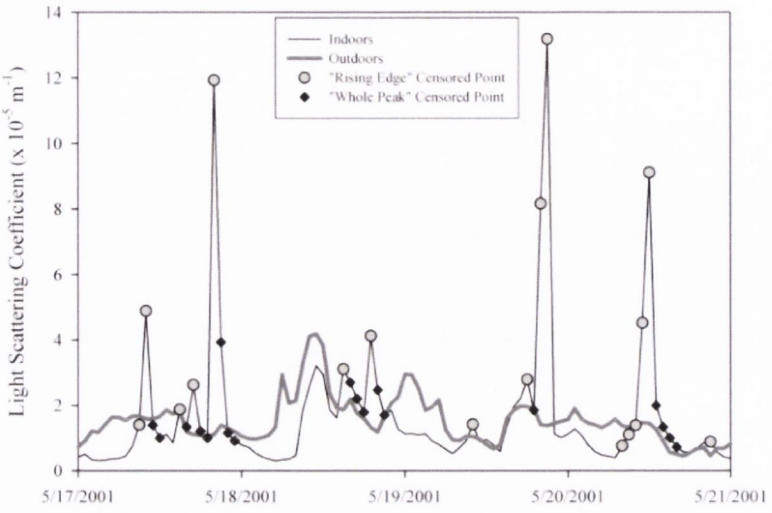

Figure 2.17 Indoor and outdoor concentrations during monitoring event (Allen et al., 2003)

K, used in Equation 2.39, was found to increase significantly when windows were closed, the author suggested that this was due to the lower air changes per hour and therefore particles had a longer time to deposit on surfaces. An average k of 0.20 ± 0.16 h^{-1}, is significantly less than Wallace (1996) who reported a value of 0.59 h^{-1} for $PM_{2.5}$ but closer to the range in 0.15 h^{-1} for summer values and 0.10 h^{-1} for winter values by Long et al. (2001).

Another modelling technique is Artificial Neural Networks (ANN) which can provide an intelligent and robust modelling technique, finding hidden links between input data in order to predict a target variable. In the case of indoor/outdoor air modelling the target data would be the indoor air quality with inputs including: outdoor concentrations, meteorological data and building characteristics. ANNs are based upon the Levenberg - Marquardy Algorithm (Marquardt, 1963, Levenberg, 1944), see Equation 2.41, which is an alternative to the Gauss-Newton Algorithm for calculating a numerical solution to the issue of minimising non-linear and linear functions, over a space of parameters for the function.

$$\left(J^T J + \lambda diag(J^T J)\right)\delta = J^T[y - f(\beta)] \qquad \text{Equation 2.41}$$

Where:

J – Local gradient of f with respect to β at X_i

β- Parameters

y – Independent and dependent variables

δ - Increment

ANNs have previously been used to predict future concentrations of air pollutants outdoors (Wang and Chen, 2002, Wang et al., 2003, Lu et al., 2003, Grinn-Gofroń et al., 2011), to predict health effects severe enough to cause hospital visits with air pollution (Bibi et al., 2002, Wilson et al., 2004), to link indoor pollutant concentrations to illness (Sofuoglu, 2008), and relationships between traffic and air pollution concentrations (Bell et al., 2004). While not as common, ANNs have also been used for the prediction of indoor air quality using outdoor data (Kindangen, 1996). Sun and Hoff (2009) used ANNs to accurately predict long term (5 year) air quality of CO_2, NH_3 and H_2S outdoors and the indoor air quality of swine deep pit buildings in Nevada, United States. Another piece of work used ANNs to predict air flows inside naturally ventilated buildings due to different ventilation strategies. The prediction of air flows could easily be adjusted to include pollutants in the ANN. Stavrakakis et al. (2011) also used ANNs to predict the size of windows necessary in buildings in order to provide occupational comfort of those working within naturally ventilated buildings using a range of metrological variables and CFD.

2.10 Input parameters for mass balance models

The previous section discussed a selection of method that can be used for modelling indoor air quality. This section focuses on the input parameters that were previously utilised for mass balance models.

2.10.1 The penetration rate

The penetration rate is the removal of pollutants due to physical deposition or chemical transformation and has units of h^{-1}. The penetration factor is the fraction of the pollutant that penetrates through the building and is not removed from ambient air, as described by Equation 2.42;

$$P = \frac{a}{a + K} \qquad \text{Equation 2.42}$$

where a is the air exchange and K is the decay rate, providing no indoor source or resuspension are present. Values close to unity indicate that the building shell does not remove pollutants - if the value is above 1 this may be due to indoor activities or sources (Thatcher and Layton, 1995). Values between 1 (Cristy and Chester, 1981) and 0.7 (Dockery and Spengler, 1981) have been found in literature for gaseous pollutants in studies based in the United States. The study by Thatcher and Layton (1995) however, suggests that these values may be incorrect due to the studies not accounting for the effect of indoor sources, deposition or resuspension. They noted that their own study would have found P values of 0.2-0.6 if these effects had not been accounted for (Thatcher and Layton, 1995). Once these effects were accounted for, average values over six separate monitoring periods gave values very close to 1.

2.10.2 Air exchange rates

The air exchange rate or number of air changes per hour (ach) will determine the quantity of pollutants which enter a building and the length of time these pollutants remain in the building. Air exchange rates are denoted by a or λ in the majority of models with units of h^{-1} but they may also be called air changes per hour or ach. In naturally ventilated buildings ach are affected by differences in temperatures between indoors and out (which creates convective behaviour patterns), or whether windows are open or closed, as well as any pressure differences, between indoors and out. Wind speeds can also increase the ach due to increased pressure differences.

The ach is determined by the filtration factor, penetration rate and reactivity rate for a particular building. For mechanically ventilated buildings three rates are considered - the makeup air, the return air and infiltration air - while for naturally ventilated buildings only infiltration rates are needed. Make-up air exchange rate (λ_m or a_m) is the contribution to the total air changes per hour by air brought in through a forced ventilation unit which usually includes a filtration system. The rate can be controlled

from a central unit and adjusted to meet temperature or exchange rate requirements. The return air exchange rate (λ_m or a_r) is air which is drawn out of the building and returned back into the system, passing through the filtration system as it re-enters the building. The final type of air exchange is due to natural filtration (λ_f or a_f) through the building via open doors, windows and leakage through the building structure. This natural infiltration of air is present in both mechanically ventilated and naturally ventilated buildings. For example, Drakou et al. (2000) used the following achs for their study; energy efficient buildings have air exchange rates of 0.2 h^{-1}, closed windows 1 h^{-1}, windows partly open 2 h^{-1} and a fully open window 6.4 h^{-1}.

2.10.2.1 Infiltration air exchange rates (a_f)

In mechanically ventilated offices infiltration exchange rates can be as low as 0.2 ach or 1 air change every 5 hours (Hayes, 1991) and range up to 18.9 ach for shops with large open doors or offices with windows which are opened. For an average naturally ventilated office building the British Research Establishment recommended rates of 0.41 to 1.5 ach with the higher values being used when occupants opened windows within the building (Dimitroulopoulou et al., 2008). The higher rate of 1.5 ach was used for modelling infiltration rates at mechanically ventilated offices in studies by Dimitroulopoulou (2001) as well as Dockery and Spengler (1981) with the same rate being used for naturally ventilated offices. The rates in UK homes were lower than those used for commercial buildings, with an average rate of 0.29 ach from a sample size of 385 (AIVC, 1994) although other studies such as Hayes (1991) concluded the opposite, finding that offices/shops often had inoperable windows and tighter sealed buildings. The AIVC sample showed mean infiltration rates of 0.68 which were higher than those measured in other countries, e.g. France (0.18), Norway (0.25), Netherlands (0.51) and Belgium (0.41). In cities such as Hong Kong, air exchange ranges of 0.3 to 3.9 ach have been recorded for mechanically ventilated shops and offices (Chao and Chan, 2001). The increased rates due to infiltration are due to different building practices and amount of time doors/windows are left open. If a naturally ventilated building has 1 ach with windows closed it is suggested that this will increase to 2.4 ach with windows partly open and 6.4 ach with windows fully open (Chaloulakou and Mavroidis, 2002). The infiltration rate will decrease during out of work hours when all doors and windows are closed and infiltration only occurs through gaps in the building fabric. For example, in a study by Kukadia and Palmer (1998) the ach decreased from 1.2 during working hours to 0.4 in out of working hours. Very similar rates were utilised

by Long et al.(2001) with I/O ratios of 1.2 for PM_2 during the day, dropping to 0.3 at night.

Finally, the air exchange rate can be calculated for naturally ventilated buildings using the deposition velocity of the pollutant (K) and the surface area of the room (A) divided

$$\lambda_r = \left(\frac{A}{V}\right) K$$ Figure 2.18

by the volume of the room (V) as shown in Equation 2.42 (Roed and Goddard, 1990);

2.10.2.2 Return air rates (a_r)

Return air rates, a_r, are only seen in mechanically ventilated buildings and are usually high compared to makeup or infiltration exchange rates. A study of 21 European mechanically ventilated buildings found average return air rates for energy efficient buildings recording 9 ach and 5 ach for non-energy efficient buildings (AIVC, 1994) for return air alone. For return rates of this level, make up air was calculated to be 1 ach for energy efficient systems or 10% of the combination of return plus makeup air. In the case of the non-energy efficient building a higher percentage of air about 34% or 2.64 ach was due to makeup air (Hayes, 1991). This is consistent with another study by Grot and Persily (1986). Higher return air rates increase the number of times that air goes through filters on the building which can greatly increase the removal rate of the filter (Fadeyi et al., 2009).

6.1.1.1. Make-up air exchange rates (a_m)

Make-up air exchange rates are the amount of outdoor air passing through a filter, (as well as possibly a heating or cooling unit) due to forced mechanical ventilation. Even if the ventilation system is turned off, for instance outside of working hours a small amount of outdoor air will enter the building through this system. As stated in the previous paragraph an energy efficient mechanical ventilation system will draw in a higher percentage (10%) of make-up air compared to the rate of return air compared to a non-energy efficient system (47%) (Hayes, 1991). Fadeyi et al. (2009) found make-up rates of 1-2 h^{-1}, which is similar to the rates found by other studies which ranged from 0.7 to 2 h^{-1} (Chaloulakou and Mavroidis, 2002, Sidheswaran et al., 2012, You et al., 2012, Dimitroulopoulou et al., 2006, Ekberg, 1995).

2.10.3 The reactivity or decay rate

The reactivity or decay rate (generally symbolised by K) for pollutants is used to model for example the effect of deposition for $PM_{2.5}$ or NO_2 interactions with other compounds which is the more likely source of decay for that pollutant. Its units are per second s^{-1} or per hour h^{-1}. The rate of K is a function of the surface materials in the room i.e. carpet or wooden floors as well as the surface area to room volume ratio. The greater the surface area of a room for a specific ratio, the greater the decay rate will be. The proportion of K due to deposition can be calculated using Equation 2.43;

$$K_{dep} = \frac{A\,V_d}{V} \qquad \text{Equation 2.43}$$

The use of V_d is an alternative way to describe deposition as when it is multiplied by the internal surface area divided by the volume as in Equation 2.43, the result is a value which accounts for the dimensions and conditions of the room in question, and therefore can be easily applied to any other room provided if A and V are known. V_d values of 1 - 0.004 was given by Karlsson (1994) for NO_2 but this figure can be adjusted for any room by multiplying it by A/V. Other studies have used K values of 0.99 h^{-1} (Yamanaka, 1984), using a A/V value of 0.9 which is recommended for offices. This results in a V_d of 1.1 mh^{-1} or 3 x 10^{-4} ms^{-1} (Dimitroulopoulou et al., 2001). Average removal rates of 0.8 h^{-1} for NO_2 were found in the 1980s by several authors although these rates varied up to 6.5 h^{-1} as can be seen in Figure 2.19 (Spicer et al., 1989b, Özkaynak et al., 1982).

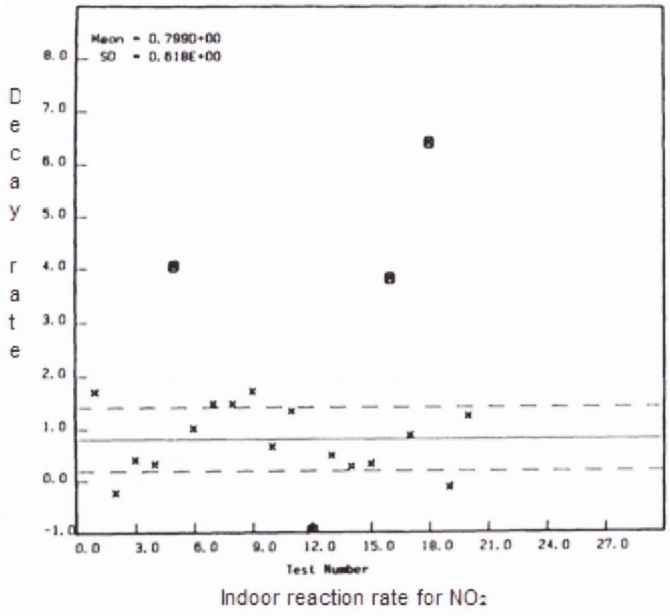

Figure 2.19 Removal reaction rates NO_2 (Spicer et al., 1989a)

Values of V_d were given by Drakou (2000) at levels of 0.0062 cm s^{-1} for NO_2, 0.0006 cm s^{-1} for NO and 0.051cm s^{-1} O_3 (Drakou et al., 2000). These values had been rounded down by 5 % from the values previously given by Nazaroff and Cass (Nazaroff and Cass, 1986) due to greater understanding of pollutant behaviours between 1986 and 2000. Drakou (2000) found that V_d decreases with increasing ventilation rate as shown in Figure 2.20, for a full chemistry case (FC) or simplified or no chemistry (NC) case. The effect of changing ach is noticeable up to 4 h^{-1} due to the lower deposition velocities seen as ach increases; the opposite is true to O_3 which results in increasing I/O ratio with increasing ventilation rates. Weschler et al. (1994) found ach in a Californian commercial building of between 0.3 to 1.9 h^{-1} with a decay rate of 0.1 h^{-1} for NO_2 in low lighting levels and no indoor pollution sources.

Comparison of air pollutant concentration under different ventilation senarios and different UV radiation levels. [a], [b], [c]: No Chemistry cases, [d], [e], [f]: Full Chemistry cases (λ_{UV}=0.15%),[g], [h], [i]: Full Chemistry cases (λ_{UV}=25%).
Simulation input parameters:
No Chemistry and Full Chemistry model
Indoor temperature=24°C and RH=50%

				Air exchange rate (h^{-1})	Case	
Constant outdoor air pollutant concentrations (ppbv):	NO=84	NO_2=40	O_3=30	0.2	0.2 FC	0.2 NC
Initial indoor air pollutant concentrations (ppbv):	NO=91	NO_2=34	O_3=12	0.5	0.5 FC	0.5 NC
Air pollutant decomposition rate (h^{-1}):	NO: 0.04	NO_2: 0.4	O_3: 3.3	1	1 FC	1 NC

Figure 2.20 a ach relationship with V_d (Drakou et al., 2000)

The reduction in indoor concentrations of NO compared to outdoors concentrations due to chemical reaction is shown in Equation 2.44. While giving the reduction in NO, it also

enables increases in NO_2 due to available NO and O_3 in the environment to be calculated;

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad \text{Equation 2.44}$$

The reaction rate for the increase in NO_2 is 4.43 x 10^{-4} s $^{-1}$(Atkinson et al., 1992). This reaction rate along with the O_3 concentration and number of air changes per hour can be used to calculate the reduction in I/O ratio due to the reaction in Equation 2.44 (Weschler and Shields, 1997). Equation 2.45 assumes 1 ach although this can be easily changed and it should be noted that O_3 concentrations are given in ppb;

$$\frac{I}{O} = \frac{2.8 \times 10^{-4}}{2.8 \times 10^{-4}} + O_3 \text{conc} \times 4.43 \times 10^{-4} \qquad \text{Equation 2.45}$$

Note: 1 ach = 2.8 x 10^{-4} s^{-1}

For example, if the O_3 concentration is 20 ppb (and assuming negligible surface reactions for NO) then the I/O ratio is 0.03, or explaining why the indoor concentration of NO can be low (Weschler and Shields, 1997).

Modelled indoor concentrations of NO_2 and NO are often miscalculated due to the lack of inclusion of heterogeneous chemical reactions on surfaces, photolysis and other sink reactions in models (Nazaroff and Cass, 1986, Hayes, 1991, Phillips et al., 1993). The reduction in NO_2 due to reaction with O_3 shown in Equation 2.46, where the reaction rate is 7.87 x 10^{-7} s $^{-1}$ (Atkinson et al., 1992);

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad \text{Equation 2.46}$$

This reaction is only important during night-time hours (outdoors or indoors) or in the absence of sunlight in areas such as ventilation ducting, raised floors and dropped ceilings (Weschler and Shields, 1997). When sunlight or strong indoor lighting is available the NO_3 is photolytically unstable and will further degrade acting as a source for NO_2 in future reactions.

Heterogeneous reactions are important for NO_2, particularly in the naturally ventilated buildings with lower air exchange rates as pollutants. One site which had very low indoor NO_2 concentrations compared to outdoors reported a damp feeling in the

building. The heterogeneous reaction in Equation 2.47 (Weschler and Shields, 1997) increases with increasing relative humidity or damp on the surfaces within the building (Brauer et al., 1993).

$$H_2O(surface) + NO_2 \rightarrow NO_3^- + H^+ + HONO(aq) \qquad \text{Equation 2.47}$$

The reaction in Equation 2.47 can act as a source of NO due to the following reaction in Equation 2.48 where NO_2 and HONO are used (Spicer et al., 1989a), with up to 15 % of NO_2 being utilised and reemitted as NO. Building materials which increase these reactions are ceiling tiles, plywood, plasterboard, bricks, polyester carpet, wool carpet, acrylic carpet and Masonite. Some of these removal rates for NO_2 are included in Figure 2.21. Weschler (2001) found that synthetic carpets showed a removal rate almost in order of magnitude more than surfaces coated in Teflon and that materials which absorb water can also significantly influence reaction rate. At an RH of only 50 % vinyl – coated wall paper was found to release HONO and the level of this release increased at RH = 70 %.

$$HONO + NO_2 \rightarrow NO_3^- + H^+ + NO \qquad \text{Equation 2.48}$$

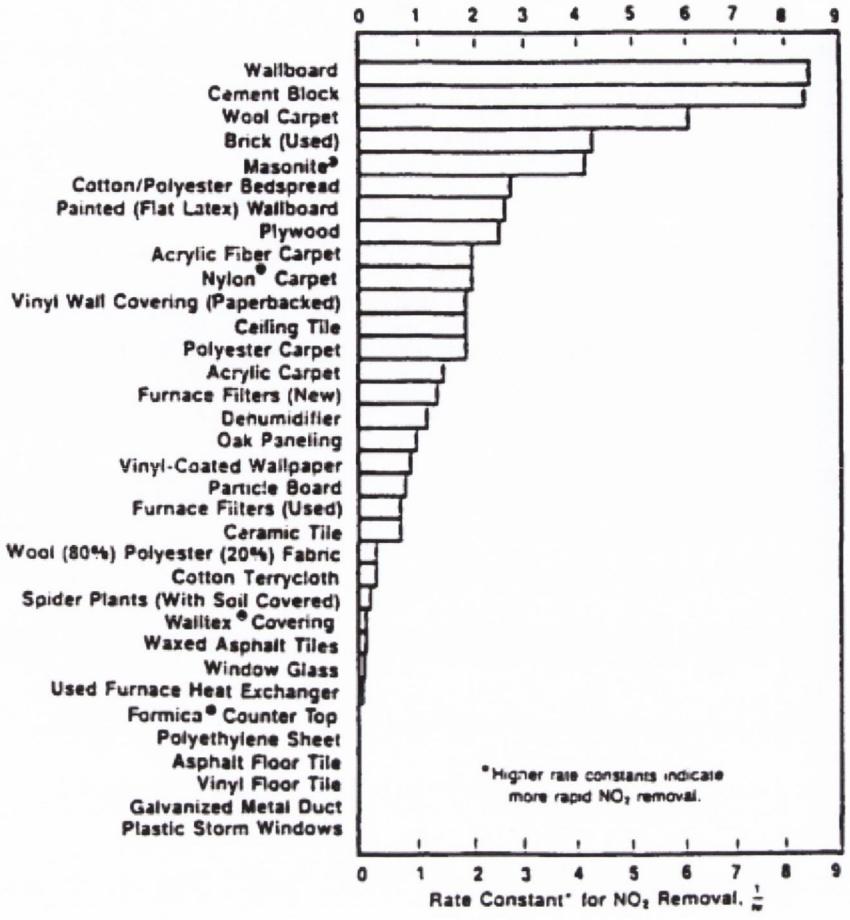

Figure 2.21 NO2 removal rates for various materials (Spicer et al., 1989b)

Heterogeneous reactions due to jute carpet backing was found to reduce NO_2 concentrations significantly 34-57 % by converting it to NO (via Equation 2.49 and Equation 2.50) due to the low molecular weight polysaccharide (ROH) present in the backing (Spicer et al., 1989a).

$$ROH + NO_2 \rightarrow +HNO_2 + Products \qquad \text{Equation 2.49}$$

$$2HNO_2 \rightarrow +NO_2 + H_20 + NO \qquad \text{Equation 2.50}$$

More recent work done in 2001 found NO_2 decay rates in a no carpet situation k = 0.07 to 0.15 h^{-1} (V_d = 4 x 10^{-4} to 9 x 10^{-4}) and in the carpeted situation k = 0.89 to 1.3 h^{-1} (V_d = 56 x 10^{-4} to 81 x 10^{-4}) (Wainman et al., 2001).

2.10.4 Decay rates $PM_{2.5}$

Decay of $PM_{2.5}$ is generally due to various types of settling or deposition rather than the chemical reactions described previously for NO_2. The deposition of particles is a function of their size, with the deposition time of larger particles being faster than smaller size fractions according to Fogh (1997). The equation $V_d = 0.48 + 0.60\ d_p$, (d_p = particle diameter, μm) was given by Fogh (1997) in order to calculate value of V_d for different size particles. For $PM_{2.5}$ a value $V_d = 1.98$ is calculated using this equation. A deposition or removal rate of $0.5h^{-1}$ for fine particles above 1 μm and less than 0.05 h^{-1} for particles under 1 μm was utilised for the mass balance model by Dockery and Spengler (1981).

Sulphate particles in almost unoccupied buildings showed deposition velocities of 0.003 to 0.005 cm s^{-1} which results in a decay rate of 0.3 to 0.5 h^{-1} assuming a surface area to volume ratio of 3 m^{-1} (Sinclair et al., 1990, Weschler and Shields, 1989). These results vary from other work completed by other authors (Nazaroff et al., 1990a, Ligocki et al., 1990, Nazaroff et al., 1990b) which found results in order of magnitude smaller, while work by PTEAM found results between the two at 0.16 h^{-1}(Allen et al., 2003). The decay or deposition rates for $PM_{2.5}$ vary due to the type of surface they come in contact with, the air flow rate when they make contact as well as near surface turbulence (Wallace, 1996). Due to these contributing factors chamber studies of deposition may not be able to fully describe patterns behaviours for specific buildings. K for the range of 0.7 to 3 μm range from 0.22 to 0.66 h^{-1} and is highly affected by particle size.

Chen and Zhao (2011) found gravitational settling due to velocity factors of 3.51×10^{-5} for PM_1 and 3.06×10^{-3} for PM_{10} while for deposition caused by the values were found to be 1.12×10^{-3} for PM_1 and 2.64×10^{-4} for PM_{10}. These results show an increase in gravitational settling with particle size while thermophoresis (setting due to different particle types exhibiting different responses to the force of a temperature gradient) settling increases with decreasing particle size.

2.10.5 The building fabric filtration factor

The building fabric filtration factor (f_{inf}), is a measure of the fraction of ambient particles that penetrate indoors and remain suspended. In naturally ventilated buildings f_{inf} may be taken as 1 as the building has no filtration system, and gaseous pollutants should also use f_{inf}=1 (Dimitroulopoulou et al., 2001). The literature recommends a building fabric filtration factor of 0.2-0.7 for mechanically ventilated offices and shops which is lower than the figure of 1 as is used for many homes (Ng et al., 2005, Özkaynak et al., 1996). Abt et al.(2000) found lower rates again, although over a wider particle size range 0.7-10 μm, of 0.12-0.5. Fine particulate infiltration for air conditioned residential buildings was found to be weak at less than 0.20, although the same study also looked at sulphates and found an even weaker effect at less than 0.05 (Dockery and Spengler, 1981). Hoek et al.(2008) reviewed 152 residential European buildings infiltration factors for $PM_{2.5}$, which ranged between 0.3 to 0.5 with the mean f_{inf} being 0.4 over homes located in Birmingham, Amsterdam, Athens and Helsinki.

If no source is present then f_{inf} is equal to the indoor concentration over the outdoor concentration as described by Equation 2.51. If an indoor source is present f_{inf} can be calculated using Equation 2.51 (Bennett and Koutrakis, 2006, Allen et al., 2003, Chen and Zhao, 2011).

$$f_{inf} = \frac{ap}{a + K} \qquad \text{Equation 2.51}$$

In order to calculate f_{inf} a regression of the indoor concentrations on the outdoor concentrations can be carried out. Using the equation of the line ($y = mx+c$), the slope (m) gives f_{inf} while the intercept provides the concentration of an indoor source present as shown in Equation 2.52.

$$C_{in} = f_{inf} C_{out} + S \qquad \text{Equation 2.52}$$

2.10.6 Indoor source

The indoor source (S) can be calculated (Equation 2.53) from the intercept of linear regression of the outdoor concentration on the indoor concentration with the slope of the equation being the filtration factor (F_{inf}) (Hoek et al., 2008, Chen and Zhao, 2011) Dockery and Spengler (1981) developed an empirical model for respirable particulate sources within a residential building; the number of air changes per hour will affect dilution of a source. Therefore, as well as the potential indoor sources such as cooking, cleaning, movement of people, photocopying etc the flow rate of air must also be considered Equation 2.53.

$$\frac{\bar{S}}{q} = B_3(N_{cig}) + B_4(AN_{cig}) + B_5(A) + B_6 \qquad \text{Equation 2.53}$$

Where:

$B_{3\text{-}6}$ (B_3 = 0.88, B_4 = 1.23, B_5 = -2.39 and B_6= 15.02) are constants to be determined by multiple regressions of indoor concentrations on the outdoor concentrations and include home characteristics that could produce particulates.

N_{cig} = estimated number of cigarettes smoked per day

A = indoor variable for fully air conditioned buildings

The separate process also calculates B_1 which gives the proportion of respirable outdoor particles which penetrate indoors to be 70%. This is calculated via a further regression of the indoor concentration on the outdoor concentrations, with B_1 being the slope of the resulting equation. It found that if full air conditioning was used rather than natural ventilation the penetration of the building shell reduces to just 31%. It was also found that for every cigarette smoked in the house 0.88 µg m^{-3} of particulate is released. The study also found that although air conditioning reduces the penetration of outdoor particles it enhances the effects of smoking with an extra 1.23 µg m^{-3} rise in concentrations. Therefore, if air conditioning is turned on, a total rise of 2.11 µg m^{-3} per cigarette can occur. The constant B_6 which represents non air conditioned, non-smoking homes returned a source increase of 15.02 µg m^{-3} for other activities which would create particulates, such as cleaning or cooking. The miscellaneous source reduces unlike in the case of smoking if air conditioning is present to 2.39 µg m^{-3}; however the author noted that this parameter had a large standard error.

2.10.7 Room volume and area

The interior surface area (A) accounts for the surface area of all walls, as well as furniture and other items within the room. Shops for instance filled with stock would have a large interior surface area while large open offices with only desks would have a lower one. The ratio of the interior surface area to room volume (A/V) can be multiplied as in Equation 19 in order to get K_{dep}. For a room with volume of 14 m^2, the unfurnished interior surface area was 35 m^2, this increased to an interior surface area of 47 m^2 in when in a furnished state (Thatcher et al., 2002). Previous work done on A/V ratios found values of 2-4, 2 and 3.4 m^{-1} for two studies in the United States and a third in Demark respectively, while another American study in an office found a significantly lower ratio of 0.9 m^{-1} (Thatcher et al., 2002, Schneider et al., 2004, Sabersky et al., 1973). This value of A/V of 0.9 m^{-1} was also used as a model parameter by Dimitroulopoulou et al (2001) for an office and a classroom situation while a range of 0.33 to 0.5 m^{-1} was found for a residential building by Roed and Goddard (1990) . Hayes(1991) used a A/V of 1.8 m^{-1}. Here is was stated that with increasing room volume the ratio of A/V decreases as the interior wall surface area will not increase to the same extent (i.e. lower surface area to volume ratios with increasing room size) Finally, Drakou et al. (2000) used A/V ranging from 0.5 to 3 m^{-1}, using smaller ratios for larger buildings.

2.10.8 Filter efficiency

Filter efficiency (e) is considered for mechanically ventilated systems which have filters placed in the air ducts in order to reduce the concentration of pollutants entering the building. Similar to the penetration factor, the closer the filter efficiency is to 1 the less effective the filter is. Fadeyi et al. (2009) found filter efficiencies of 0.35, although with an increase of return air rate from 7 h^{-1} to 14 h^{-1} the efficiency increased significantly. There are several types of dry filters with different efficiency rates: Flat panel (0.20-0.35), Continuous roll (0.25), Bag filters (0.4-0.9), HEPA (High Efficiency Particulate Air) Filters (0.01), ULPA (Ultra Low Penetrating Air) Filters (0.01) (Engineering toolbox, 2012). A study carried out in the late 1980s found secondary, (i.e. return air) filtration rates for 0.75 for secondary filters in a HVAC system fine particles for office buildings in the Wisconsin, USA (Weschler and Shields, 1989). The filtration rate for larger coarse particles was much higher at 0.995 yet for primary filtration the study found little or no filtration occurred. Many studies use P, the penetration factor, instead of a separate filter efficiency although certain studies have calculated separate filter efficiencies (Hayes, 1991, Chaloulakou and Mavroidis, 2002). For gaseous pollutants specific filter

types can be utilised in order to achieve reductions, for instance activated carbon filters are known to reduce NO_2, volatile organic compounds and O_3 concentrations (Fadeyi et al., 2009, Sidheswaran et al., 2012, Gao et al., 2011).

Heavily laden particulate filters can have their surface area increased from 0.34 m^2 to over 600 m^2 due to particles caught in the filter which results in a large area for surface reactions to occur and which can therefore reduce NO_2 concentrations (Weschler, 2004).

2.10.9 Summary of modelling parameters

The following four tables summarise the literature review of some of the input parameters found for mass balance models. The input parameters summarised are; penetration factor, air exchange rate, decay rate, deposition velocity and infiltration factor.

Table 2.4 Summary of Penetration factors from literatures

Source	Thatcher and Layton, 1995	Cristy and Chester, 1981	Dockery and Spengler, 1981
P	0.2-0.6	1	0.7

Table 2.5 Summary of air exchange rates from literature (h^{-1})

Source		Drakou et al.,2000	Hayes, 1991	Dimitroulopoulou et al., 2008	Dockery and Spengler, 1981	Chaloulakou and Mavroidis, 2002	Fadeyi et al.,2009	AIVC, 1994
Natural air changes	Closed window	1		0.41		1		
	Partially open window	2				2.4		
	Open window	6.4	18.9	1.5		6.4		
Mech air changes	Energy efficient	0.2	0.2					
	Normal			1.5	1.5		1-2	
	Energy inefficient							
Return air changes	Energy efficient		9					9
	Energy inefficient		2.64					5

Table 2.6 Summary of decay rates and deposition velocity from literature

Source	Karlsson (1994)	Yamanaka., 1984	Drakou.,2000	Weschler et al.,1994
V_d (NO_2) ms^{-1}	1 - 0.004		0.0062	0.1
K (NO_2) h^{-1}		0.99		
	Fogh et al.,1997	Dockery and Spengler, (1981)	Allen et al., 2003	Wallace., 1996
V_d ($PM_{2.5}$) ms^{-1}	1.98			
K ($PM_{2.5}$) h^{-1}		0.5	0.16	0.22-0.66

Table 2.7 Summary of infiltration factors from literature

Source	Dimitroulopoulou et al., 2001	Ng et al., 2005	Abt et al.,2000	Hoek et al.,2008
Natural ventilation	1		0.12-0.5	0.4
Mechanical ventilation		0.2-0.7		

2.11 Conclusions

In urban areas, where traffic concentrations are high, there is a serious difficultly for local authorities to control the sources of NO_2 and $PM_{2.5}$. While mitigation measures can be conducted to provide sinks for these sources as outlined in Section 2.2 and ensure that the concentrations are kept under the legal limits discussed in Section 0, it is clear that pollution is a real issue in many cities worldwide.

There is a clear lack of research on the influence of outdoor pollutant concentrations on those inside buildings. The research that is conducted often focuses on residential properties. Much of the research that was found relating to commercial buildings was frequently conducted in the 1990's and required updating (Ekberg, 1996, Ekberg, 1995, Field et al., 1992, Phillips et al., 1993). Ireland stands out; review of previous work uncovered only one minor study on the air quality indoor/outdoor relationship. This study, monitored three days of data, looking at the indoor/outdoor relationship of PM_{10} but did not monitor NO_2, one of the pollutions of most concern for Ireland with respect to achieving legislative annual mean limits (European Commission Joint Reserach Centre, 2008). Those working in commercial buildings in Dublin urban city centre spend on average 40 hours per week in some the parts of the city where air quality is a real concern. It is necessary to gather information on the relationship between indoor and outdoor concentrations in order to learn which building techniques, locations and ventilation strategies provided the best reductions of outdoor concentrations.

A second gap in the knowledge base that is outstanding is the lack of a modelling technique designed for use by the average consumer rather than an air quality

professional. The current techniques demand a high level of detailed information that those working in office or shop buildings would not have access to. Therefore this research aims to set out a technique that uses freely available data and computer programmes coupled with easy to navigate techniques.

3. Monitoring sites and methodology

3.1 Introduction

It is estimated that the urban population spends up to 90% of their days indoors (Dimitroulopoulou et al., 2001). A large proportion of the time awake is spent in the workplace. Statistics show that 60% of the work force in Dublin city centre commute more than 5 km to work and as the city centre air monitoring sites in Dublin show higher air pollutant concentrations than surrounding areas, those working in the city centre may be exposed to higher ambient pollutants in the area they work in than their residence (EPA, 2011). Therefore, a review of the indoor pollution concentrations in urban workplaces is necessary as the only previous work found on this area for Dublin was compiled by the AIRMEX study in, which reviewed two work environments for $PM_{2.5}$ in the Dublin city centre, but no buildings with respect to NO_2 (European Commission Joint Research Centre, 2007).

This research aimed to study a representative selection of buildings to show typical working environments for those working in Dublin city centre. This chapter deals with the criteria for the choice of buildings and the monitoring methodology followed in order to collect samples accurately. The aim of this research was to use only widely available information, that is, information that staff working in a shop/office would have easy access to or could easily find by speaking to their building maintenance staff, in combination with air monitoring inside and outside the building. Many previous researchers have monitored sources, air flow rates, deposition, etc., in detail from residential buildings, but as this monitoring was conducted in commercial buildings many more constraints were imposed by the occupants of the buildings. The monitoring could not interfere with how business was conducted or the productivity of staff. As well as an agreement for access from building staff, the choice of buildings was constrained by those which had suitable outdoor monitoring locations, i.e. a footpath wide enough to place the air monitoring equipment and access to electricity overnight. This work aimed to study an equal number of mechanically ventilated and naturally ventilated buildings. Therefore, once several buildings had been monitored the choice of buildings shifted somewhat in order to ensure this was met. This was due to a large number of the initial buildings monitored being mechanically ventilated. Further detail on the choice of buildings is contained within Section 3.2.

3.2 Site characterization

People spend 40 plus hours a week in their place of work, yet little information available on the quality of air in Irish commercial buildings in urban areas. This study was undertaken in order to gain a greater understanding of the air quality in such places of work. The 2011 CSO statistics state that 227,429 people are at work in Dublin city centre and therefore affected by results of this research (CSO, 2011). Understanding what building characteristics influence the quality of indoor air can lead to better choices in future with respect to building design, urban planning and on a personal level choice of workplace.

10 sites were chosen for monitoring, five mechanically ventilated and five naturally ventilated. A brief summary of the ten sites are displayed in Table 3.1 Site summaries, opening hours of monitoring sites and

Site No.	Ventilation Type	Run 1	Run 2	Building age (years)	Building use	Opening hours	Glazing
1	Natural	Ground	Ground	>50	Shop	10 am-5 pm	Single
2	Mechanical	Ground	Roof	~ 45	Office	8 am-6 pm	Single
3	Mechanical	Roof	Ground	~ 5	Office	8 am-6 pm	Double
4	Mechanical	Ground	Roof/Ground	~ 5	Shop	8 am-8 pm	Double
5	Mechanical	Roof	N/A	~5	Office	8.30 am–5pm	Double
6	Natural	Ground	Ground	~180 (refurbished)	Office	10am-6pm	Single
7	Natural	Ground	N/A	~1900 (refurbished 1990)	Shop	8am-5pm	Single
8	Natural	Ground	N/A	>25	Shop	8 am-7 pm	Single
9	Natural	Roof	Ground	~44	Office	9 am-6 pm	Single
10	Mechanical	Ground	Roof	~40 (refurbished 2001)	Office	9 am-6 pm	Double

Table 3.2 Dates of monitoring and the building locations in Figure 3.1. The sites include a sports centre, a college canteen, two shops, several office buildings and an exhibition space within a building, all of which are located along busy street canyons in the city centre of Dublin. The sites were selected to monitor a diverse group of natural and mechanically ventilated buildings across a range of ages. Two monitoring runs were carried out at some sites while only one was deemed necessary at others. In general if a site had a mechanical ventilation system two runs were carried out in order to monitor the major entry points of outdoor pollutants at ground level and roof level air intake i.e.

through the front door and through the ventilation system. Two runs were also carried out at the naturally ventilated sites 1, 6 and 9 due to a variety of reasons. At site 1 no overnight data was collected during run 1 due to concerns regarding the safety of the equipment but after reviewing data it was decided that overnight data was necessary to understand the full behaviour of pollutants. For this reason monitoring was repeated at site 1. Monitoring was repeated at site 6 due to unusual NO_2 concentrations, which confirmed the patterns from run 1. Re-monitoring of a site was not always possible but on this occasion and with site 1 the building staff agreed to a second run of monitoring. At site 9 roof level monitoring took place as a result of an access agreement with member of staff in this building who was developing a NO_2 monitoring technique that required roof level data to calibrate his own results. Therefore, it was agreed to monitor here in exchange for access to the indoor and ground level site.

The criteria for choosing sites were based on collecting data from a wide range of parameters which are discussed in the following paragraphs. The outdoor monitoring equipment for collecting ground level air pollution data was housed in a purpose built container and needed to be placed at the door of the building and secured. This required some form of railing or similar to secure the storage container via a lock and chain. It was vital that the monitoring equipment not block the footpath to pedestrians as this would make securing a permit from the Dublin City Council for its placement difficult. At the beginning of this research it was decided to monitor commercial buildings located on canyon style streets. This meant buildings located along the River Liffey Quays' or bordering city parks were ruled out and specific areas of the city which best fitted the "street canyon style" were concentrated on for potential sites. The street canyon is a very common location for commercial buildings in Dublin and therefore was chosen to represent the greatest number of buildings possible. Street canyons create a natural vortex causing pollutants to recirculate, affecting how concentrations of pollutants behave within the canyon. While this is important information and can be studied in detail by the use of modelling packages such as '*fluent*' the aim of this particular study was to gather information which can be applied to a variety of buildings rather than only those for which the study has specifically modelled. Instead of focusing on the pollutant behaviours outdoors this work reviews the impact on indoor concentrations of $PM_{2.5}$ and NO_2 and how this changed from the concentrations at the main entry points of pollutants for the building. Furthermore, the research questions if it is possible to predict accurately indoor concentrations using only outdoor data at these locations.

The outdoor monitoring equipment required continuous power supply in order to run, which became another logistical factor in the choice of buildings. Several potential monitoring sites were ruled out as no overnight power could be supplied. The outdoor power was supplied by running an extension cord from indoors via a post-box, poorly sealed door, large key hole or ventilation opening. These features became a necessary aspect of the buildings of choice when initial surveys of possible sites were carried out. Due to the cost of the equipment, sites close to nightclubs or late bars were also ruled out as it was feared that unintentional or intentional harm could come to the monitors. Once a potential building was decided upon, permission for monitoring inside and outside of the building was requested from the occupier. Consent was withheld in some cases due to a number of reasons; noise levels, health and safety fears due to the monitors constituting a trip hazard, disturbance to work, security concerns and other unknown reasons. If permission to monitor was granted, a suitable monitoring schedule was drawn up and agreed upon with the occupants of the building.

Table 3.1 Site summary.

Site No.	Ventilation Type	Run 1	Run 2	Building age (years)	Building use	Opening hours	Glazing
1	Natural	Ground	Ground	>50	Shop	10 am-5 pm	Single
2	Mechanical	Ground	Roof	~ 45	Office	8 am-6 pm	Single
3	Mechanical	Roof	Ground	~ 5	Office	8 am-6 pm	Double
4	Mechanical	Ground	Roof/Ground	~ 5	Shop	8 am-8 pm	Double
5	Mechanical	Roof	N/A	~5	Office	8.30 am–5pm	Double
6	Natural	Ground	Ground	~180 (refurbished)	Office	10am-6pm	Single
7	Natural	Ground	N/A	~1900 (refurbished 1990)	Shop	8am-5pm	Single
8	Natural	Ground	N/A	>25	Shop	8 am-7 pm	Single
9	Natural	Roof	Ground	~44	Office	9 am-6 pm	Single
10	Mechanical	Ground	Roof	~40 (refurbished 2001)	Office	9 am-6 pm	Double

Table 3.2 Monitoring dates at sites and Irish grid coordinates of sites

Site No.	Run 1	Run 2	Irish grid coordinates
1	24-16 April 2010	26 – 29 July 2010	315356,233323
2	2 – 4 June 2010	15 – 17 June 2010	316006,233889
3	6 – 9 July 2010	12 – 15 July 2010	316547,234071
4	13 – 16 December 2010	27 – 31 March 2011	316493,234092
5	24 – 26 January 2011	----------	317834,233800
6	26 – 29 April 2011	27 June – 1 July 2011	316292,234156
7	3 – 6 May 2011	----------	316295,234187
8	11 – 15 July 2011	----------	316585,234103
9	18 – 22 July 2011	2 – 5 August 2011	315356,233323
10	16 – 20 January 2012	23 – 26 January 2012	316175,234220

Figure 3.1 Site locations with insert map of Dublin

3.2.1 Site 1

Site 1 is a naturally ventilated computer repair shop located on the ground floor of a four storey building. The floors above are not connected to the shop and are accessed for private use through a separate door. It has opening hours of 10am – 5pm and its front door is generally left closed although at certain times customers did leave it open. It has a normal swing door and no operable windows. The room volume was measured manually with a tape measure and found to be 105.28 m^3 (3.09 m (height) * 8.99 m (length) 3.79m (width)) with stock on shelves, a small seating area for consultation with customers and an area for computer repair behind the counter. The indoor monitors were located in the middle of the shop floor, between the customer area and cash tills behind which staff were located while not talking to customers. Tubing was extended from the monitors in order to collect data from the breathing zone of staff while the sat discussing issues with customers. The site is located on a busy road with high volumes of traffic during the day as well as taxis at night. Figure 3.2 shows the ground floor shop where Site 1 was located with the monitoring container outside. No direct indoor sources were reported on questioning staff in the building and heating was not provided by gas.

Figure 3.2 Site 1 with monitoring container outside

3.2.2 Site 2

Site 2 is a four storey mechanically ventilated building which is used as a private third level college. Monitoring was carried out in the canteen area on the 2nd floor, which has a room volume of 355 m^3 with 14 windows, each with a perimeter of 4.4 m. Consultation with the building services manager showed that windows were generally kept shut but they appeared to be poorly sealed, the building being fairly old, allowing infiltration of air into the room. The room stretched from the street side of the building right across the width of it to the back, where the monitors were placed. The canteen used a gas cooker to prepare food so an indoor source was present at peak dining times. The cooker was in an adjoining kitchen area which was separated by a ceiling height barrier wall with an opening for access to the kitchen. During the time of monitoring students were mainly on summer vacation so source concentrations may have been lower than normal. The ventilation system dates back from 1969 with the addition of a coolant system in the 2006. Solid inline panel filters are used in this unit which takes its air intake from the back of the building away.

Figure 3.3 Site 2 indoor monitoring

3.2.3 Site 3

Site 3 is a sports complex built in 2006 that utilises mechanical ventilation and is pictured in Figure 3.4. Site 4 can also be seen in this image as it was constructed as an adjoining project to site 3. The ventilation system uses both panel and bag filters on the supply air (which should achieve 95% particle removal according to the building

services manager on site) with panel filters only on the return air; these filters are changed every 3 months. The monitoring was located in one of the individual staff offices on the 2nd floor of the building with the monitors being placed upon a temporally unused desk. This gave a clear and reprehensive example of the breathing zone for a staff member working in such a space. These offices have a dedicated air handling unit which is controlled for the needs of office staff rather than members of the gym. The ventilation rates are controlled by the set point temperatures for inside which are controlled by the building services manager on site via the building management system (BMS). The office has a volume of 65 m^3 (2.92 m (height) * 4.92 m (length) 4.54 m (width)) with one wall made entirely of glass. Office hours are 9am to 5pm with the ventilation active from 7am to 7pm. The building is located on the intersection of two busy roads but also has a train line running along a 3rd side roughly at the 2nd floor height. A train line runs along the back of the building, (roughly 5 m away) with a height in line with the 1st storey of the building.

Figure 3.4 Site 3 and 4 building images

3.2.4 Site 4

This building is located directly beside Site 3 and was built with the same ventilation system specification, see Figure 3.4. The main use of this 4 storey building is as a

scientific gallery space but office space, lecture theatres and a cafe are also present. The ventilation system runs from 8 am to 8 pm and the air monitors were located on the ground floor near the road. The building contains a large glass facade as seen in Figure 3.6 and a ground floor volume of 742 m^3. It should be noted that the same train line from site 3 runs along the length of the back of this building at a height in line with the 1st story of the building above ground, although in this case the supply air is drawn from the front side of the building which runs along a very busy road. The indoor monitors were located on the open plan ground floor, close to a desk which was used by staff working at exhibition in the gallery. This desk was located out of the direct line of air flow through the front door.

3.2.5 Site 5

Site 5, see Figure 3.5, is the site monitored at greatest distance from the city centre, roughly 2 km from Grafton St. It is a newly built office space with high environmental and energy efficiency, therefore the ventilation unit was run only for occupied hours and high efficiency filters were installed. Due to restrictions, outdoor monitoring could only take place at the supply air inlet which is located on the roof of the five storey building and not at ground level. The indoor monitoring took place at the back of the building on the 1st floor in a small office space. This office had approximately five people working in it during the time of monitoring; samples were taken to be representative of the breathing zone of these staff.

Figure 3.5 Site 5

The building faces a reasonably busy road in a semi-residential area of the city. The ventilation units in the offices run from 8.30 am to 5 pm with other units supplying air to separate parts of the building running from 7 am to 7 pm. This office again had no set air flow through the ventilation unit and was run to a set point temperature similar to all other mechanically ventilated sites. The building's heating is provided by 2 gas boilers but all on site cooking (i.e. in staff canteen, which mainly consists of heating soups) is carried out by electrical units.

3.2.6 Site 6

Site 6 is located approximately 250 m from Sites 3 and 4 along the same busy road. It is a naturally ventilated 3 storey office building dating back to circa 1910. The monitored office is located on the ground floor as seen in Figure 3.6 with the monitored office seen between the two trees. The volume of the room is 160 m^3 (4.08 m (height) * 9.72 m (length) 4.05 (width)) with large inoperable windows (4.11 m (width) * 2.79 m (height)) overlooking the street. The staff in the office worked hours which were flexible but usually between 10am to 6pm. The monitors were located in the middle of the room on a disused desk.

Figure 3.6 Site 6 outdoor view

3.2.7 Site 7

Site 7 is a naturally ventilated cooking utensil shop located directly across the road from Site 6. It is a long shop with a door at the front along the street (see Figure 3.7) and a second opening to a small yard at the back of the shop which is used as a smoking area by one of the staff during break times. Monitoring took place close to the rear of the shop next to the cash register where staff spent a large amount of their working day. The shop is open from 8am to 5pm and the door to the street is left closed apart from when customers enter/exit through it. The volume of the shop is 375 m^3 (3.3 m (height) * 21 m (length) 5.42 m (width)). No gas heating is present within the site.

Figure 3.7 Site 7 outdoors

3.2.8 Site 8

This site is a naturally ventilated shop located at the opposite side of the junction to Site 3, as shown in Figure 3.8. The monitoring was carried out on the upper floor in the office area of the shop which had a volume of 51 m^3 (2.05 m (height) * 4.9 m (length) 5.15 m (width)). The shop's main use is as a pharmacy with the office space upstairs connected via a small staircase and used by staff members only. No door was in place between the downstairs and upstairs of the shop. Monitoring took place, in the breathing zone, next to a desk, used by a member of staff completing work in the office area throughout the monitoring. The shop opened from 8am to 7pm and natural ventilation was provided via the door and a small air vent in the facade of the building.

The building's heating was provided by a gas heating system and no cooking facilities were present in the building.

Figure 3.8 Site 8 outdoors

3.2.9 Site 9

Site 9 is a naturally ventilated college building that was built circa 1968. The building is six storeys high with monitoring located on fifth floor to the road front side of the building, see purple 'x' in Figure 3.9 which is located above the window location. The yellow 'x' represents the location of the roof monitoring unit while the green 'x' is directly above the front door at which ground level monitoring took place. The monitoring area was an office for staff member with a volume of 34.3 m^3 (2.97 m (height) * 3.66 m (length) 3.16 m (width)). The monitors were placed along the wall of the office, on the corner desk used by a staff member in order to give a sample of the air in the breathing zone of this individual. The office has an elevator service area beside the office attached via a door. Monitoring took place with the room window open for one week and closed for the second week in order to compare the two. Office hours were flexible from the usual 9am to 5pm, as the staff member using the office was working in engineering laboratories located in another section of the building during the time of monitoring. The building's main door, which faced onto a busy road, was located a considerable distance from the office and separated by several fire doors.

Figure 3.9 Site 9 roof top view

3.2.10 Site 10

Site 10 is located on the same busy junction at the end of the road at which Sites 3, 4 and 7 are located. It is a large 1970's office space which underwent major upgrading including a new ventilation system and facade in 2001. The ventilation system has both bag and panel filters and is in use continuously and replaced on a regular basis. Monitoring took place in a canteen area of the offices although no cooking facilities were placed here, except for a microwave and kettle. The canteen was located on the top floor of this five storey building, this was a large open plan room with monitors placed to the side of the room but sampling from the breathing zone. Ventilation was provided to the room by ceiling level vents. The air intake was located in the middle of a large area roof, however two sides of the building are surrounded by busy roads. The room has a volume of 310 m^3. The canteen was mainly in use for break times but was also used for tea/coffee sessions after large meetings. Ground level monitoring took place directly outside the building entrance as shown in Figure 3.10.

Figure 3.10 Site 10 ground level monitoring

3.3 Monitoring programme

For the naturally ventilated sites, outdoor data was gathered as close to the main door as logistics would allow i.e. electricity supply, security and not blocking the path to pedestrians. For all sites (except Sites three and four) it was possible to place the monitors directly outside the door to each building. For Sites 3 and 4 the monitors were placed a short distance away as no electrical supply would be facilitated directly outside the doors. For mechanically ventilated buildings two trials or runs were carried out to gather outdoor data at both roof and street levels while taking concurrent indoor concentrations. All ventilation supply air intakes were located at roof level. Some intakes were located to the back of the building furthest away from busy roads while others were located directly above the roads. In all roof level outdoor monitoring runs it was possible to place the monitors directly at the ventilation intake therefore getting an accurate reading of the concentrations of $PM_{2.5}$ and NO_2.

For each run, variations in pollutant concentrations were continuously monitored over 3 to 4 day durations. Wind speed/direction, temperature and humidity data were measured indoors and outdoors at each site, with additional weather data provided by *Met Eireann* at monitoring locations in Phoenix Park (310000,236100) and Dublin Airport (316900,243400), located roughly 3 and 10 km from the city centre monitoring locations respectively as shown in Figure 3.11. As with previously these coordinates are Irish grid system.

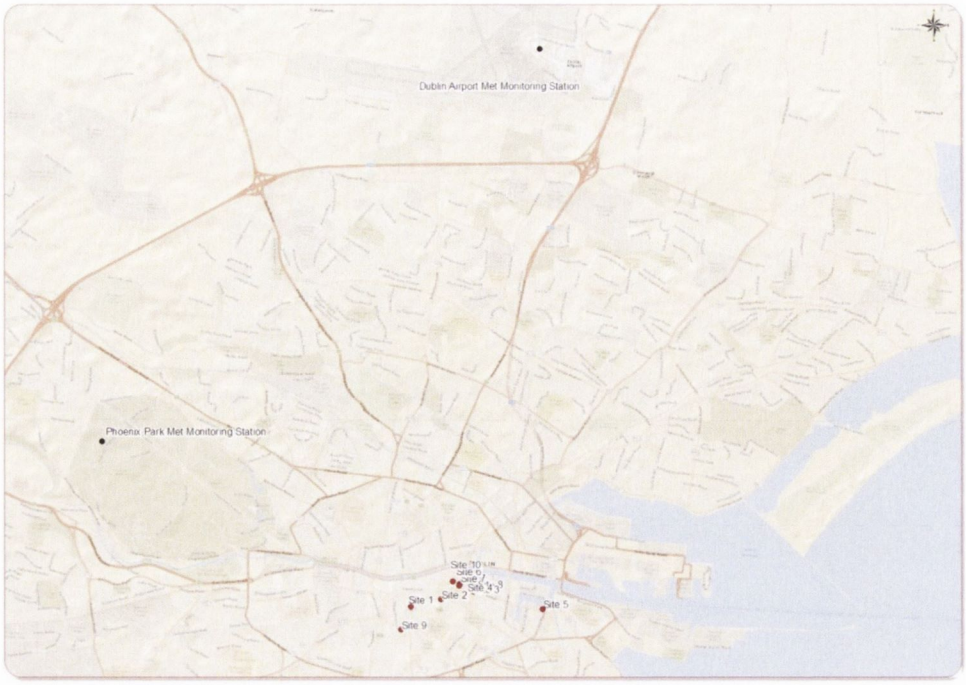

Figure 3.11 Met Eireann monitoring locations

Information such as the prevalence of open windows/doors or if a mechanical ventilation system was in use was noted for future reference. Once a site was chosen a timetable for monitoring was arranged. This was necessary as a permit needed to be requested in advance from Dublin City Council. This permit stated the date, hours and location of monitoring and must be available at all times for inspection during the monitoring process. The permit also required notification of local Gardai. Weather conditions were also a factor, for example if heavy periods of rain were forecast monitoring these weeks was avoided in order not to damage the outdoor monitors. However, sometimes due to time constraints set down by the occupants of the building this did not always occur.

3.4 Description of monitoring equipment

Two sets of monitoring equipment were used for this study, one to measure $PM_{2.5}$ and the second to measure NO_x. The two pollutants, one particulate ($PM_{2.5}$) and one gaseous (NO_2) were chosen as these two air pollutants are of most concern to Dublin City, as stated in the 2008-2012 Dublin Regional Air Quality Management Plan. The outdoor monitoring equipment was housed in a specially fabricated steel container (see

Figure 3.12) which had two compartments; one to store the NO_x analyser (Teledyne, M200E) and the second for the PM monitor and external pump for the NO_x analyser.

Figure 3.12 Box containing outdoor monitoring equipment

The function of the container was to protect the monitors from adverse weather conditions and to provide security for the monitors. Temperature was regulated to close to ambient conditions within the container by the installation of ventilation holes on the side of the container to allow the dissipation of the heat generated by equipment when running continuously. The container was repainted silver from the original black colour to reflect the sun and reduce heat generation inside the container further. For the $PM_{2.5}$ monitor (Environmental Devices Corporation, EPAM-5000, Haz-Dust) known as a *Haz-Dust* it was important to ensure that the tubing extended vertically for the $PM_{2.5}$ monitor. This prevented particulate matter being obstructed by twists in the tubing and not reaching the impactor; for this reason sampling was carried out by extending tubing out of the containers via a small hole on the lid of the container rather than the side. Indoor and Outdoor monitoring was carried out at a height between 1-1.5 m but the tubing was kept to the minimum length needed to prevent particles catching in the tubing as specified in the equipment technical manual. The supply tubing attached to the NO_x monitor had to be kept well below a maximum length of 3 m (as per manufacturer's instructions). To prevent the ingression of water, plastic sheeting was placed between the tubing and the circumference of the hole. Indoor monitors were placed in a location that would be representative of someone working in a given site (for example, on a desk in an office).

On the day that a monitoring run was due to begin, the equipment was transported from the Environmental Engineering laboratory in Trinity College to the site as early as possible in the morning. Often an agreed indoor location had been selected prior to this day but in the instances where one had not been chosen, a discussion of the most suitable location was had with the building occupiers. The noise of the pumps attached to the NO_x monitor was a concern expressed in several of the sites especially the office based ones, and so for this reason an office which normally had high noise levels was often chosen. For the shops noise was less of a concern and the main concern emphasised by the occupiers shifted to trip hazards of customers. The monitoring locations needed to be representative of someone working within the building and the monitors needed to be in a safe area where they could remain for the entire monitoring run, as well as not being close to any direct source of air pollution. Obviously, if a monitor was located next to a direct source this could cause disproportionately high concentrations compared to the rest of the building. Due to the size and weight of the NO_x monitor, placing it at floor level and extending tubing was the safest option, as shown in Figure 3.13. The Haz-Dust is much lighter and smaller and therefore could be raised higher by the use of a box or stool in order to minimise the length of inlet tubing (and therefore sampling errors). This allowed concentrations to be measured at a suitable height (1-1.5 m) without long lengths of tubing being used. An effort was made to communicate with any staff that would come in contact with the monitors the nature of the work being carried out. As well as informing the staff to the health benefits of good indoor air quality, it also provided an opportunity to ask them not to interfere with the equipment and if they saw a problem with the equipment e.g. tubing fell or a warning light came on, to contact the number provided.

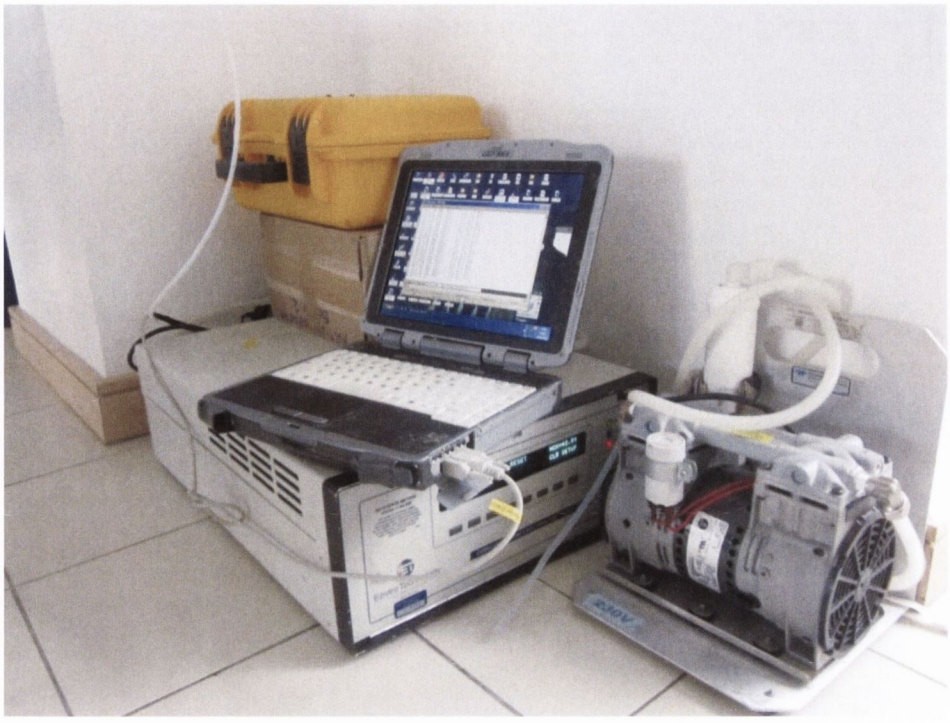

Figure 3.13 Haz Dust and NOx monitors indoors downloading to computer

3.4.1 NO_x monitoring equipment

The two NO_x monitors used to collect data were both made by Teledyne, but were two different models: M200E used for outdoor monitoring and M200EU used for indoor monitoring. The two monitors have slightly different specifications but both measured NO and NO_2 as described below. Both monitors had low noise levels for interference in readings of less than 0.2 ppb. Both monitors work on the principle of Chemiluminescence but the indoor monitor had a marginally lower limit of detection. Chemiluminescence occurs when NO is exposed to O_3 creating NO_2, some of which is in an excited state due to excess energy created in the reaction, and O_2. The laws of thermodynamics mean that NO_2 will return to its most stable state by releasing a quantum of light (*hv*) with wavelengths between 600 and 3000 nm, peaking at 1200 nm. The relationship between the light released and concentration of NO_2 is linear and reliable under the normal operating conditions of the monitors. Some NO_2 will have lost the excess energy via collisions in the reaction cell, which is called third body quenching. As this increases with higher pressures in the reaction cell the cell is kept at reduced pressure as it is an undesirable event. To measure the non-light emitting NO_2, molybdenum is heated to 315 ^{o}C, at which point it reacts with NO_2 to produce NO and a secondary form of molybdenum. This NO can be measured via chemiluminescense. The analyser switches modes every 6-10 seconds in order to measure both NO and

NO_2. NO_x concentrations are then calculated by the addition of NO and NO_2 concentrations.

3.4.2 Particulate matter monitoring equipment

Two identical Haz-Dust monitors (Environmental Devices Corporation, EPAM-5000, Haz-Dust) were used for indoor and outdoor measurement of $PM_{2.5}$. Particulate matter can be determined using two methods within the Haz-Dust, a gravimetric technique and a light scattering nephelometer technique which has a precision of± 3 µg m^{-3}. Several size fractions can be measured using the Haz-Dust by changing the impactor size; these include PM_1, $PM_{2.5}$ and PM_{10}. For this research a 2.5 µm impactor was used to prevent particulate matter with aerodynamic diameters greater than 2.5 µm from being counted via light scattering techniques. As stated in Chapter 2 $PM_{2.5}$ was chosen to monitor as due to its smaller size, it reaches deeper into the lungs and has a longer residence time. $PM_{2.5}$ is also a strong indicator of anthropogenic (man-made) emissions.

The light scattering method works on the principle of near-forward light scattering of an infra-red radiation in order to measure the concentration of particles in a certain size range. When particles come in contact with light from the infrared source they cause the light to scatter. The scattered light is then sensed by a photo detector and is proportional to the concentration of the $PM_{2.5}$ present.

The EU reference method (EN 12341) for measurement of particulate matter is by the traditional gravimetric sampling technique which is the other option available when using the HazDust. This draws air through an impactor which allows a certain size range of particulates to pass with larger size fractions prevented from passing as their streamline angles do not allow them to pass over the impaction plate. Once the particles pass through the impactor the air is then drawn through a filter which retains the particles. These filters are conditioned to a particular humidity pre weighing on a microbalance; this process will be discussed in more detail in Section 3.5.2. Once the sample is collected and reconditioned the increase of mass on the filter can be calculated and converted into a concentration.

This method provides a representative sample of the particulates in the chosen size range for the sampled environment averaged over a chosen time period such as 8, 12 or 24 hours. However, the method does not allow short term variations in air quality to be monitored. For this reason it is an unsuitable method for sampling during this research. It should be noted that both methods of measurement were used for trials at

the first two sites but due to extremely poor results (i.e. mass lost on filters compared to pre monitoring filter weight) use of the gravimetric method was ceased. The use of an optical method such as a light scattering nephelometer measures the particulate concentration without disturbing the particulate in real time. The disadvantage of this method is that readings are distorted by relative humidity, but due to its ability to provide short temporal resolution it was the chosen method for this work. Without this resolution it would not have been possible to view the dynamics between the indoor and outdoor concentrations to the levels required. To account for distortion of the particulate concentration due to humidity, calibrations were carried out for varying weather conditions to ensure the light scattering method aligns with the gravimetric method (as discussed in the following section).

3.5 Quality control and quality assurance

In order to ensure the accuracy of measurements taken by the two sets of monitors used for monitoring in parallel, certain quality control procedures were put in place that were carried out before every monitoring run, and another set of procedures carried out during the monitoring run. These procedures ensured no element was overlooked resulting in untrustworthy data. In Sections 3.5.1 and 3.5.2 the quality control procedures are set out and explained for NO_2 and $PM_{2.5}$ respectively. In addition to these, the equipment was checked several times a day during monitoring runs in case of faults occurring for reasons such as the power supply being cut, temperatures exceeding recommended operating conditions or air supply tubes being tampered with.

3.5.1 Quality control of NO_2 measurements

In the days prior to a monitoring trial both NO_x monitors were run side by side in the Environmental Engineering Laboratory at Trinity College, with their inlet tubing connected via a t piece ensure both monitors sampled the same air during this calibration period. After the monitors were run for several hours they were connected to a zero air scrubber. This removes all NO and NO_2 from the air and gives the monitors a baseline value from which they can calculate concentrations. The readings taken by the monitors stabilised after 5-10 minutes, and stability was checked via the stability output reading (*'TST' – 'NOx STAB')* on the user interface of the monitor. If this value is equal to or below 0.2 it could be concluded that the air entering the monitor is at a constant value. If the monitors indicated a non-zero (0 ±2 ppb) value after the monitor has stabilised it was necessary to zero calibrate the monitors using the zero air scrubber. This was done by simply pressing *'ZERO' – 'ENTR'* and then *'EXIT'* on the user interface (see Figure 3.14) while the scrubber was connected.

Once completed further spot checks were carried out to check for variance between the concentrations measured by the two monitors. If a difference was shown, a further calibration was done using compressed gas 450 ppb nitric oxide in nitrogen, provided by *Air Liquide*. The procedure was similar to the zero calibration; the gas was connected to the intake of the monitor and allowed to stabilise as described above. If this did not read 400 ppb ± 0.5 % NO the monitors were calibrated using the following commands on the user interface; *'TST' – 'NOx STAB' – 'SPAN'*, then *'ENTR'* and *'EXIT'*. Once calibrated, the monitors continued to run with spot checks carried out. On all occasions prior to monitoring, this procedure meant that both monitors were reading the same concentrations within a 1 ppb tolerance.

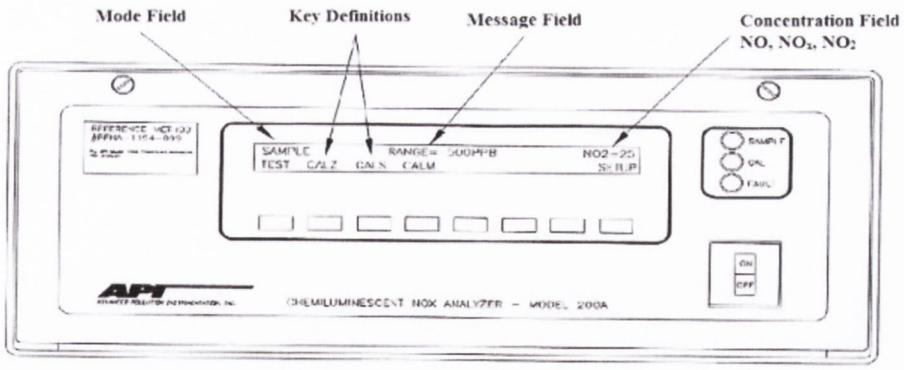

Figure 3.14 User interface of NOx monitor

Table 3.3 Test specification for NO_x monitor

Parameter	Units	Nominal Range	Parameter	Units	Nominal Range
Time	hh.mm.ss	-	Rcell Temp	°C	50 ± 1
Calz Range	ppb	50 - 20,000	Box Temp	°C	0-48
NOx Stab	ppb	< 0.2	PMT Temp	°C	7 ± 1
Sample Flow	cc/m	500 ± 50	IZS Temp	°C	50 ± 0.4
Ozone Flow	cc/m	60 - 90	Moly Temp	°C	315 ± 5
PMT	mV	0 - 5000	Rcell Temp	In-Hg-A	50 ± 1
Norm PMT	mV	0 - 5000	Samp	In-Hg-A	25 - 30
Azero	hvps	-170	NOx Slope	-	1.0 ± 0.3
HVPS	v	450 - 900	NOx Offset	mV	0.0 ± 150
DCPS	mV	2500 ± 200	NO Slope	-	1.0 ± 0.3
Rcell Temp	°c	50 ± 1	NO Offset	mV	0.0 ± 150
Box Temp	°c	Aug-48			

The NO_x monitor contains a filter which requires changing every 2 to 3 weeks in heavily trafficked areas or prior to every calibration. The filters were changed by lowering the front panel of the monitor and unscrewing the filter casing in order to remove the old filter. This was replaced with a new 47 mm 5 µm filter, with the fibrous side of the filter facing outwards.

The monitors were also serviced by the manufacturing company on an annual basis and more frequently if interface data suggested it was required i.e. if the NO_x or NO SLOPE was outside the tolerance of 1.0 ± 0.3, by the flashing of a red warning light. In this circumstance the local company representative was contacted and a service was arranged if the issue could not be resolved remotely.

At the beginning of each monitoring trial, the first 30 minutes of data collected at each site was excluded to allow the ozone generator within the analyser to power up. The NO_x data was automatically averaged over 15 minute and 1 hour intervals.

3.5.2 Quality control of $PM_{2.5}$ measurements

Prior to each monitoring run the Haz-Dusts were manually zeroed using a zero air attachment as shown in Figure 3.15. This is carried out by simply attaching a zero filter to the top of the impactor sleeve, entering the particle size chosen to monitor and time step to monitor it in and then the '*Manual-Zero*' option in the extended options menu. This manual zeroing takes 100 seconds and creates a baseline for the Haz-Dust to check itself automatically every 30 minutes to reduce any drift.

Figure 3.15 Zero air attachment

Prior to carrying out the zero air calibration compressed air was used to remove particles of dust which deposit on the impactor, impactor tube or near the optical sensor. After dust has been removed, the optical sensor is cleaned using foam tipped buds and a cleaning solution as in Figure 3.16.

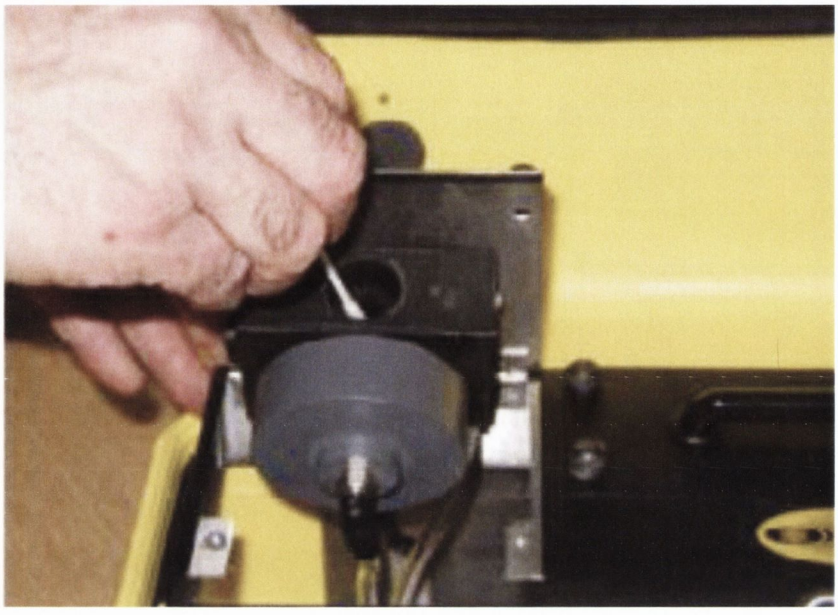

Figure 3.16 Cleaning of the optical sensor

The solution on the foam tipped buds was also used to remove any residual particles deposited on the monitors sensing equipment. The flow rates of the monitors were checked regularly against the target flow rate of 4 litres/minute. Again, this was carried out by attaching an airflow adaptor to the impactor sleeve. Choosing the '*check battery status*' option allowed the flow rate to be checked, although the battery had to be fully charged during this check. If this rate was not achieved then the pump could be adjusted easily to reach the desired rate.

As with the NO_x monitors the first 30 minutes of each data set from the beginning of each monitoring trial was discarded in order to allow the monitors settle and any particles in the tubing to be pulled though the system. Once a year the particulate monitors were returned to their manufacturers for full calibration and servicing of the components such as the pump. During the monitoring trials readings were taken every second and recorded as one minute averages. Table 3.4 contains the specification of the Haz-Dust monitor.

Table 3.4 Haz-Dust specification

Calibration	Gravimetric reference NIST traceable - SAE fine test dust
Accuracy	± 10% to filter gravimetric SAE fine test dust
Sensing range	.001-20.0 mg/m³ or .01 - 200.0 mg/m³ (optional)
Particulate size range	.01 - 100 µm
Precision	± .003 mg/m³ (3 µg/m³)
Sampling flow rate	1.0 - 5.0 litres/minute
Filter cassette	47mm FRM style
Digital output	RS-232
Operation temperature	-10°C to 50°C

The procedure for calculating the particulate concentration using the gravimetric technique was open to error, therefore quality control had to be tightly adhered to. Firstly filters were placed in a desiccator, a sealed container or cabinet containing desiccant material which is used for preserving moisture sensitive items, in order to control the effect of humidity on the filters. The filters were left there for at least 24 hours before pre-weighting them using the microbalance. Electrostatic charge was then removed from the filters by the use of a radioactive ionizing unit stored in the micro balance chamber (*Thermo, Cahn C-33 micro balance*). Storing the ionizing unit (S*taticmaster* 3c500) in the chamber also reduces electrostatic on the balance pan. The balance is left on continuously as recommended by manufacturers to increase stability and precision. Transferring of the filters from the desiccators to the microbalance was carried out by a stainless steel tweezers so as not to contaminate the filter. Again, the electrostatic charge on the filter was decreased by the use of stainless steel rather than plastic tweezers. Both sides of the filter were gently placed near the ionizing unit before being placed onto the microbalance pan and the chamber door shut. Once positioned on the pan, the microbalance was allowed to settle for three minutes before a stabilised reading was noted. The procedure was repeated three times and required all three readings to be within 0.005 mg. Once weighed the filter was placed in the cassette contained within the Haz-Dust for the monitoring period which had to begin immediately. Once monitoring was complete the filter was carefully removed and placed onto a particulate free Petri dish in the desiccator for 24 hours before the post sampling weight could be measured.

While weighting the filter atmospheric pressure, relative humidity and temperature in the room were recorded for use in calculation of the filter weight change (Equation 3.2) pre and post sampling. The air buoyancy correction (Equation 3.1) could then be applied which accounts for the effect of these conditions on the filter as measured mass changes are so small (with the resulting high sensitivity to particulate concentrations being measured).

$$\text{Filter volume} * (\text{Pa}_2 - \text{Pa}_1) * 10^9 \quad = \text{Air bouyancy correction} \qquad \text{Equation 3.1}$$

$$3.484 * \text{pressure} - \left(\frac{(0.00252 * \text{temp} - 0.02058) * \text{RH}}{273.2 + \text{temp}}\right) = \rho a \qquad \text{Equation 3.2}$$

The buoyancy correction was added to the weight change of the filter in order to find the adjusted weight. The weight change of the field blank was then accounted for by adding this to the adjusted filter weight. The volume of air which passed though the filter was calculated by multiplying the flow rate and sample duration and dividing by 1000. Once this had been calculated, the adjusted filter weight was divided by volume of air passed through it in order to calculate the concentration of PM retained by the filter.

3.5.3 Relative humidity correction

Relative humidity affects the measurement of particulate matter by light scattering measurement due to the increase in mass of the particle from condensing humidity (Jamriska et al., 2008, Kittelson et al., 2004, Kim et al., 2002, Both et al., 2011). A correction factor (CF) for outdoor $PM_{2.5}$ as seen in Equation 3.3;

$$CF = 1 + 0.25\frac{RH^2}{(1 - RH)} \qquad \text{Equation 3.3}$$

may be applied on an hourly basis in order to counteract the increase in average particle size associated with condensational growth of the particulates (where RH is the relative humidity) (Ramachandran et al., 2003). The correction has been applied in several countries such as India (Bangalore), the USA (Los Angeles/Minneapolis) and southern Italy with success. This correction is only necessary when the relative humidity is above 60% when using light scattering measurement devices; below this value little or no effect is seen on the particles. Unfortunately, Ireland regularly experiences relative humidity above this level. For example, the average annual relative humidity at 3 pm in Dublin measured over a 29 year period is 72 %. Relative humidity measured in the middle of the night in Dublin regularly reaches above 90 %. The above correction factor is non-systematically distorted for relative humidity below 95 % (see Figure 3.17).

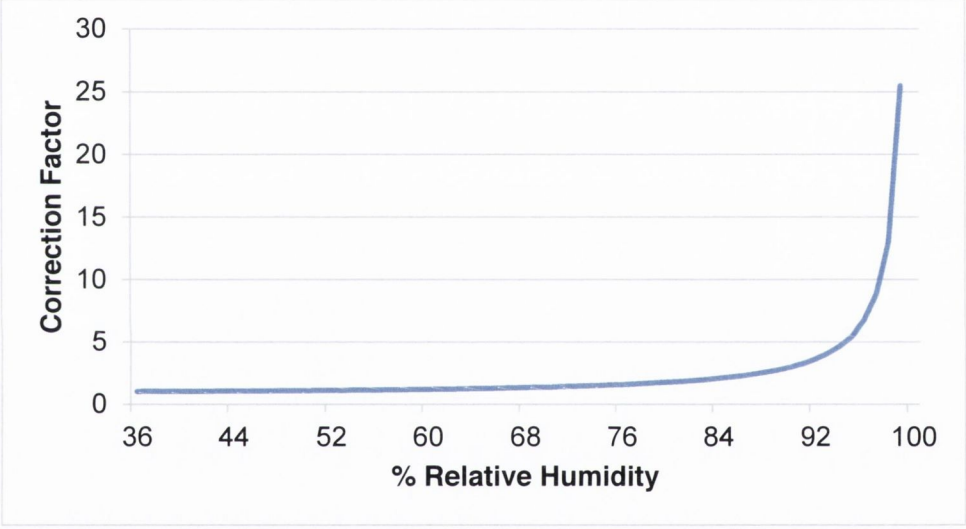

Figure 3.17 Relative humidity correction curve from application of Ramachandran et al. (2003)

On a number of occasions continuous logging of relative humidity was carried out at the sites. Unfortunately, this was not possible at all sites due to security of relative humidity data collector. Meteorological data, including relative humidity, was collected from several local sources including weather station data from other research groups and Met Eireann as well as spot checks carried out beside the device as the container which held the other equipment was heated by the running of the equipment, and therefore the readings would not represent the environment outside the container. Table 3.5 contains corrected working hour averaged concentrations for all runs.

The second correction factor which is applied to data is used to account for the use of a light scattering nephelometer rather than the preferred gravimetric method which is set

out in ISO 9096 (International Organization for Standardization, 2003). Initially it was hoped to monitor using both gravimetric and light scattering methods at each site but the movement of filters from sites back to the laboratory caused disruptions to the calculated concentrations using the gravimetric method. The filters were removed from the monitoring equipment and returned to the laboratory in a covered Petri dish. However, mass was found to be lost on several of the filters from the pre-sampled weight. Removing the monitors from site was not an option, due to the reduced monitoring time at each site and hence, it was decided to do a calibration to correct for the differences between gravimetric sampling and light scattering. This calibration was done by running the HazDust monitors in several locations within the Trinity College campus both indoors and outdoors at various times of the year. 37 samples were taken in total with the results plotted on Figure 3.18 of light scattering measurements against gravimetric measurement of the same sample. An R^2 of 0.9208 was found using a 3rd degree polynomial fit to the sampled data. Note, it was decided to pass the best fit line through the origin as 0 concentration should be the same whether it was calculated by gravimetric or light scattering methods. In order to differentiate the gravimetrically corrected data from uncorrected data, the corrected data is denoted by a '*' in Table 3.5.

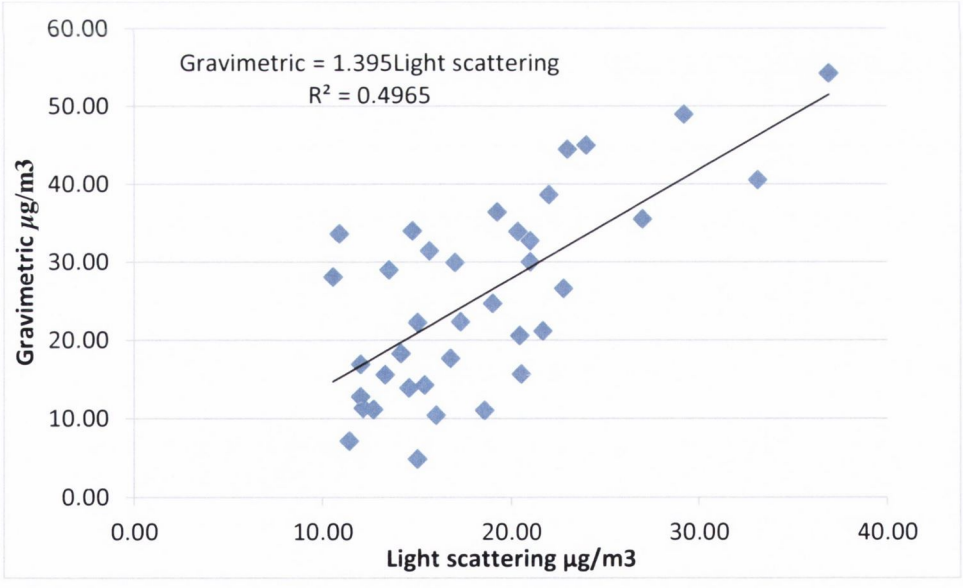

Figure 3.18 Gravimetric measurement V Light scattering

Table 3.5 shows the effect of applying the resulting correction (Gravimetric = 1.395 Light scattering) to the data collected from the 10 sites with Figure 3.19 showing an example of the different corrections applied to outdoor PM concentrations monitored at Site 1 across a 2 day period. The RH correction causes a more significant reduction in

times of higher RH while the gravimetric correction varies with concentration with some runs recording an increase in data and others recording a decrease. The daily average concentrations increase with the correction due to the under estimation of the light scattering device.

Table 3.5 Daily average concentrations for $PM_{2.5}$

	Indoor $PM_{2.5}$	Outdoor $PM_{2.5}$	Outdoor $PM_{2.5}$ RH	Indoor $PM_{2.5}$*	Outdoor $PM_{2.5}$*	Outdoor $PM_{2.5}$RH*
S1R1	23.79	24.02	17.67	33.19	33.51	24.66
S1R2	15.67	12.69	10.27	21.87	17.71	12.74
S2R1	15.24	34.95	31.68	21.92	49.39	44.19
S2R2	8.93	8.08	7.06	12.46	11.28	9.92
S3R1	6.20	11.24	12.72	8.66	19.48	12.00
S3R2	7.70	15.91	8.74	26.99	22.20	3.30
S4R1	16.75	17.94	6.01	23.54	25.73	11.13
S4R2	25.83	15.31	9.60	36.03	21.36	13.20
S5R1	6.68	10.21	5.42	9.04	14.15	8.02
S6R1	19.06	27.74	24.36	25.82	37.86	33.47
S6R2	11.73	17.70	15.26	16.36	24.69	20.61
S7R1	29.36	20.28	16.16	40.95	28.30	24.66
S8R1	9.90	21.21	13.03	13.75	29.11	19.10
S9R1	17.30	5.26	4.10	24.22	7.26	5.11
S9R2	12.50	7.01	5.53	17.58	11.48	8.96
S10R1	11.60	14.83	7.90	16.18	19.99	11.93
S10R2	6.25	7.23	3.72	9.15	10.97	5.29

Note: S1R2 = Site 1 run 2

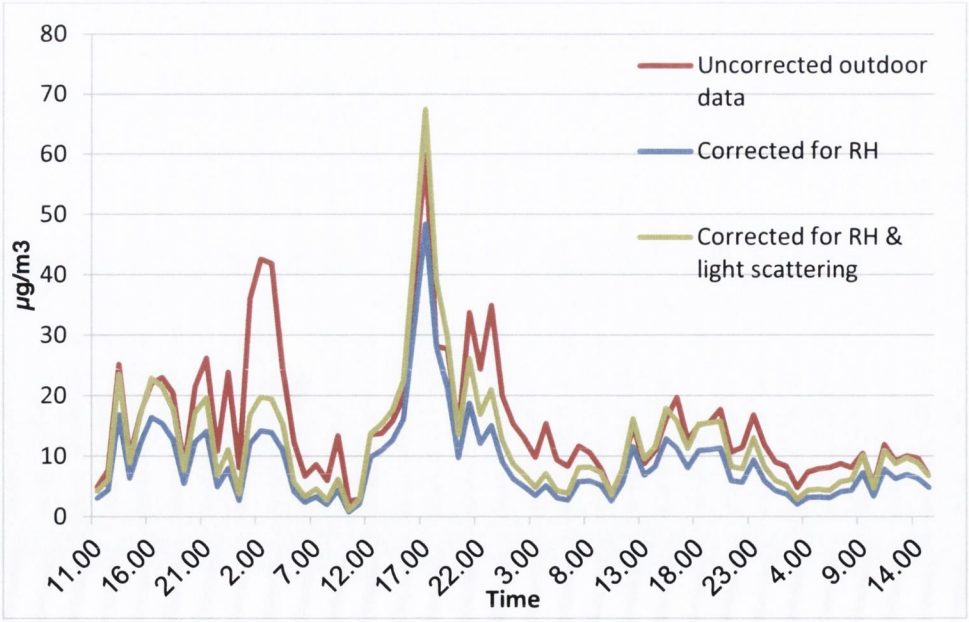

Figure 3.19 Site 1 Run 2 effect of correction on $PM_{2.5}$

4. Analysis of Monitoring Results

4.1. Introduction

This chapter deals with the results of the monitoring of the ten Sites which covers a total of 67 days of monitoring among the different Sites. First, working hours concentrations are calculated using the opening hours of the buildings in question in order to assess the typical air pollution exposure to the workers. Unlike residential buildings, most commercial buildings are only occupied during the day with exceptions including bars and hotels. The ten buildings studied in this research operated variable hours with the earliest opening at 7 am and the latest closing at 8 pm. The analysis of these results was conducted by looking at several aspects including the daily averaged concentrations, indoor/outdoor ratios at each site, the lag time between peaks outdoors and their paired indoor peak and the relationship of NO_2/NO_x indoors and outdoors. Each of these sections will give an insight into the relationship between indoor and outdoor pollutants in the commercial buildings monitored for this study. Before analysis took place, two corrections were applied to the $PM_{2.5}$ data, one to correct for relative humidity and another to correct for use of a light scattering device, the details of which are contained in Chapter 3. Throughout this chapter the concentrations for $PM_{2.5}$ are in $\mu g\ m^{-3}$ and NO_2 in ppb.

4.2. Trends of indoor and outdoor concentrations in monitored data

4.2.1. Diurnal concentrations at Sites and average working hours concentrations

Diurnal trends in the concentrations of air pollutants are well recognised. These exist seasonally, weekly and daily. Hatzianastassiou et al. (2007) found concentrations of NO_2 to be highest during warm sunny weather with weak winds and high solar irradiation. This would indicate summer concentrations should be higher than winter, however, data collected from the EPA and Dublin City Council on NO_2 suggests the opposite. Concentrations were found to be higher during winter months for both NO_2 and $PM_{2.5}$ than during summer months. This may be due to the influence of vehicles in the city which emit higher concentrations of $PM_{2.5}$ and NO_2 in winter months due to cold starts and overall higher number of vehicles on the road (Artíñano et al., 2004). For example, a study in Birmingham, UK, found higher percentages of $PM_{2.5}$ in PM_{10} for

winter months due to higher concentrations of traffic and higher re-suspension rates of soil particles and surface dust (Harrison et al., 1997).

Figure 4.1 shows outdoor ground level concentrations for NO_2 taken at the same location in Dublin (outside Sites 3 and 4) during this research but at 3 different times of the year; in December, in March and finally in July. December shows the highest concentrations with July consistently showing the lowest. The concentrations for March fall in-between with some days showing higher concentrations and others showing lower. The plot also shows the daily trend for NO_2 with concentrations sharply increasing in the morning after a night-time dip; highest concentrations are seen during this morning period due to high traffic concentrations during rush hour. Smaller peaks are also seen during evening rush hour and often at lunch time when traffic concentrations increase.

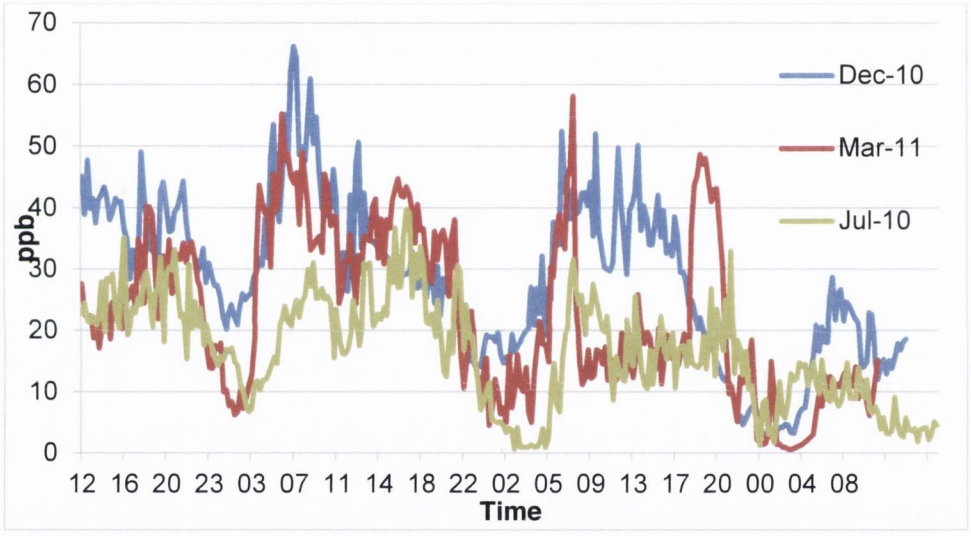

Figure 4.1 Summer/Winter NO_2 concentrations

4.2.2. Indoor and outdoor NO_2 and $PM_{2.5}$ time series

Analysis of the collected data from the 10 monitoring sites is contained within this chapter. Before detailed analysis is carried out Figure 4.2 to Figure 4.32 show time series plots of each run carried out for indoor and outdoor data with a very brief summary underneath. Attention is drawn to unusual behaviour with the plots but detailed analysis has been reserved for discussion in future sections of this chapter.

The daily diurnal patterns are mentioned frequently in the section with respect to NO_2 as they are generally strong with peaks occurring in the morning. These peaks are heavily influenced by the availability of O_3 and UV light. The concentrations then drop significantly at night when these are unavailable. The pattern also shows smaller peaks

occurring during evening rush hour. Concentrations begin to drop off after this, reaching minimum concentrations between 12 am and 3 am depending on the time of year. The diurnal patterns are in general pronounced for the collected NO_2 data although there is a particular lack of night time drops and rush hour peaks seen for indoor $PM_{2.5}$ data. The data presented here for $PM_{2.5}$ has been corrected for RH and use of the light scattering devices as detailed in Chapter 3. In some sites the correction for RH on outdoor data reduces concentrations to values below indoor concentrations, as indoor RH is below 60 %. For instance, this occurs at Site 4 Run 1 where indoor $PM_{2.5}$ concentrations are noticeably higher than outdoors.

Site 1 (Naturally ventilated shop)

Site 1 run 2 (26 – 29 July 2010) shows very similar patterns and trends for indoor and outdoor concentrations of both air pollutants in Figure 4.2 and Figure 4.3. This was a naturally ventilated shop, which often left its door open during the day. This resulted in the close relationship between indoors and outdoors. Site 1 shows a clear diurnal trend for both indoor and outdoor NO_2 concentrations see Figure 4.2. Indoor concentrations of NO_2 are above outdoor concentrations during many of the non-working hours, showing a baseline level of 10 ppb which they do not go below. Indoor concentrations exceed outdoor concentrations in the middle of the day. This may be due to sources within the building or chemical interactions. Run 1 was not included as no overnight data was collected due to restrictions in the first round of monitoring; these were resolved for the second run. The lack of data from run 1 makes it difficult to get a clear picture of the interaction between indoor and outdoor, therefore the data is not included here.

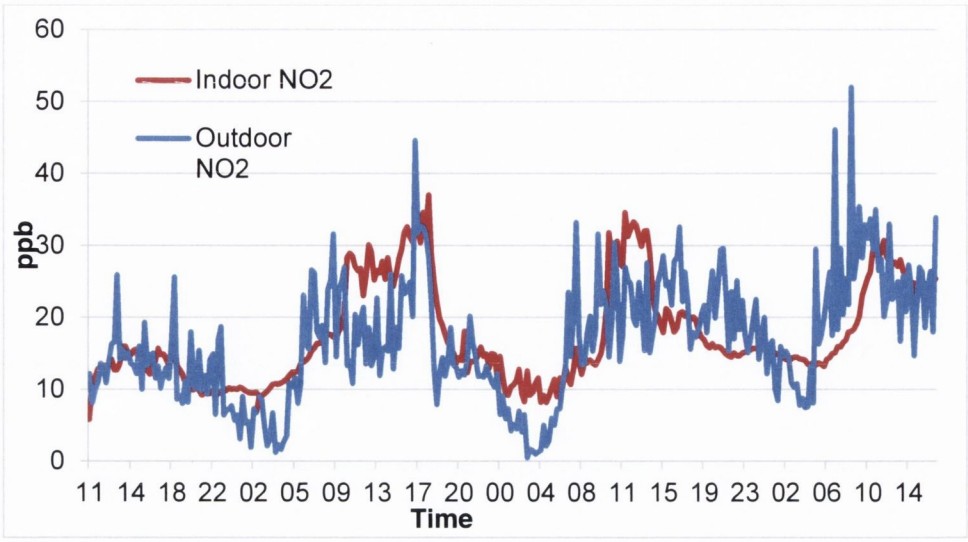

Figure 4.2 NO_2 Site 1 Run 2

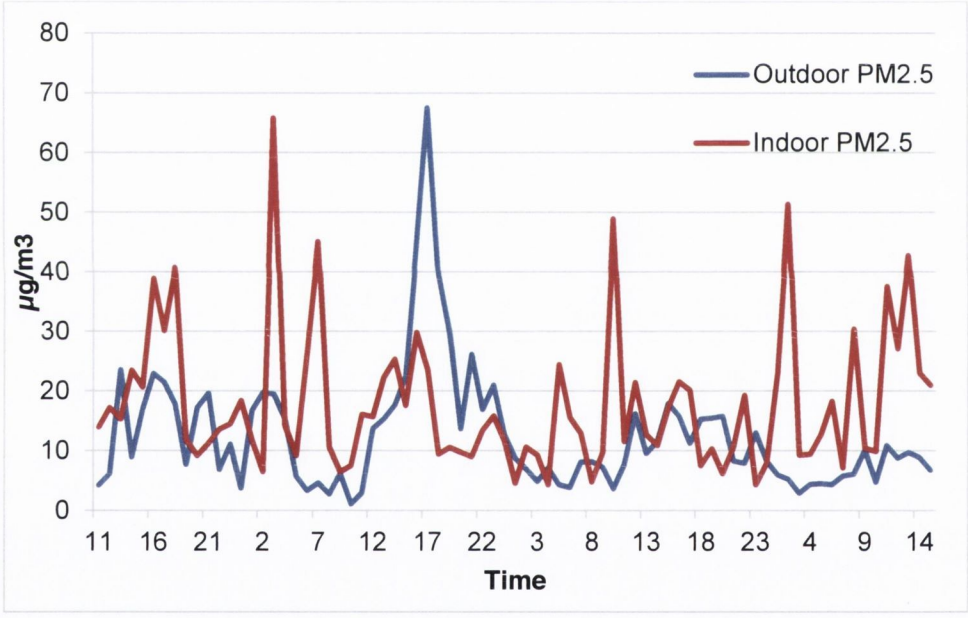

Figure 4.3 $PM_{2.5}$ Site 1 Run 2

Site 2 (mechanically ventilated office)

Site 2 run 2 (15 – 17 June 2010) also shows a close relationship for indoor and outdoor NO_2 concentrations although an indoor source during the day increases indoor concentrations slightly. Unusually there are increases in the NO_2 concentrations both indoors and outdoors for the second night of monitoring which drops sharply just before dawn. This rise was also seen in EPA data from another city centre monitoring site at Winetavern Street. Similar to Site 1, Site 2 run 1 only had data collected for day

time hours and therefore was excluded from the plots shown here as the full relationship between indoor and outdoor is unclear.

Over the week of monitoring for $PM_{2.5}$ more stable concentrations can be seen for indoor data which stay in the range of 10 – 20 µg m^{-3} for the majority of monitoring with little signs of a daily diurnal trend. The trend outdoors is more pronounced with sharp peeks aligning with evening rush hour followed by reductions in concentrations overnight.

Figure 4.4 NO_2 Site 2 Run 2

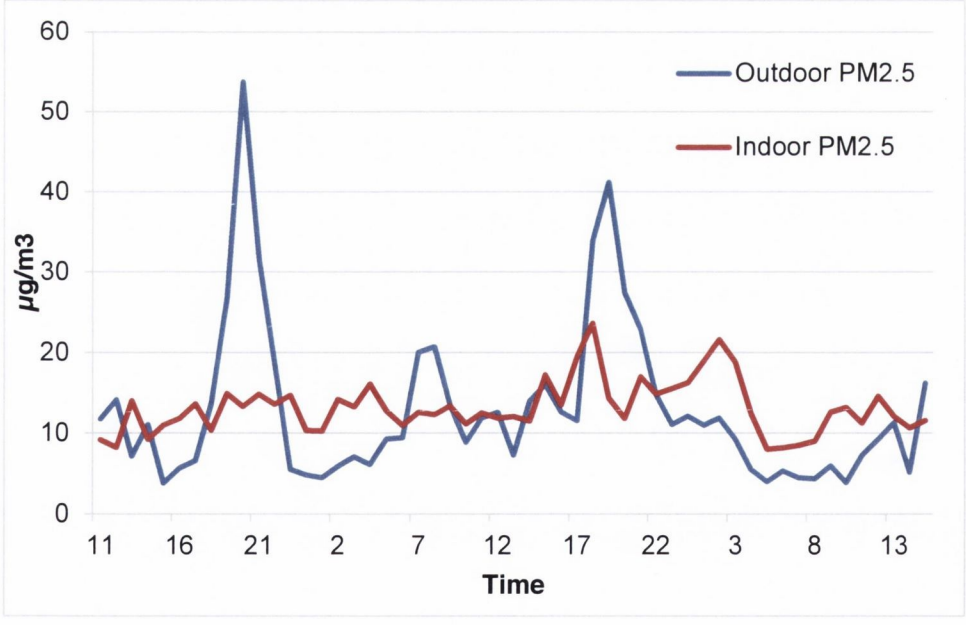

Figure 4.5 $PM_{2.5}$ Site 2 Run 2

Site 3 (mechanically ventilated office)

Site 3 run 1 was carried out with outdoor monitoring equipment on the roof beside the air intake; the indoor NO_2 levels are smoother and higher than outdoors. Diurnal trends, with the concentration reducing nightly and increasing upon sunrise and morning traffic, can be seen both indoors and outdoors.

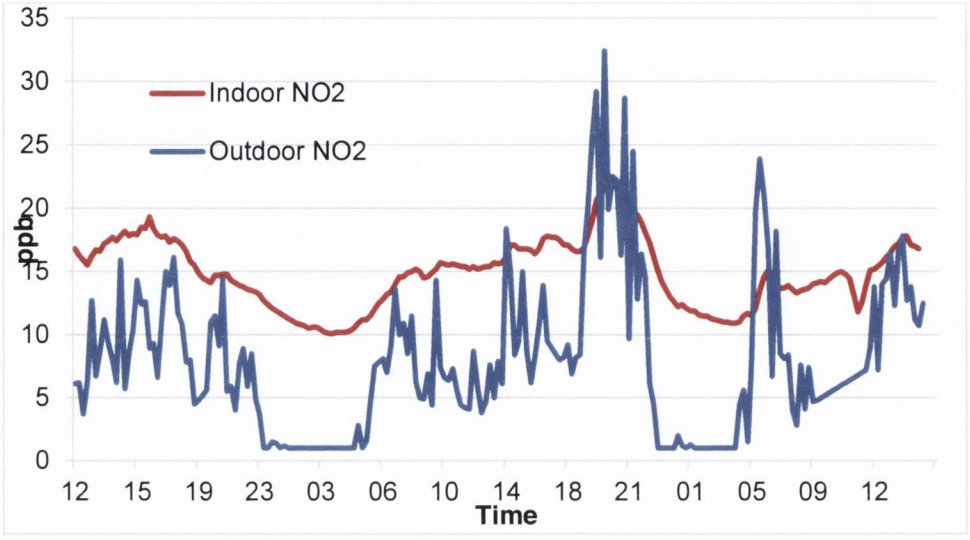

Figure 4.6 NO_2 Site 3 Run 1

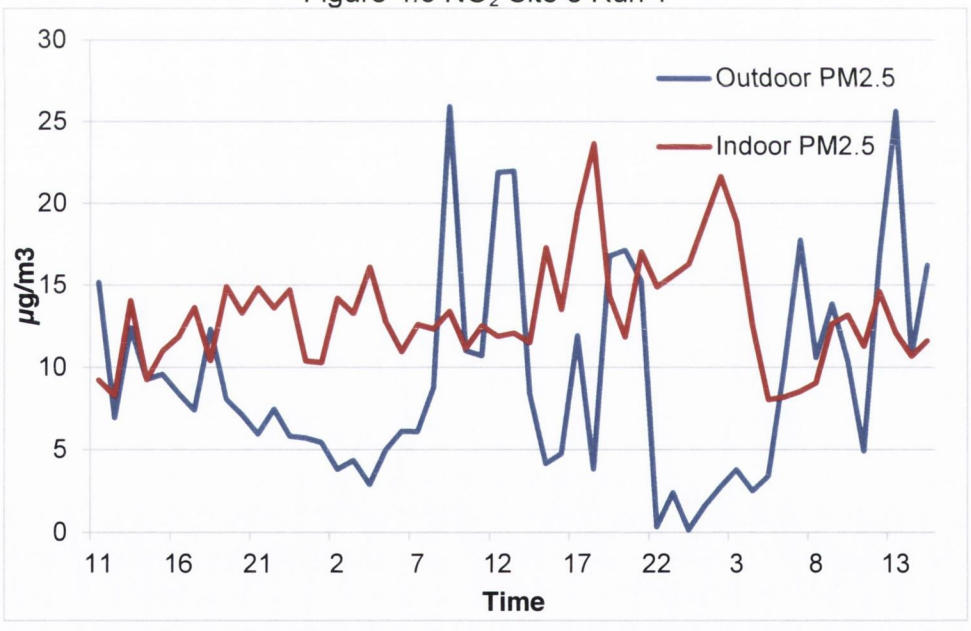

Figure 4.7 $PM_{2.5}$ Site 3 Run 1

Outdoor $PM_{2.5}$ concentrations show a greater diurnal trend than indoor concentrations. Sharp increases indoors can be seen several times during working and non-working time periods with no linked outdoor increases; during working hours this may be explained by staff re-suspending particulates but overnight no clear explanation is available.

A strong day and night-time trend is clear at Site 3 run 2 with indoor NO_2 concentrations staying higher than outdoors throughout the night. For run 2 the outdoor monitor was moved from the roof to the street level. The indoor concentrations had a marginally higher correlation to the outdoor concentrations at street level, during run 2, compared to the correlation between indoor and roof level concentrations during run 1 (0.712 versus 0.732) as well as a much smaller estimate for the difference between the two when conducting a 2 Sample T-Test (2.125 versus 6.914).

Indoor and outdoor $PM_{2.5}$ concentrations for Site 3 run 2 remained largely within a range of 5 – 20 μg m^{-3}. The indoor results show two sharp spikes throughout the run, one which occurred at the start of the working day and may be due to movement of staff within the room and a second which occurred at the end of the previous working day. A slight diurnal variation is present showing concentrations outdoors and indoors reducing to below 10 μg m^{-3} in the middle of the night and rising again in the morning.

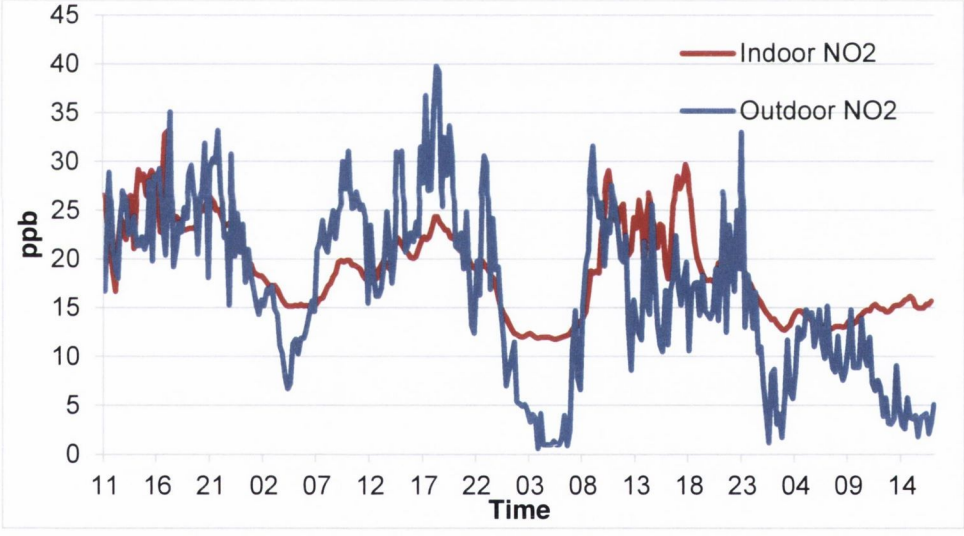

Figure 4.8 NO_2 Site 3 Run 2

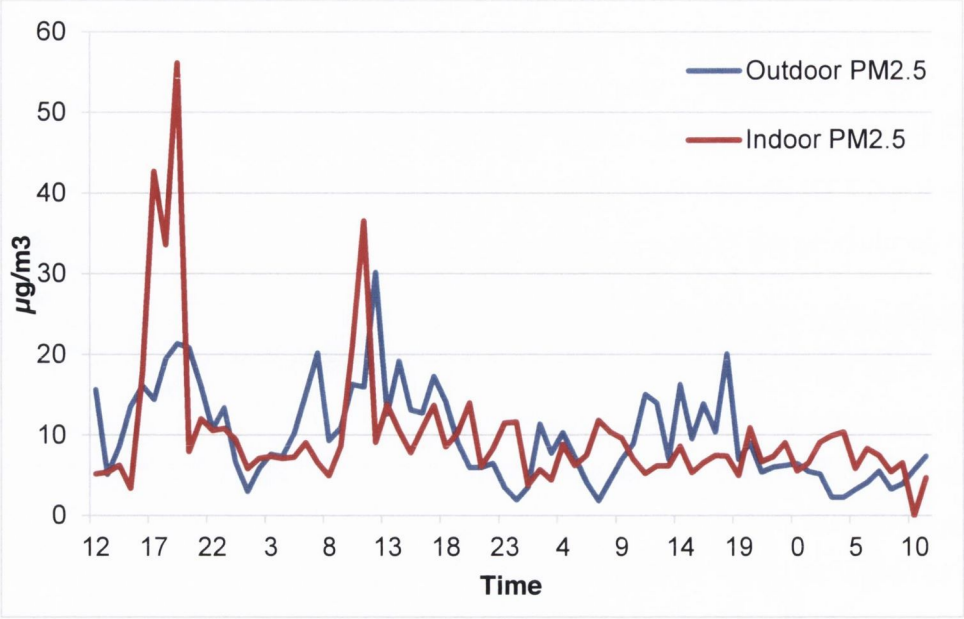

Figure 4.9 $PM_{2.5}$ Site 3 Run 2

Site 4 (mechanically ventilated office)

Site 4, a mechanically ventilated building which was built in the last five years, shows very strong diurnal patterns indoors and outdoors. The indoor pattern is a smoothed out and reduced version of outdoor concentrations which were taken at road side see Figure 4.10. As seen in many other sites, the indoor concentrations of NO_2 here do not dip below 10 ppb, even if the outdoor concentrations drop significantly below this level. $PM_{2.5}$ during run 1 (13 – 16 December 2010) saw elevated concentrations for indoors compared to outdoors with significantly less diurnal fluctuations see Figure 4.11.

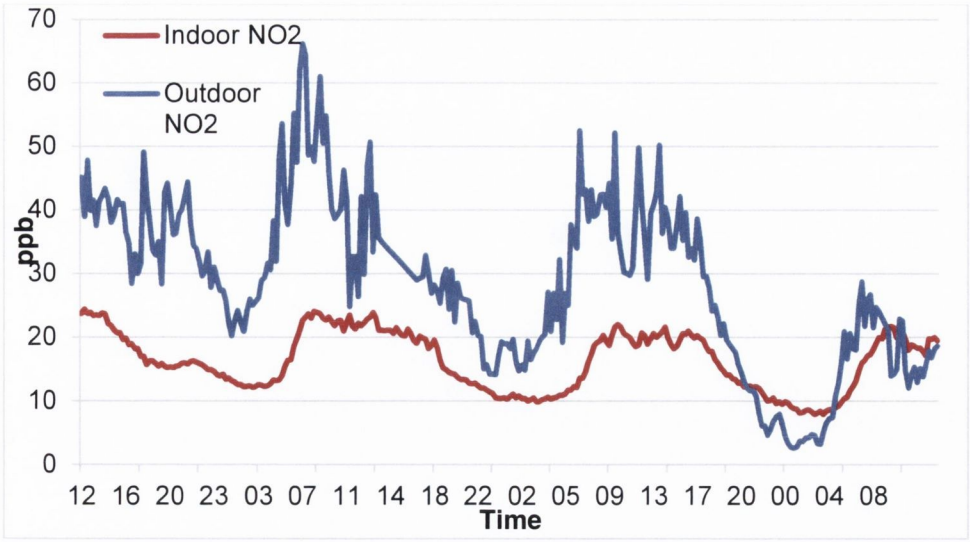

Figure 4.10 NO_2 Site 4 Run 1

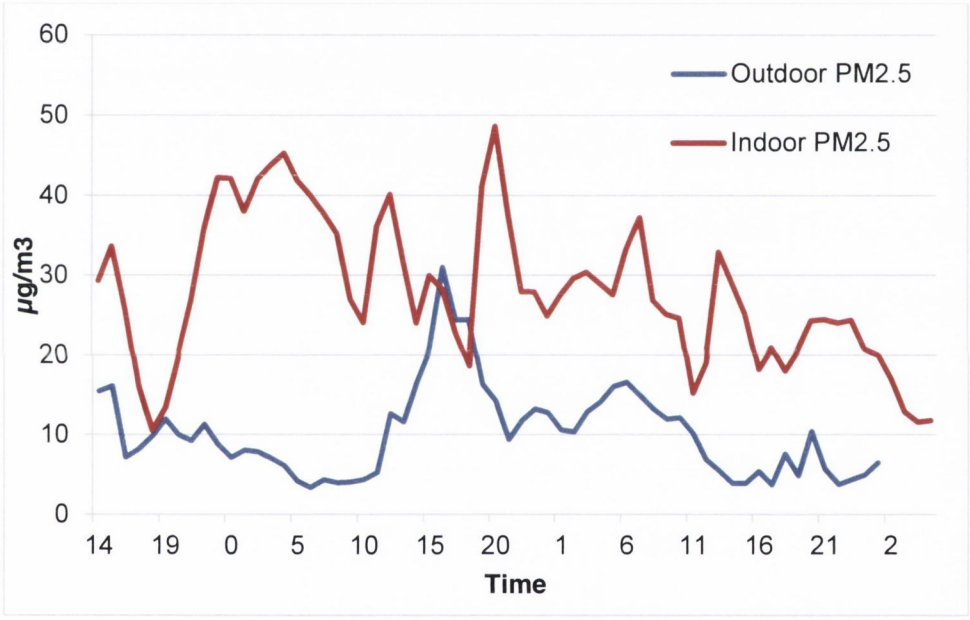

Figure 4.11 $PM_{2.5}$ Site 4 Run 1

$PM_{2.5}$ concentrations indoors at Site 4 run 2 (15 – 17 June 2010) (Figure 4.11) fluctuate around a mean value a slight diurnal trend for the second half of monitoring. However, the first half shows substantial increases in concentrations. Outdoor ground level concentrations show a diurnal trend and are much reduced compared to indoor concentrations. These would be the opposite of what would be expected by the usual trends, especially as this building has a filtration system in place to remove $PM_{2.5}$. The highest $PM_{2.5}$ outdoor concentrations were seen over the second evening of monitoring and some of the lowest concentrations were seen at evening rush hour for the 3rd day.

Site 4 run 2 was conducted using both ground level and roof level indoor monitors. However, as there was a malfunction of the NOx monitor which was placed at air inlet

(roof) level, only PM readings were obtained for all three monitoring locations in parallel, see Figure 4.13. The concentrations between indoor and outdoor were much closer during this run which was conducted in March rather than December for run 1. Indoor concentrations showed considerable spikes during this run see Figure 4.13, the reasons for which will be assessed later in the chapter. These increases were also seen for roof level concentrations, although a correction for RH, which has only been applied to the outdoor data, reduced these concentrations.

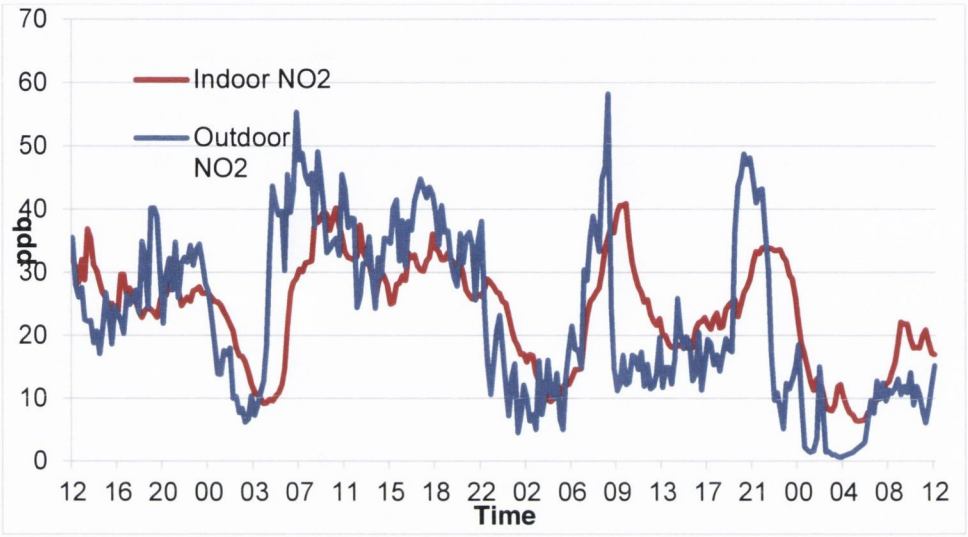

Figure 4.12 NO_2 Site 4 Run 2

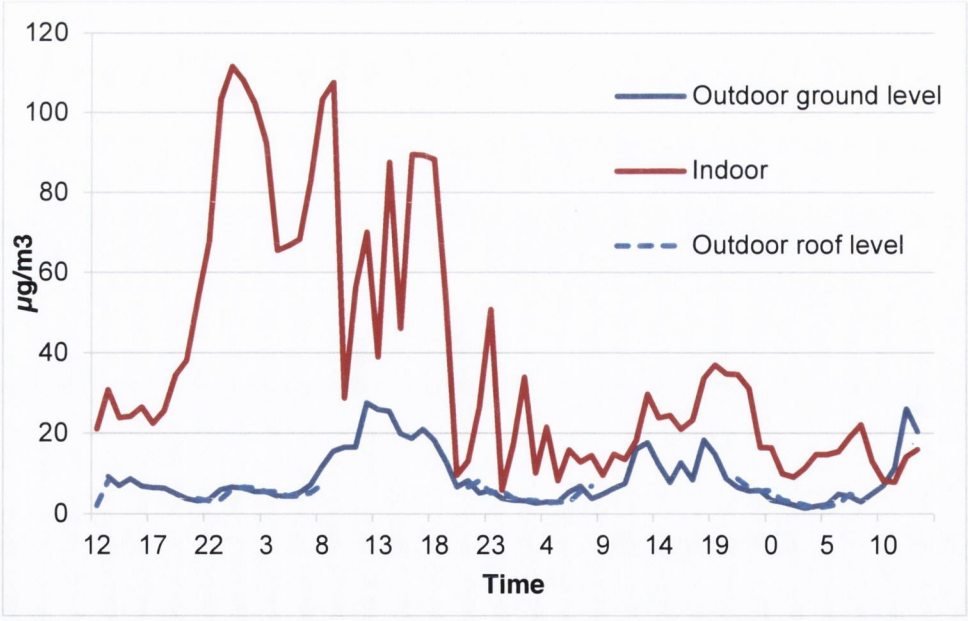

Figure 4.13 $PM_{2.5}$ Site 4 Run 2

Site 5 (mechanically ventilated office)

Site 5 shows two very different relationships throughout run 1 (24 – 26 January 2011) for indoor and outdoor NO_2 concentrations see

Figure 4.14. The first half of the data set shows a normal diurnal trend with concentrations at night, rising early in the morning with rush hour and the presence of UV from sunlight, while the second half shows a very different pattern which has an increasing trend within the peaks and troughs. Staff in the building were questioned for any unusual activities which may have contributed to the change in the pattern but no reason was put forward. The relationship will be discussed in greater detail throughout this chapter.

$PM_{2.5}$ indoor concentrations are often higher than outdoor concentrations which were taken at roof level,

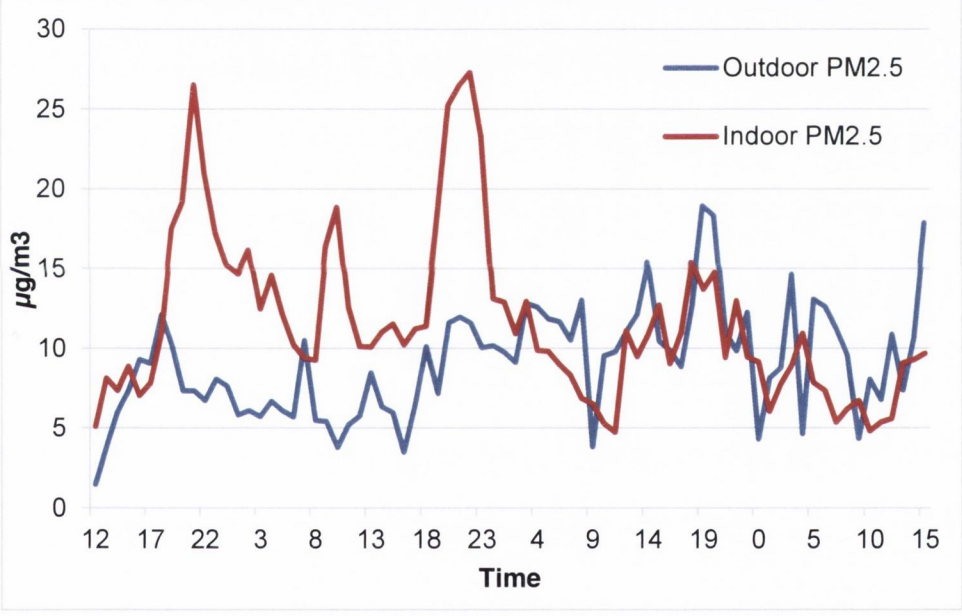

Figure 4.15. The times when these peaks occur are correlated with the troughs seen in NO_2 data and like the NO_2 data are not seen for the final night. Street level concentrations were unable to be collected due to access agreements with building staff. Indoor and outdoor concentrations seem to have little interaction although this will be discussed in this chapter

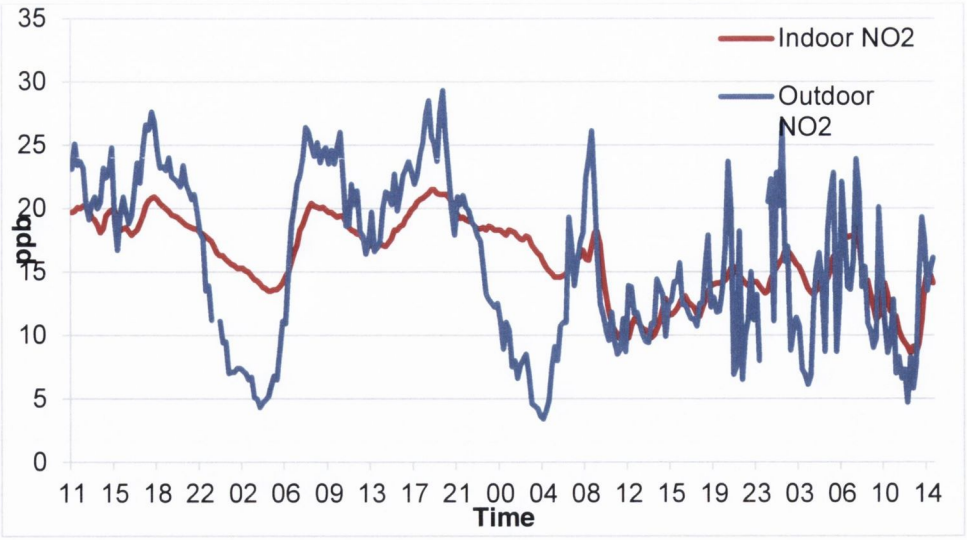

Figure 4.14 NO_2 Site 5 Run 1

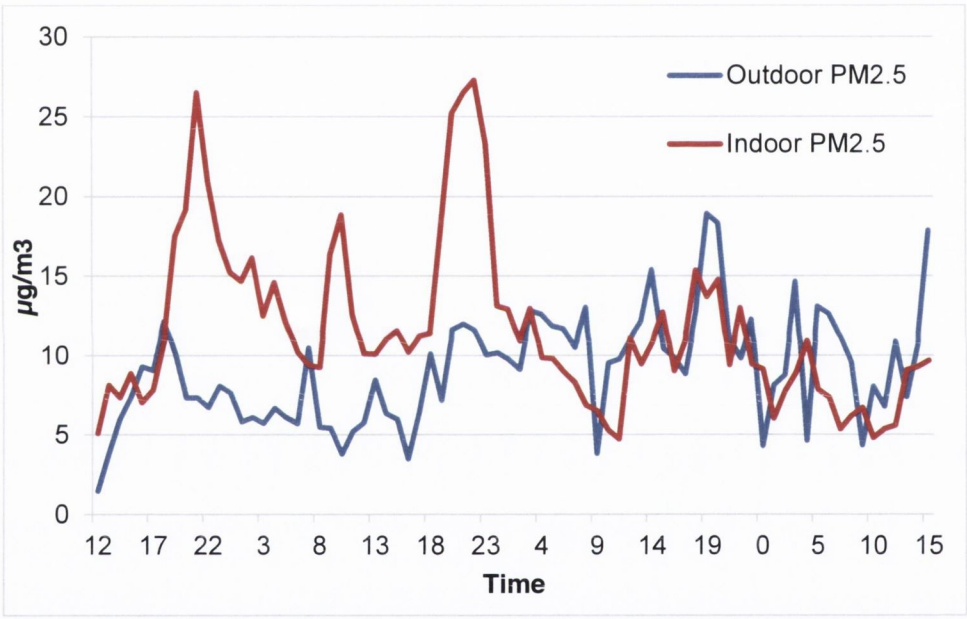

Figure 4.15 $PM_{2.5}$ Site 5 Run 1

Site 6 (naturally ventilated shop)

At Site 6 NO_2 concentrations were found to be significantly reduced indoors compared to outdoors, see Figure 4.16 and Figure 4.18 but when a secondary axis is used to compare the run 2 data in Figure 4.19 it reveals that even though concentrations are significantly reduced the diurnal trend outdoors is followed indoors. As with NO_2 for run 1 there is a considerable reduction of outdoor concentrations when they infiltrate into this naturally ventilated building for run 2. The diurnal pattern is clear outside but due to the scale on the plot in Figure 4.18 the pattern is not as clear for indoor concentrations, therefore Figure 4.19 contains a plot with indoor concentrations placed on a secondary axis. The data was collected on 26 – 29 April 2011 for run 1 and 27 June – 1 July 2011 for run 2.

Indoor and outdoor $PM_{2.5}$ concentrations for run 1 were very similar. However, concentrations outdoors reduced during the night due to less traffic while concentrations indoors show a lesser reduction see Figure 4.17. Similar to run 1, run 2 had indoor and outdoor concentrations for $PM_{2.5}$ in the same range with some slight reductions in concentrations outdoors overnight, as shown in Figure 4.20. Run 2 saw much greater noise in the monitored $PM_{2.5}$ compared to the data collected in run 1.

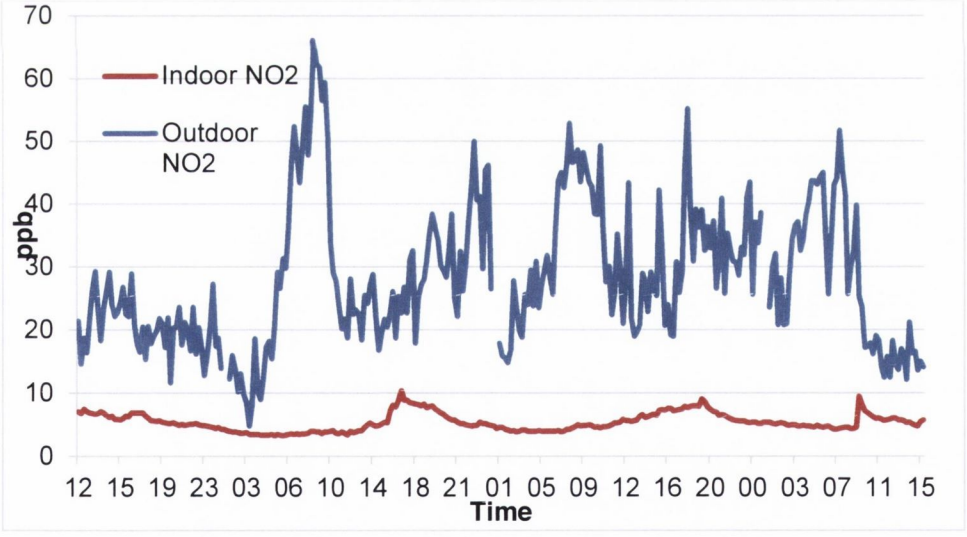

Figure 4.16 NO_2 Site 6 Run 1

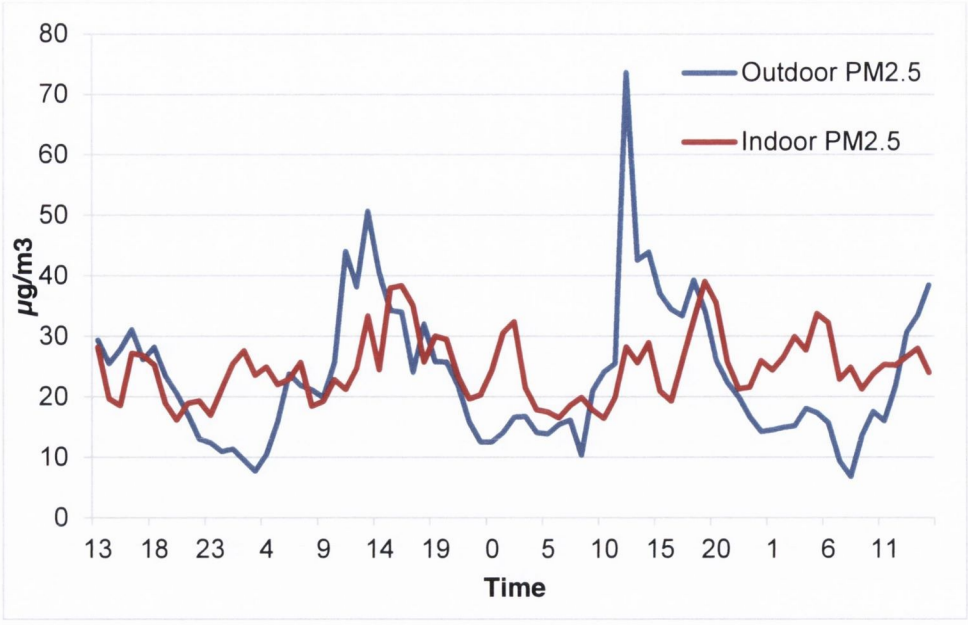

Figure 4.17 $PM_{2.5}$ Site 6 Run 1

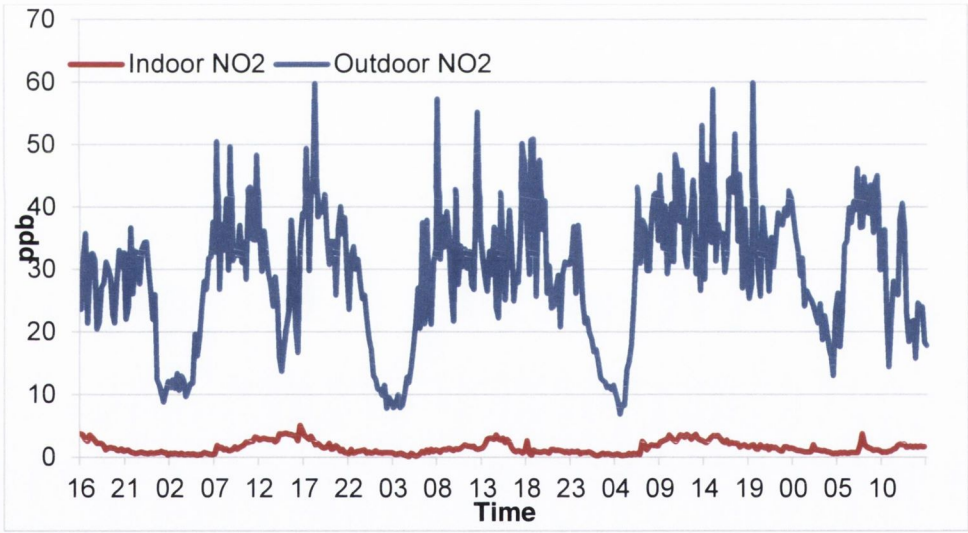

Figure 4.18 NO_2 Site 6 Run 2

Once plotted on a secondary axis, the similarities between indoor and outdoor for NO_2 in run 2 can be seen. A lag is visible between outdoor increases in the morning, and reductions in the evening occurring indoors, see Figure 4.19. This will be discussed later in the chapter.

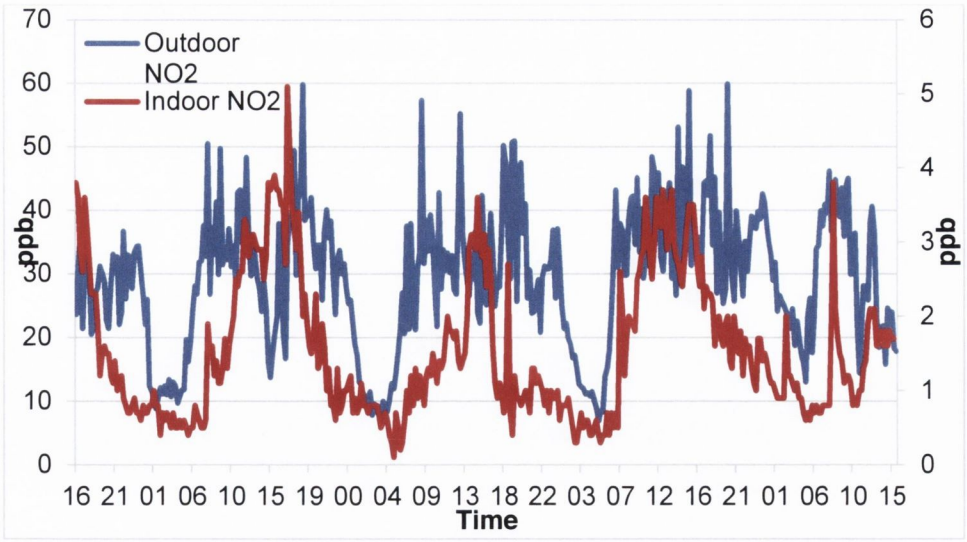

Figure 4.19 NO_2 (with secondary axis) Site 6 Run 2

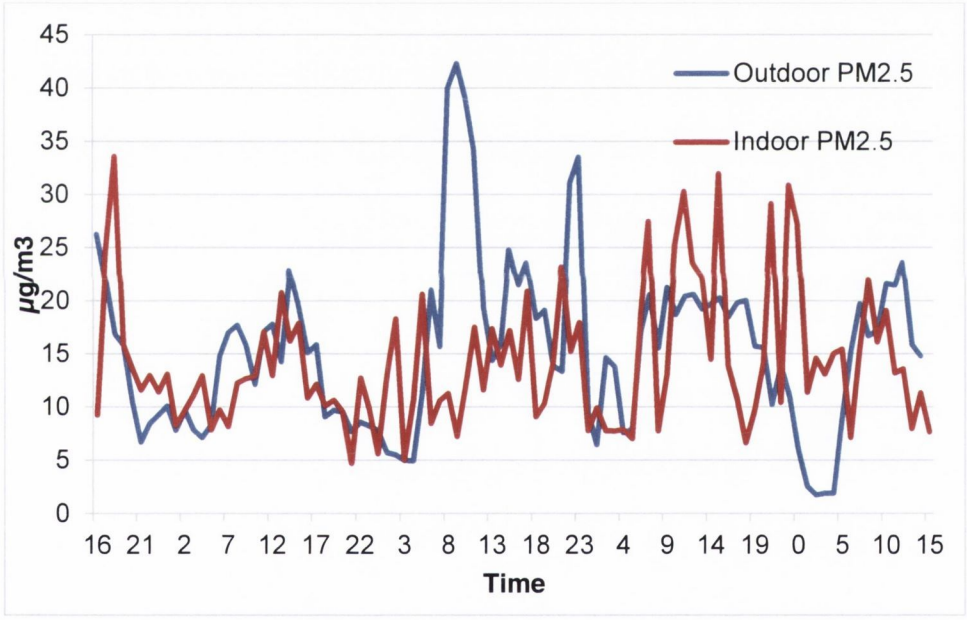

Figure 4.20 $PM_{2.5}$ Site 6 Run 2

Site 7 (naturally ventilated shop)

As with many other naturally ventilated sites there are strong daily diurnal NO_2 patterns with indoor concentrations not going below 10 ppb during the night-time period, as shown in Figure 4.21. Although some high peaks can be seen for indoor $PM_{2.5}$ concentrations (Figure 4.22) the concentrations for indoors and outdoors show an overall close relationship for this naturally ventilated shop. Again, as many other sites, outdoor concentrations showed slight reductions in concentrations while indoor concentrations did not. Data was collected at Site 7 during 3 – 6 May 2011.

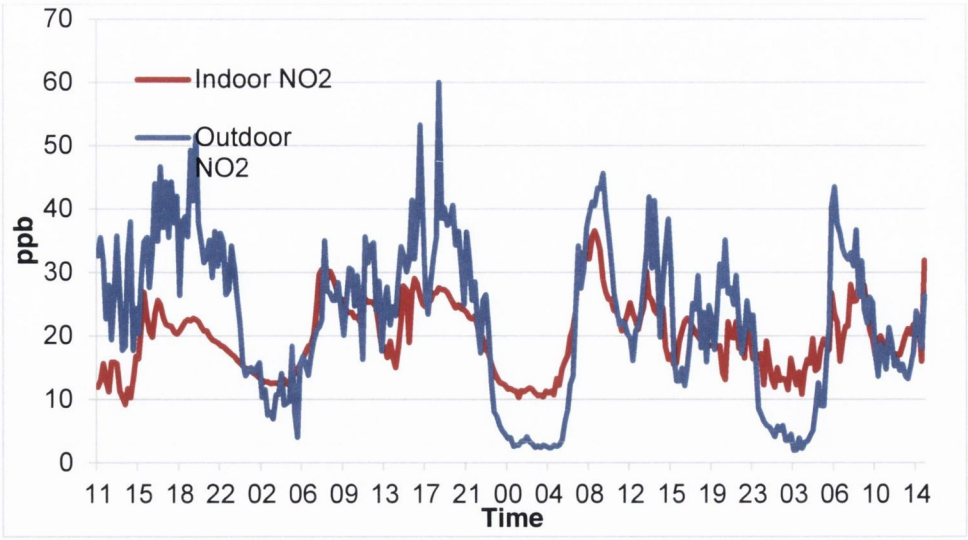

Figure 4.21 NO_2 Site 7 Run 1

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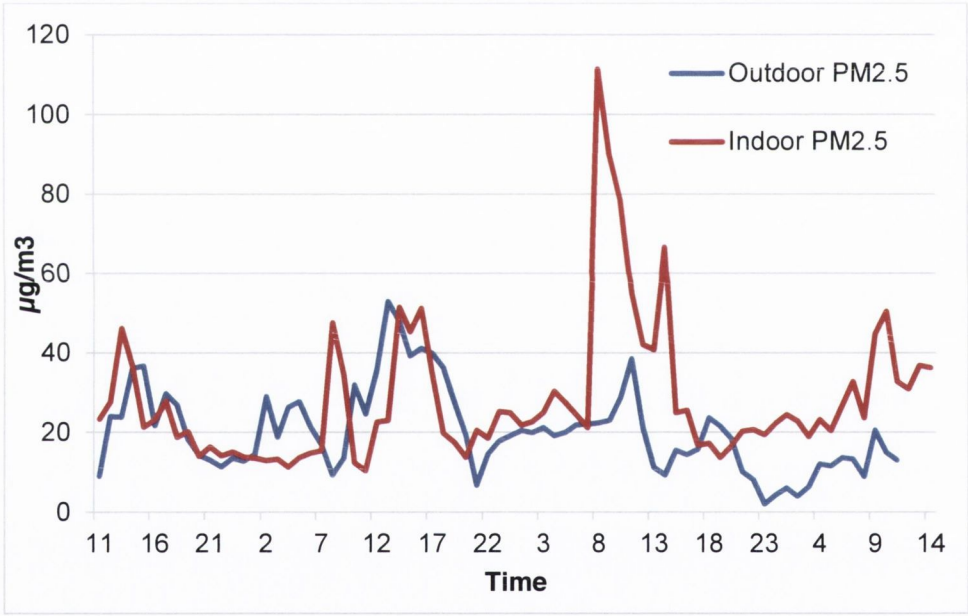


Figure 4.22 $PM_{2.5}$ Site 7 Run 1

Site 8 (naturally ventilated shop)

Site 8 (11 – 15 July 2011) showed a stronger diurnal NO_2 pattern indoors while outdoors shows different patterns with increases during the night-time hours and lulls during the day, see

Figure 4.23. The first night of outdoor monitoring of NO_2 was interrupted due to staff unplugging the outdoor monitors. $PM_{2.5}$ data was not interrupted as the monitor has a back-up battery for use when an electricity supply is not available.

Outdoor concentrations of $PM_{2.5}$ at Site 8 were generally within the range of 10 – 20 µg m^{-3} with outdoor concentrations having some peaks and lulls outside of this range, see Figure 4.24. The largest of the outdoor peaks occur in the morning during rush hour. Again a small diurnal pattern can be picked out within the outdoor time series with a similar pattern revealed indoors.

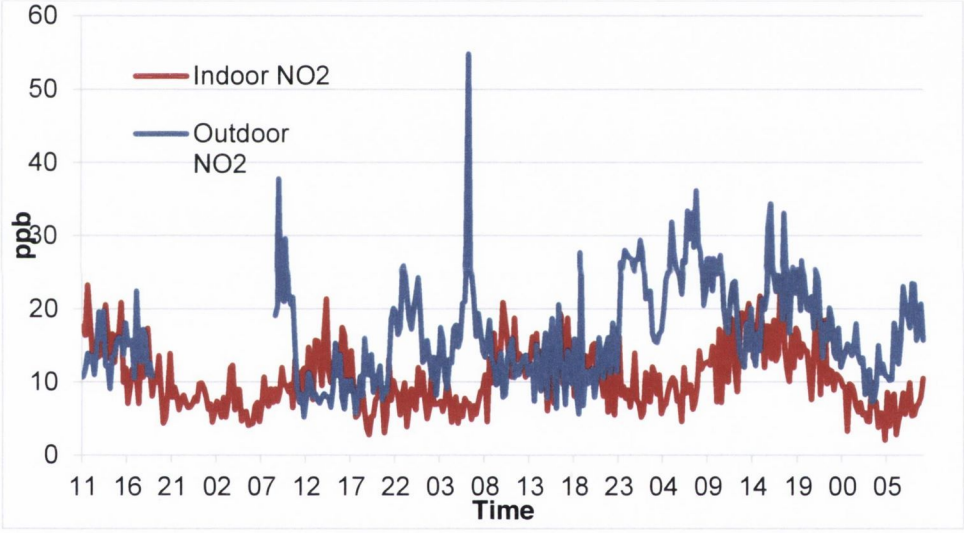


Figure 4.23 NO_2 Site 8 Run 1

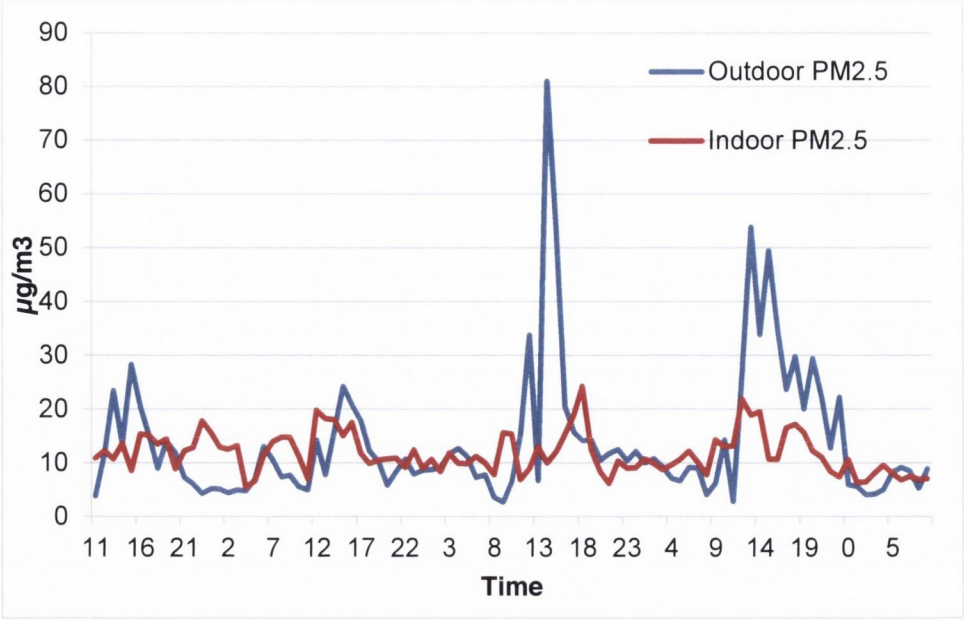


Figure 4.24 $PM_{2.5}$ Site 8 Run 1

Site 9 (naturally ventilated office

Although Site 9 is a naturally ventilated building, outdoor concentrations were taken at roof level for during run 1 (18 – 22 July 2011) in order to complement another research project being carried out in the building at the same time whereby another monitor was being calibrated against the rooftop concentrations of NO_2. The data for this run was included as some interesting results can be obtained as the indoor office was located on the floor of the building below the roof. This data showed low indoor and outdoor concentrations of NO_2 (see Figure 4.25) with a breakaway from the diurnal pattern shown on the final night of monitoring outdoors. Indoor $PM_{2.5}$ concentrations were much higher than the roof level concentrations outside with levels falling in between 15 – 40µg m^{-3} indoors and between 2 and 14 µg m^{-3} outdoors, see Figure 4.26. The final day of data outdoors was at very low concentrations - this may be linked to the extremely wet weather conditions during this period without the same reductions indoors.

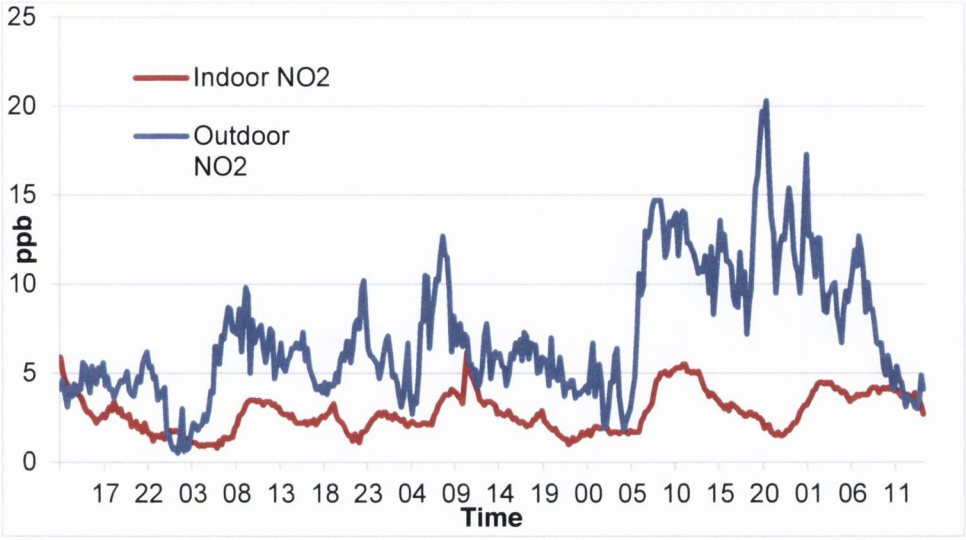


Figure 4.25 NO_2 Site 9 Run 1

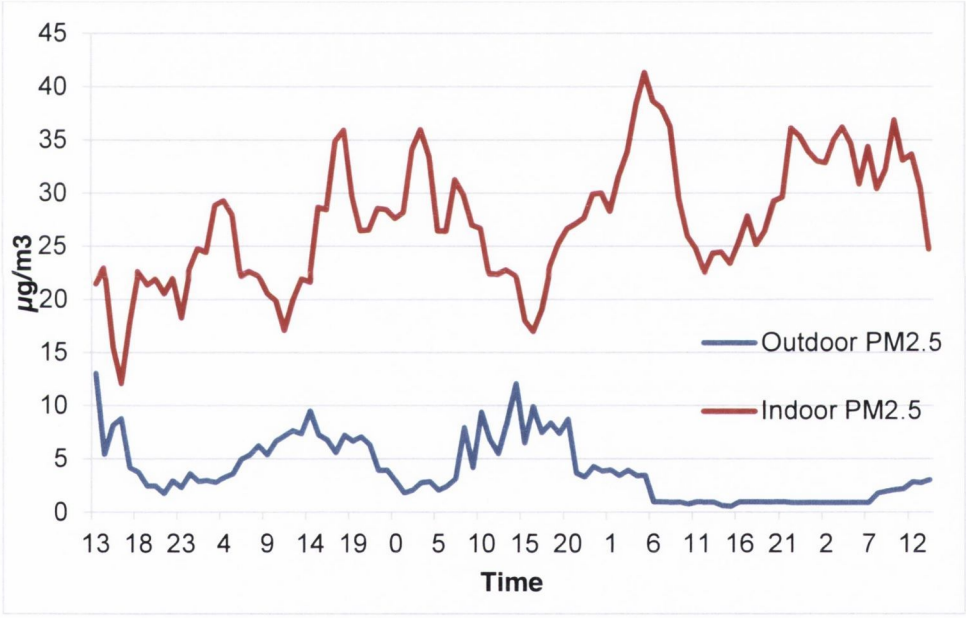


Figure 4.26 $PM_{2.5}$ Site 9 Run 1

Indoor concentrations show a strong pattern for NO_2 in run 2 (see Figure 4.27) with no such pattern shown for outdoors. This monitoring took place during 2 – 5 August 2011. Further investigations are carried out later in this chapter to show whether it was an issue with the monitors, or local sources that gave rise to these unusual patterns.

Outdoor concentrations were again lower than indoors for run 2, even with outdoor concentrations being taken at street level near a trafficked street. Indoor concentrations are slightly reduced compared to run 1; this may be due to the greater opening of a window in the office which increased the number of air changes per hour.

This indicates a form of indoor source for $PM_{2.5}$ within the building which will be discussed later.

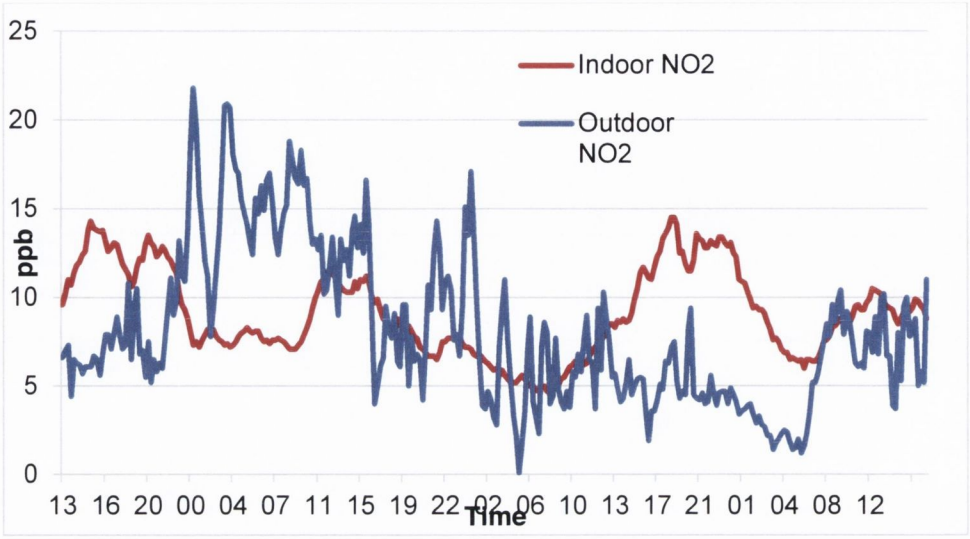


Figure 4.27 NO_2 Site 9 Run 2

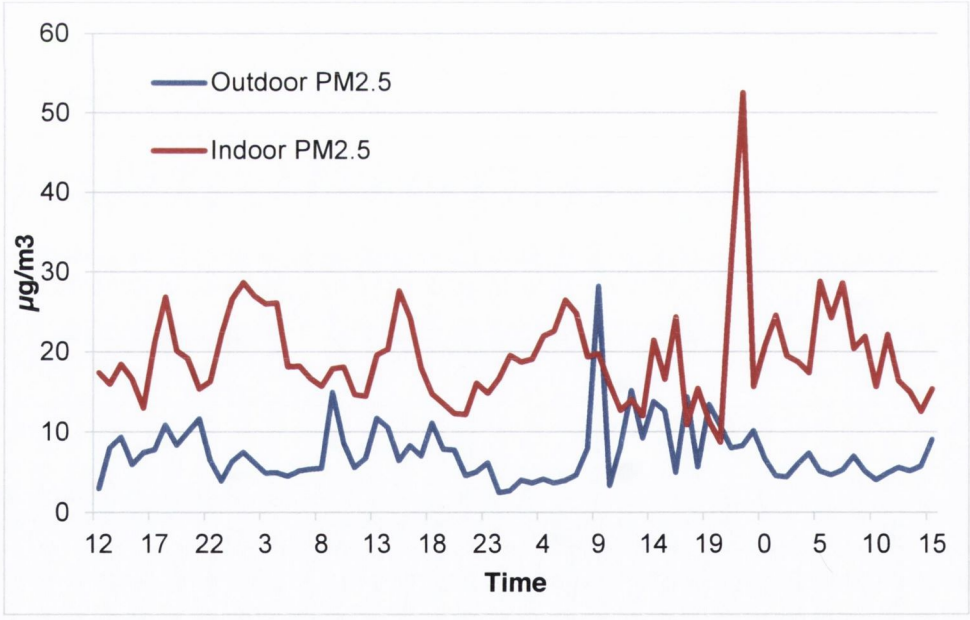


Figure 4.28 $PM_{2.5}$ Site 9 Run 2

Site 10 (mechanically ventilated office)

A strongly linked relationship can be seen here for indoor and outdoor concentrations of NO_2 for run 1 (16 – 20 July 2012) which was monitored at ground level, see Figure

4.29. As this is a mechanically ventilated building a drop in concentrations would be expected due to air being supplied from roof level. These were similar results to those collected at Site 3, another new mechanically ventilated building.

Indoor and outdoor $PM_{2.5}$ concentrations for this run, see Figure 4.30, have a slight diurnal pattern indoors, with the pattern being less obvious outdoor. The outdoor pattern shows a lot of noise around a mean concentration of 8 µg m^{-3}. An even greater reduction in concentrations would be expected for $PM_{2.5}$ compared to NO_2 as both panel and bag filters were fitted in the building's ventilation system to remove $PM_{2.5}$. However indoor concentrations are often greater than outdoors. This, combined with the reduction in concentrations due to the ventilation supply being located at the roof of the building, which has been shown to reduce concentrations due to its vertical distance from local sources, should have promoted a reduction in concentrations of $PM_{2.5}$ indoors.

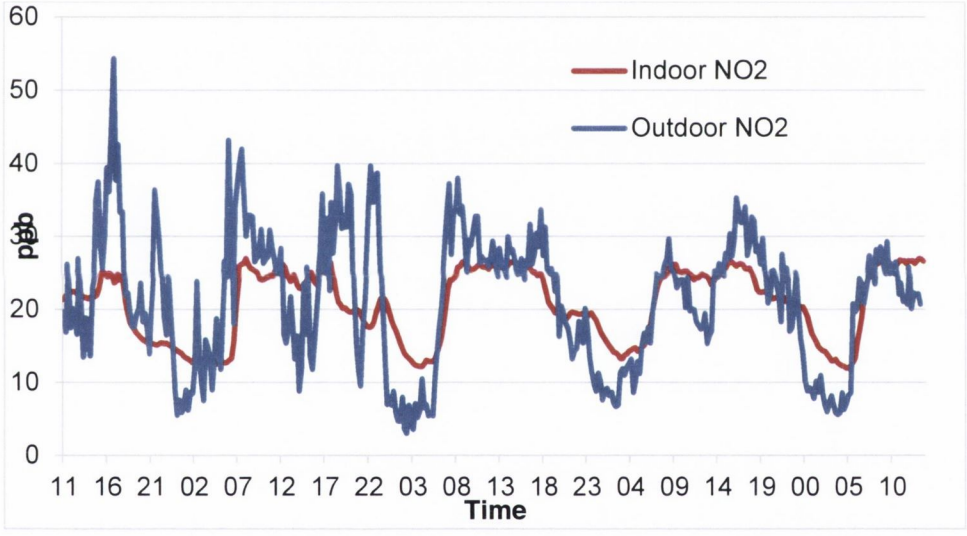


Figure 4.29 NO_2 Site 10 Run 1

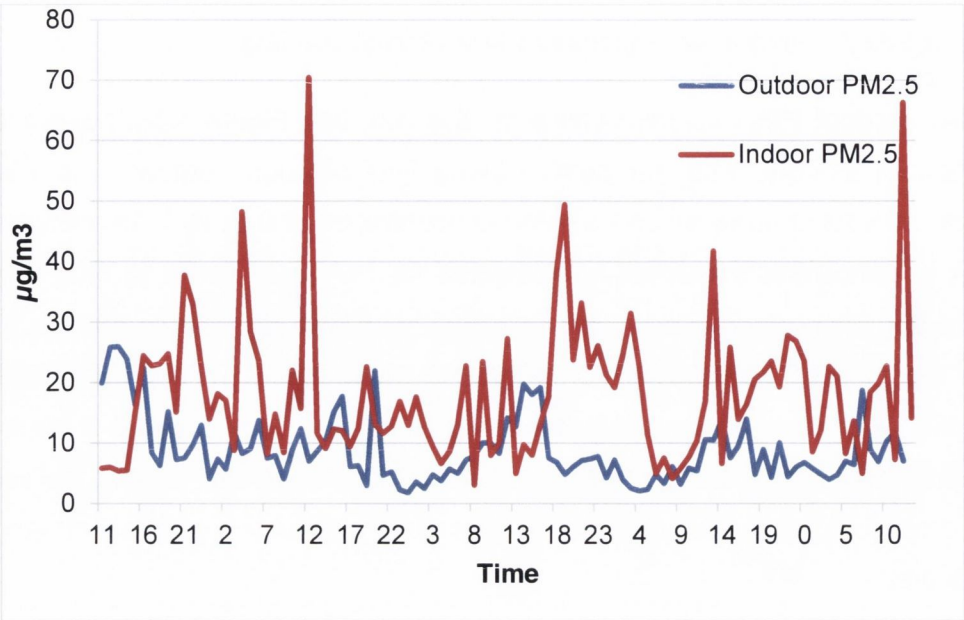


Figure 4.30 $PM_{2.5}$ Site 10 Run 1

This roof level outdoor data for run 2 was taken at the air intake for the ventilation system and shows significantly lower NO_2 concentrations than indoors although both follow the same diurnal pattern, see Figure 4.31. Indoor concentrations indicate that either a major source is present in the building or air from street level impacts the concentrations indoors more than the ventilation intake which is designed to bring cleaner roof level air into the building.

Similar to NO_2 results the $PM_{2.5}$ show significantly higher concentrations indoors compared to outdoors with indoor concentrations decreasing throughout the night and increasing with staff returning to work, see Figure 4.32. Such a clear pattern is not visible for outdoor roof level data.

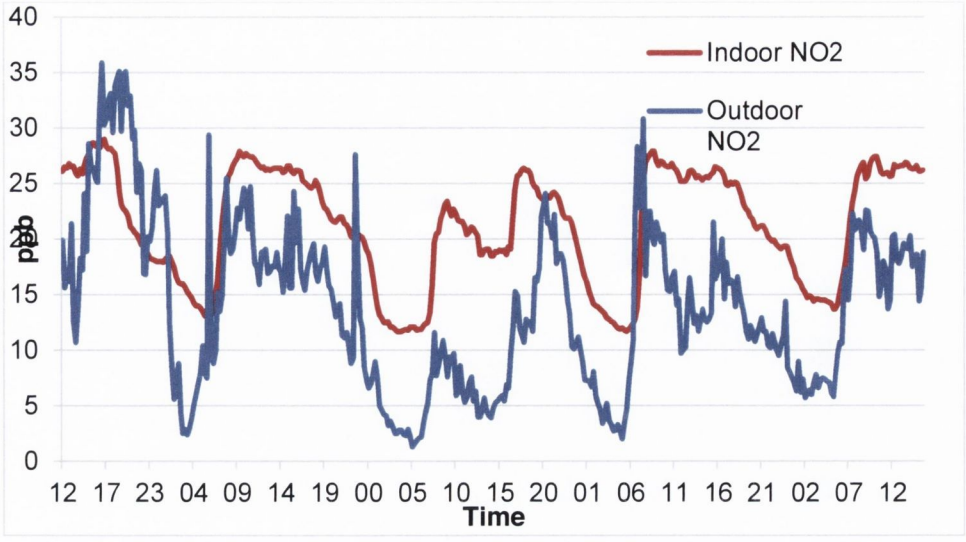


Figure 4.31 NO_2 Site 10 Run 2

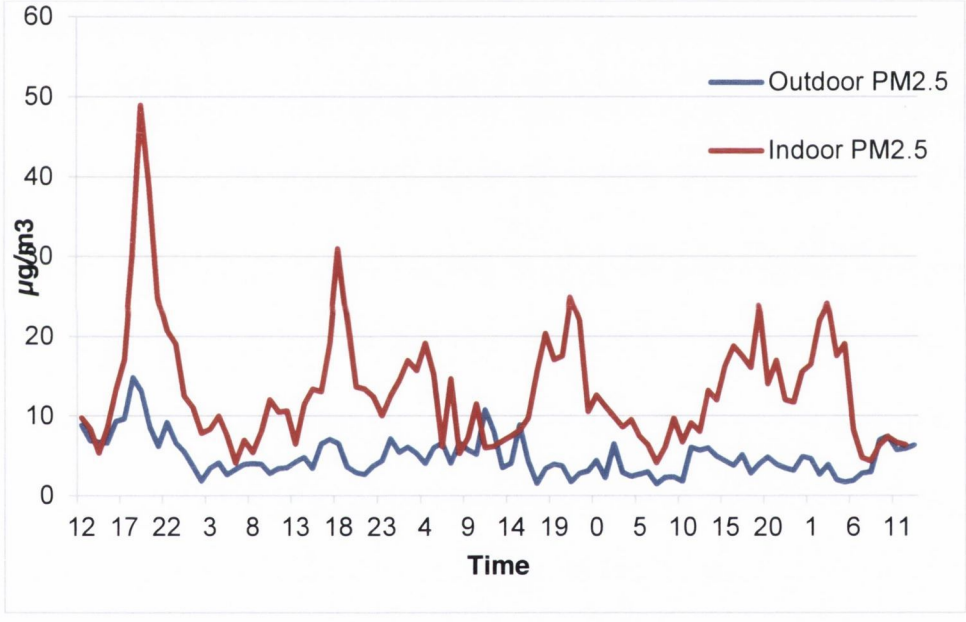


Figure 4.32 $PM_{2.5}$ Site 10 Run 2

In summary naturally ventilated $PM_{2.5}$ sites show close relationships between indoor and outdoor concentrations. However, this is not true for mechanically ventilated sites. Sharp spikes occur indoors at night for $PM_{2.5}$ which are not accountable for in the site logs. $PM_{2.5}$ indoor concentrations showed less diurnal fluctuations compared to outdoors; mechanically ventilated sites showed a greater propensity to having a diurnal pattern in $PM_{2.5}$ data. Instead naturally ventilated $PM_{2.5}$ data showed a steady fluctuation around a mean concentration. This is more than likely due to the use of the ventilation system during certain hours and not during others.

For NO_2 in all buildings a clear diurnal pattern can be seen. Mechanically ventilated buildings showed reductions overnight indoors which did not drop below 10 ppb and while this level was seen in some naturally ventilated buildings it was not as strong as the mechanically ventilated sites. Mechanically ventilated buildings with roof level intakes showed higher indoor concentrations compared to outdoors. The mean day time concentrations indoors are closer to ground level concentrations indicating that these may have a greater influence on the indoor concentrations. This is particularly clear for Site 10.

4.2.3. Average working hours concentrations

Public health awareness on indoor air quality lags significantly behind that of outdoor air quality with current legal limits for air quality in Ireland only covering outdoor air quality. Recent discussions in the EU have indicated that indoor air quality legislation may be considered in the near future although no official publications have been made on the subject to date. For comparative purposes current outdoor air quality limits shall be used for both indoor and outdoor limits as these are the concentrations which have been considered as safe to be exposed to with respect to human health. In Ireland the 1 hour limit for NO_2 is 105 ppb, which cannot be exceeded more than 18 times per year and the average annual exposure limit is 21 ppb. No 1 hour or daily limit is set for $PM_{2.5}$ but the annual mean limit is set at 25 μg m^{-3}. As people spend a large proportion of their day inside at work, it would seem reasonable to compare their indoor exposure against such exposure limits. The EU limits vary from limits in other areas of the world. For instance in the United States, where annual mean limits are higher for NO_2 at 53 ppb, 1 hour limits for NO_2 are lower at 100 ppb and $PM_{2.5}$ annual mean limits are considerably lower at 15 μg m^{-3}. Unlike in the EU the United States also legislates for a 24 hour limit value for $PM_{2.5}$ set at 35 μg m^{-3}. Three American States have indoor air quality regulations, namely New Jersey, California and Washington, while twenty-five other states have Occupational Safety and Health Administration enforcement policies.

In order to calculate the air pollution exposure of staff working in the buildings monitored during this research, the average concentrations over the hours that the staff are present in each respective building have been used. It should be noted that the average working hours vary between sites with some sites beginning their working day at 10 am and others at 7 am. However, this method was chosen as against using a set working day for all sites (for example 9 am to 6 pm), as using such fixed hours would not yield truly representative exposure calculations. For some sites this would lengthen the working day while others it would shorten it and would also mean that

peak concentrations may be mistakenly included or rejected as working hours, again distorting exposures. There are no indoor air pollution limit values set for the protection of human health, only outdoor limit values.

The following sections present the analysis of average pollutant concentrations over the working days for both $PM_{2.5}$ and NO_x at all the Sites with comparisons made to the annual limit values. However, exceedances of these values over a run do not indicate annual exceedances will occur, especially if it occurs during winter when both NO_2 and $PM_{2.5}$ are increased as part of the annual diurnal cycle. These cycles can be seen in Sections 4.2.4.1 and 4.2.5.1 in which a comparison is made between annual Dublin City Council (DCC) and EPA data

Chapter 5 will detail the reductions between indoors and outdoors specifically, focusing on the concentration differences at Sites both indoors and outdoors.

4.2.4. $PM_{2.5}$ average working hours concentrations

Table 4.1 (as well as Figure 4.33) contains the average $PM_{2.5}$ concentrations for corrected and uncorrected data during working hours for all Sites. All data has been corrected for the use of the light scattering device (denoted with a * when corrected in the table. Outdoor data has also been corrected for RH as mentioned previously. This correction has made a significant difference at several sites.

Table 4.1 Working hours averaged concentrations for $PM_{2.5}$ ($\mu g\ m^{-3}$)

	Indoor $PM_{2.5}$	Outdoor $PM_{2.5}$	Outdoor $PM_{2.5}^{RH}$	Indoor $PM_{2.5}^{*}$	Outdoor $PM_{2.5}^{*}$	Outdoor $PM_{2.5}^{RH*}$
S1R1	23.79	24.02	17.67	33.19	33.51	24.66
S1R2	15.67	12.69	10.27	21.87	17.71	12.74
S2R1	15.24	34.95	31.68	21.92	49.39	44.19
S2R2	8.93	8.08	7.06	12.46	11.28	9.92
S3R1	6.20	11.24	12.72	8.66	19.48	12.00
S3R2	7.70	15.91	8.74	10.45	22.20	12.20
S4R1	16.75	17.94	6.01	23.54	25.73	11.13
S4R2	25.83	15.31	9.60	36.03	21.36	13.20
SrR2 Roof	25.83	13.62	10.21	36.03	52.44	14.24
S5R1	6.68	10.21	5.42	9.04	14.15	8.02
S6R1	19.06	27.74	24.36	25.82	37.86	33.47
S6R2	11.73	17.70	15.26	16.36	24.69	20.61
S7R1	29.36	20.28	16.16	40.95	28.30	24.66
S8R1	9.90	21.21	13.03	13.75	29.11	19.10
S9R1	17.30	5.26	4.10	24.22	7.26	5.11
S9R2	12.50	7.01	5.53	17.58	11.48	8.96
S10R1	11.60	14.83	7.90	16.18	19.99	11.93
S10R2	6.25	7.23	3.72	9.15	10.97	5.29

Note: S1R2 = Site 1 run 2

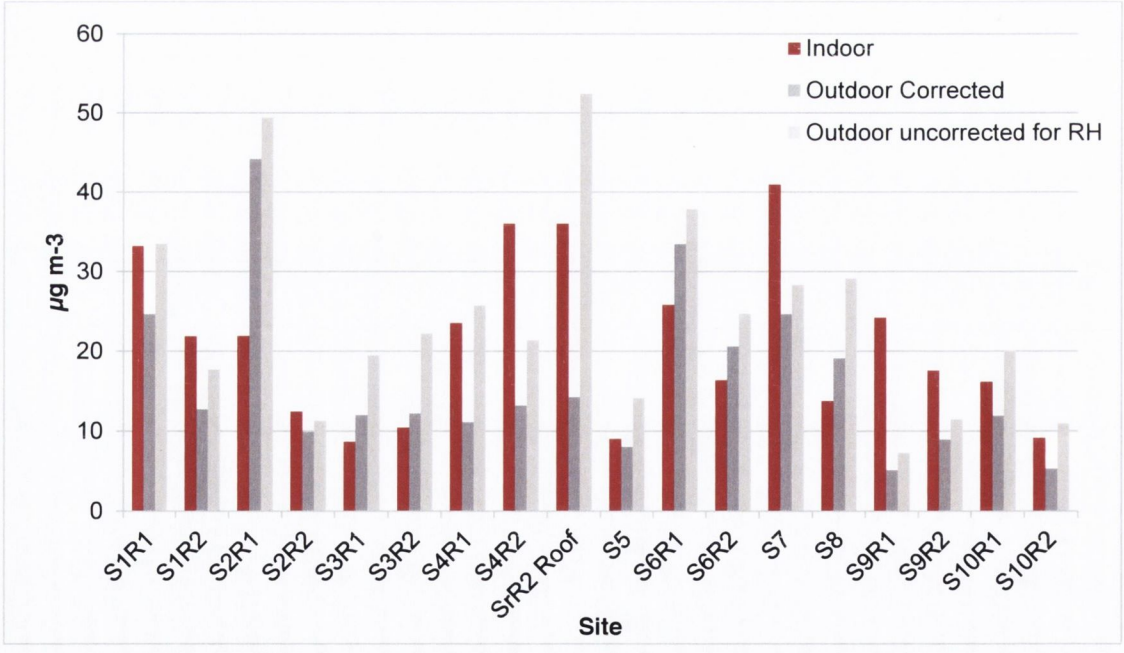


Figure 4.33 $PM_{2.5}$ working hours average concentrations

Site 1 run 1 (indoor and roof outdoor),Site 2 run 1 (outdoor), Site 4 run 2 (indoor and roof outdoor), Site 6 run 1 (outdoor) and Site 7 (indoor) exceeded the annual mean

$PM_{2.5}$ limit value set out by the CAFE directive (25 µg m^{-3}) for air quality. Apart from Site 1 run 1 and Site 4 run 2, which were monitored in April and March respectively, the rest of these exceedances occurred during the summer which usually records lower particulate concentrations (as seen later in Figure 4.34) as combustion boilers used for heating the houses are turned off. Greater review of these data sets found that Site 4 run 2 produced some indoor concentrations for up to 108 µg m^{-3} during day 2. Removing day 2 and recalculating the indoor and roof level average working hours concentration returns a value of 21.0 µg m^{-3} for indoors and a value of 14.24 µg m^{-3} for roof level, both of which are inside the recommended limit. The exceedances seen for Site 4 were correlated with recorded outdoor concentrations. However, the outdoor exceedances are greatly reduced when the correction for relative humidity is applied. According to literature this correction is not necessary for indoor environments (Ramachandran et al., 2003). While these concentrations were above the limit if the average runs indoor concentrations are taken for both run 1 and run 2, the average concentration drop below the limit to 31 µg m^{-3} for Site 4.

The same issue caused the exceedances indoors of the 25 µg m^{-3} limit in Site 7 without linked exceedances outdoors. In this instance increases over 2 hours and another 15 minute period during the morning of day 3 caused the high peaks when indoor concentrations exceeded 100 µg m^{-3}. Reviewing the data set without these 2 short burst of high concentrations from the average daily indoor concentrations, as was done with Site 4 run 2, returns a concentration of 34.17 µg m^{-3}. These concentration increases may be attributed to a member of staff who smoked cigars daily outside the back door; due to rain which occurred at this time the smoker may have been further inside the door during this particular morning causing spikes in the concentration. Alternatively, cleaning may also have caused the spikes in concentrations although no cleaning was reported when staff were questioned.

Site 10 run 2 and Site 5, both of which were mechanically ventilated with systems installed in the last ten years, had some of the lowest daily average concentrations with indoor concentrations under 10 µg m^{-3}. It should be noted that both these runs were carried out during periods of rain which has been known to flush out particulates from the air therefore lowering concentrations (Byrd et al., 2010). This has also been observed in other Irish studies such as Kourtchev et al. (2011) which looked at $PM_{2.5}$ in Cork and witnessed lower outdoor concentrations in summer compared to winter months. Both Site 10 and Site 5 had low outdoor concentrations to match the indoor concentrations. In Site 5 outdoor concentrations of 14.15 µg m^{-3} reduced to 8.02 µg m^{-3} when the relative humidity correction is applied while Site 10 run 2 saw outdoor

concentrations at an average of 10.97 μg m^{-3} before corrections for relative humidity were applied and an average of 5.29 μg m^{-3} after relative humidity corrections were applied.

The location of Site 5 is the furthest from the city centre and during its monitoring run winds were coming from the west whereby air would have travelled across the city centre before reaching the site. Site 9 is one of the most centrally located Sites and like Site 10 run 2 was monitored in winter when EPA average $PM_{2.5}$ concentrations are higher in the city and consequently a higher outdoor concentration would be expected. Both runs for Site 9, a non-ventilated building, showed significantly greater indoor concentrations compared to corrected outdoor concentrations (2 sample T-Test value =35.10 for run 1 (with estimate of difference = 23.46 μg m^{-3}, P-Value=0.0); T-Value of 14.29 for run 2 (with estimate of difference = 12.10 μg m^{-3}, P-Value=0.0). The outdoor concentrations were some of the lowest recorded throughout all sampling runs. During the monitoring runs several periods of rainfall were recorded which could explain the reduced outdoor concentrations as discussed above in relation to Site 10 and Site 5. Unlike these sites, Site 9 was monitored during July which would be in the middle of the non-heating season and therefore usually records lower outdoor concentrations. Section 4.2.4.1 compares data collected at EPA and Dublin City Council (DCC) stations with the data collected at these Sites.

Outdoor monitoring for Site 2 run 1, a mechanically ventilated building whose system was installed in the 1960s, was carried out at street level and showed the greatest day time average outdoor $PM_{2.5}$ concentrations. This building used a mechanical ventilation system with air intake located on the roof which was fitted with a panel filtration system. Average working hours indoor concentrations were found to be within 1μg m^{-3} yet a significant difference between ground and roof level concentrations was found. The combination of reductions due to vertical displacement of the particulates, which was found to be 73 % at 20 m by Wu et al., (2002) and 80 % at 20 m by Väkevä (1999). The influence of an indoor source or street level concentrations entering the building can be seen during the second run as outdoor concentrations measured at the ventilation air intake are below indoor concentrations.

Site 3 showed low average working hour's indoor concentrations for both runs with small reductions from average working hour's outdoor concentrations. Outdoor concentrations would be expected to be increased for run 1 compared to run 2 as run 1 was measured at roof level while run 2 was measured at street level. As mentioned above reductions of particles with height have been measured in many research

studies, although these measurements were not taken simultaneously and therefore the lack of vertical reduction may be due to difference pollutant concentrations over the two weeks. The outdoor average daily concentrations returned the almost the same value for run 1 and run 2 of 12.0 and 12.20 μg m^{-3} respectively. Testing was carried out over two separate weeks and therefore the data is not directly comparable but as outdoor concentrations were relatively stable over the two runs of monitoring this result indicates minimal reduction in concentrations between ground and roof level. Site 3 is located less than a 100 m from a busy train station and the ventilation intakes are located only metres from the train line at similar height as the trains leave the station and pass over a bridge. A high proportion of the trains passing run on electricity (the local 'Dart' trains), but all commuter trains i.e. non-dart trains, still run on diesel engines. These diesel trains often idle at the nearby train station as it is initial station for several train lines and therefore creating a source of $PM_{2.5}$ and NO_x. Station timetables show 91 journeys which are made into and out of Pearse Street train stations by commuter trains, which are diesel powered, on a weekday. Out of these 91, 83 of the journeys have Pearse Street station as their initial or final station. As mentioned above the other type of train passing through the station are Dart trains that run on electricity and hence are not a local source of combustion, but as the trains pass they are a source of $PM_{2.5}$ through re-suspension and the friction between the train and the line.

4.2.4.1. Comparison with Dublin City Council data at Coleraine Street

The EPA in conjunction with Dublin City Council (DCC) collects daily data readings for $PM_{2.5}$ at two Dublin locations, Coleraine Street and in Marino using time averaged gravimetric measurements and has kindly provided this data for comparative purposes before its publication. Averaged 24 hour concentrations for each run were plotted against the data collected from DCC. The data is measured by a "Leckel SEQ 47" or "Partisol" depending on the site, whereby both gravimetric monitors automatically switch filters at midnight and the filter is left in place for 24 hours beginning at midnight. Due to the collection method no real time breakdown is available unlike the collection methods used for this research and the DCC method for other pollutants such as NO_2. The Coleraine Street site is located roughly 1 km North and 1 km West of the sites while the Marino site is roughly 3 km North-East of the city centre. Figure 4.34 plots the DCC recorded data for 2011 and the first 5 months of 2012. Much greater fluctuations and higher average concentrations can be seen from January until the end of May with concentrations stabilizing over the summer months with higher concentrations again occurring in November. Coleraine Street shows higher concentrations over all with

Pearson's r = 0.836 and the results of a 2 sample t-test returning an estimate for the difference of the 2011 results of 2.257 μg m^{-3}.

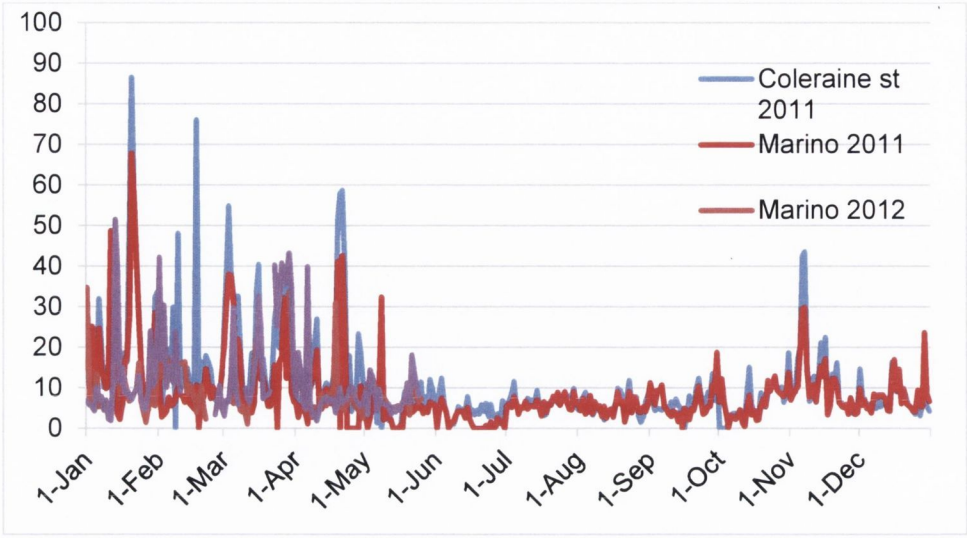


Figure 4.34 Particulate matter 2011 and 2012

The location of the DCC monitoring site at Coleraine St. in Table 4.2 is north of the River Liffey and more westerly than the 10 Sites monitored in this study, but is the closest site available for comparison with respect to $PM_{2.5}$. For Sites 9, 10 and 5 averaged concentrations were within 2 μg m^{-3}. Site 4 run 2 found elevated concentrations for the DCC Site but without similar concentration increases for the outdoor street level monitored data. Site 4 run 2 was the only run where indoor, roof and ground level concentrations were monitored simultaneously due to the availability of an extra set of monitors. The heightened concentrations seen in DCC's data were also seen in the roof level concentrations which had a run average of 23.66 m^{-3} for roof level concentrations and 26.72 m^{-3} from DCC data. This was one of the highest run average concentrations and was caused by a day and a half of highly elevated concentrations followed by a decrease to seasonal averages. This increase was also picked up by monitors indoors but interestingly not at ground level.

Table 4.2 Averaged DCC (Coleraine St.) v Site measurement during monitoring periods

Site	Outdoor	DCC
S1R2	12.52	4.58
S2R2	12.95	7.82
S3R1	9.28	4.65
S3R2	9.96	6.25
S4R1	10.24	14.65
S4R2	9.09	26.72
S4R2 Roof	23.66	26.72
S5R1	9.09	10.07
S6R1	23.40	15.61
S6R2	15.45	4.36
S7R1	20.33	7.33
S8R1	13.91	7.41
S9R1	3.89	5.91
S9R2	7.39	7.44
S10R1	8.91	10.23
S10R2	4.86	7.55

For many of the Sites this research recorded higher concentrations compared to the DCC Site. This can be explained due to the location of the monitors at the Coleraine St. being placed within a storage yard roughly 20 m from the road behind the building compared to the monitoring which was carried out in this project which used roadside monitors. For instance, the site with results closest to the DCC data was Site 9 which was the monitoring site whose door was furthest away from the road.

4.2.5. NO_2 average daily concentration

A far greater number of NO_2 sites show exceedances of the annual mean limit value for averaged working hours than were seen for $PM_{2.5}$. However due to over-night reductions bringing these averages down the entire run averages have only two exceedances of the annual mean limit. No site exceeds the maximum 1 hour concentration limit of 105 ppb with the highest maximum 1 hour values recorded at Site 4 run 2 of 38.58 ppb for indoors and Site 2 run 1 at 79.55 ppb for outdoors. Figure 4.35 shows the averaged NO_2 concentrations with Table 4.3 showing the maximum one hour concentrations for comparison against the legislative limit. The annual mean limit of NO_2 in the United States is considerably higher for NO_2 at over twice the EU limit at 53 ppb which would mean all sites are below the legal limit of what is considered appropriate for the protection of human health. No data were included for Site 4 run 2

as the monitors placed at roof level were found to report unreliable results and negative concentrations, therefore these data were discarded.

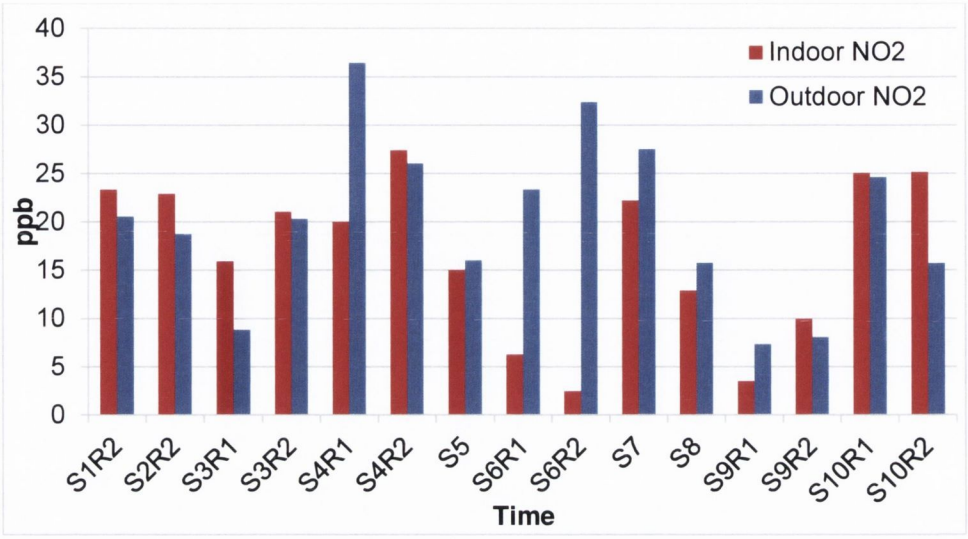


Figure 4.35 NO_2 working hours averaged concentrations

Table 4.3 Maximum 1 hour NO_2 concentrations during working hours

Site	Max 1 hour outdoor NO_2	Max 1 hour indoor NO_2
S1R1	27.03	30.55
S1R2	32.15	32.88
S2R1	79.55	36.43
S2R2	34.48	30.9
S3R1	14.85	18.65
S3R2	35.38	29.75
S4R1	53.33	23.68
S4R2	47.28	38.58
S5R1	25.05	20.3
S6R1	42.13	9.18
S6R2	43.95	4.03
S7R1	43.05	34.4
S8R1	28.38	19.3
S9R1	13.65	5.35
S9R2	17.38	13.83
S10R1	44.9	26.8
S10R2	29.55	28.4

Average concentrations over the run show some seasonal pattern with averages in summer months generally being below that of winter ones. As discussed above, the 1 hour limit for NO_2 is 105 ppb, which cannot be exceeded more than 18 times per year and the average annual exposure limit is 21 ppb. No exceedances of the 105 ppb limit were recorded during monitoring although 9 of the 17 runs showed indoor working hours averaged concentrations were above the annual mean limit for human health. The maximum 1 hour averaged concentrations outdoors were produced for Site 2 run 1 at 79.55 ppb with Site 4 run 2 producing the highest indoor concentration of 38.58 ppb.

The highest working hours averaged concentration, see Figure 4.35, was recorded at Site 2 run 1 for outdoor monitoring with concentrations 38.22 ppb. The monitors were located on a busy street with high traffic volumes, bus stops and a junction close to the monitoring site which would increase the NO and NO_2 emissions due to the stop/start behaviour of the traffic. Site 2 saw exceedances of the annual mean limits both during working hours and the entire run averages again this site was monitored in summer months and therefore concentrations may rise further during the winter.

Site 4 run 1 and Site 6 also saw high outdoor concentrations, with monitoring taking place at street level during all these monitoring runs. A significant increase can be seen for Site 3 between roof and ground level concentrations over the two runs unlike the case with $PM_{2.5}$ where little increase was found. An increase in indoor concentrations was also recorded between the two runs, although this was not as significant as the increase measured outdoors when monitors were moved to ground level.

Sites 9 and Site 6 significantly reduced indoor concentrations of NO_2 compared to outdoors. Neither building was fitted with a mechanical ventilation unit and both were built over 40 years ago. Site 9 showed NO_2 concentrations with average run 2 concentrations at 9.94 ppb and run 1 concentrations of 3.51 ppb. The increase between the two runs may have been due to the opening of a window located in the small office where indoor concentrations were being measured. This increased the number of air changes per hour and therefore allowed a greater number of pollutants into the room. Site 6 showed a unique behaviour for this data set, i.e. sharp drops in indoor concentrations of NO_2 compared to outdoors. This is likely to be due to heterogeneous reactions on the surface of walls, floor and ceilings of buildings reducing NO_2. Inside this office is a very large surface area due to collections of occupants' papers, equipment and various other items in the room. The floor is

carpeted and walls are painted, with dividers placed in both halves of the room to separate the 8 desks. Half the room can be seen in Figure 4.36. The monitors were located on the closest desk although they were not present at the time the image was taken. The second half of the rectangular room contains a large glass case which is used as a display area overlooking the street. Glass has been known to increase heterogeneous reaction rates. Having the display case rather than just a window triples the surface area in which these reactions can take place. This case is not sealed and is left open to the room. Heterogeneous reaction rates depend on the materials, surface area and increases with increasing relative humidity, therefore older damp offices may have increased reaction rates. If materials show dampness i.e. damp wall or carpeting, the reaction rate of NO_2 to HONO increases (Baughman and Arens, 1996). Materials which have been found to have high reactivity with respect to NO_2 include; Masonite (hardboard), ceiling tiles, plasterboard, carpet (polyester, wool and acrylic), oak panelling and curtains (Weschler and Shields, 1997, Nazaroff and Cass, 1986). In buildings with low air exchange rates surface reactions become more prominent as the air has the time required for these to occur. In mechanically ventilated buildings with higher movement of air gas phase reactions become more important. Sites 6 and 9 are both naturally ventilated and carpeted older buildings, so heterogeneous reactions may be a cause of the significant reduction in NO_2. Site 6 did show higher RH than other sites indoors (~50%) and upon questioning staff in the office said it is often damp in there.

Figure 4.36 Site 6 office

Site 10 saw a significant reduction in NO_2 concentrations between roof and ground level, with ground level concentrations being almost 10 ppb higher than roof level, and indoor concentrations remaining stable within its diurnal cycle over both runs with average concentrations during working hours of 25.08 ppb. If non-working hours data is included (as EPA limits are for data averaged over the full year including night time data) the concentrations reduce to 20.70 ppb for run 1 and 21.24 ppb for run 2 which are just about at the limit value. These measurements were made at the peak concentration time of the year in January and therefore it would be expected that during the summer period concentrations would be reduced.

Two runs were carried out at Sites 1 and 4 using equipment in the same positions. The second run was done at Site 1 as no overnight data was collected during the first run. For Site 4 a second run was done in order to collect roof, street and indoor data simultaneously. Unfortunately, the roof level monitors results were unreliable and therefore the results have not been included. Site 1 showed only a marginal decrease in outdoor concentrations as both runs were carried out in the non-heating season where ambient concentrations are considered to be lower and more stable, see

Figure 4.37. Site 4 on the other hand showed an increase of 10 ppb in outdoor concentrations which may be due to seasonal trends as run 1 was carried out in

December and run 2 was carried out in late March. Both outdoor runs showed concentrations which were well above the annual limit value of 21 ppb, although if night time reductions are included the averages decrease to 28.48 ppb for run 1 and 22.84 ppb for run 2. On review of the DCC/EPA NO_2 data for the year 2011 both Winetavern and Coleraine Streets recorded annual mean concentrations below the limit values of 13.8 ppb and 18 ppb respectively. The values recorded during the monitoring trials in early spring and winter were when concentrations are at their highest, therefore when averaged throughout the year lower values are returned. Interestingly, concentrations indoors seem unaffected by the reduction in outdoor concentrations and are 7 ppb higher during run 2 even though outdoor concentrations reduced by 10 ppb. This suggests a possible source within the building which was not present during run 1. Questioning of staff regarding new equipment etc, particularly in the small café resulted in no possible source. During both runs clear correlations can be seen between indoors and outdoors with their plots following the same trends with a strong lag visible in both.

Naturally ventilated buildings showed lower NO_2 concentrations indoors with the two naturally ventilated offices monitored during this study showing the lowest concentrations. One of these was an older damp building and it is suspected that the lower concentrations were due to heterogeneous reactions. The same happened at the other naturally ventilated office, while not as old as the first office also showed some signs of damp. These reductions were not seen in the naturally ventilated shops, possibly due to a higher number of air changes per hour caused by customers entering/leaving the shop opening the door. If these assumptions on the cause of these reductions are correct then unmonitored reaction products will be emitted which may cause other health issues. Damp increases the rate of heterogeneous reactions but encourages mould growth which is also detrimental to human health. Therefore, while naturally ventilated offices may be beneficial in one sense there are other risks associated with them.

4.2.5.1. Comparison with EPA/DCC annual data

Unlike the $PM_{2.5}$ data collected by DCC used earlier, NO_2 shows real time concentration fluctuations and therefore can be compared more readily with the data collected at the 10 monitoring sites.

Figure 4.37 shows the annual concentrations for two locations in Dublin city centre: one is the same location where $PM_{2.5}$ concentrations were monitored at Coleraine Street on the North side of the River Liffey and the second is on the South side of the river on Winetavern Street. Average annual concentrations at Winetavern Street are 34.4 ppb whilst at Coleraine Street the annual average is slightly lower at 26.4 ppb. Both sites exceeded the annual mean limit of 21 ppb with several breaches of the hourly limit of 105 ppb also visible. In winter months more exceedances of the hourly limit transpire, with only one occurring during the summer. The same pattern can be seen for the site data with higher concentrations visible during winter months when more combustion sources, heavier traffic due to unfavourable weather and natural diurnal cycles cause concentrations to be higher.

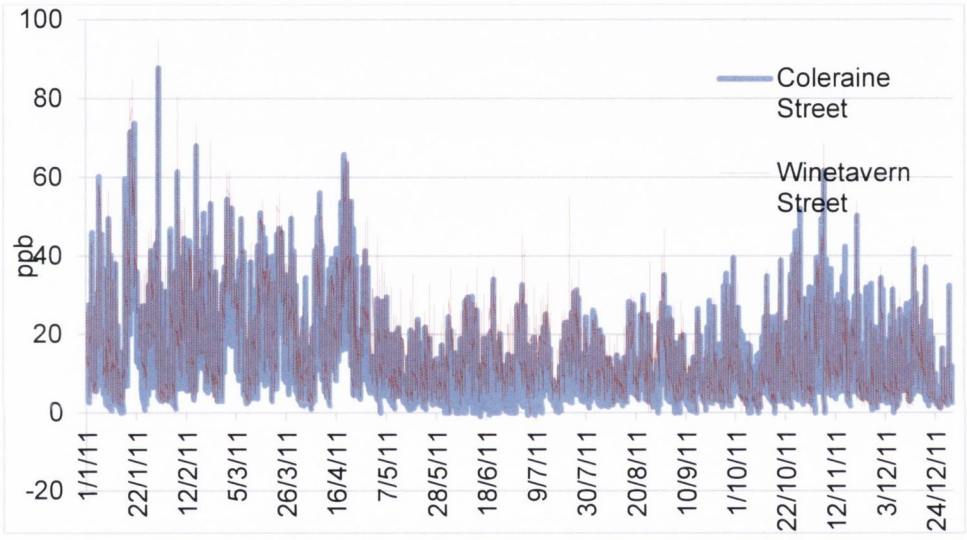


Figure 4.37 2011 NO_2 concentrations at Coleraine and Winetavern Streets

Many sites show close correlations with the data collected by the EPA/DCC. For instance, Figure 4.38 shows the comparison for Site 2 run 2. While concentrations at Winetavern Street were higher than at Site 2 during the day the same patterns can be seen with night-time concentrations, when local traffic sources are reduced, correlate particularly well.

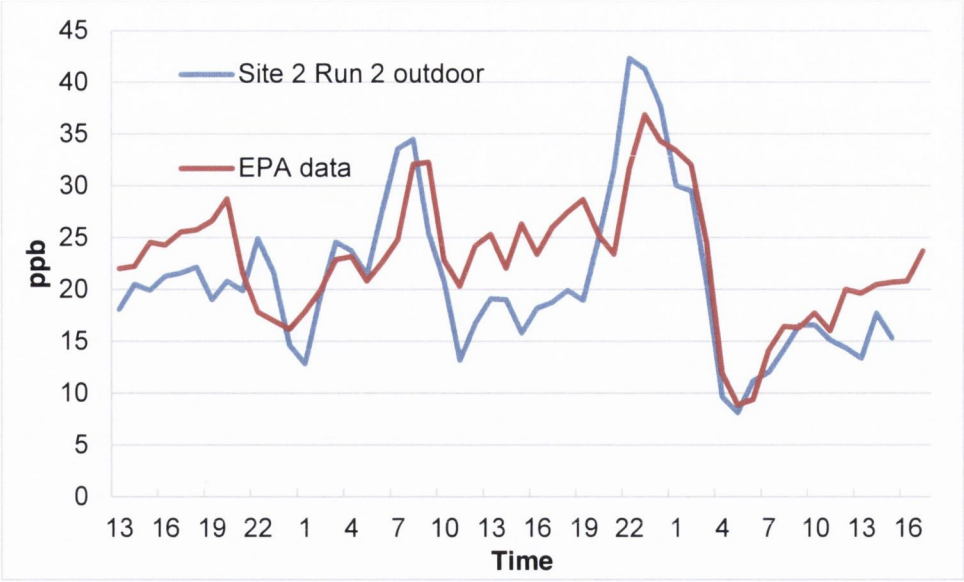


Figure 4.38 NO_2 concentrations - Site 2 run 2 versus EPA/DCC data

Site 3 produced two very different plots (see Figure 4.39 and Figure 4.40) when comparing the two runs with EPA/DCC data sets. Run 2, which were carried out at ground level, shows a strong correlation with similar peaks and dips in the data over the entire run. On the other hand run 1 shows what looks like a good fit for the first day of the run and after this some inconsistencies in the data sets emerge. Two significant spikes in NO_2 concentrations over several hours occur at Site 3 which is not matched by the EPA/DCC data. This may be due to a local source which increased concentrations in the area for a short time. The monitor's location next to the ventilation intake at this time is very close to the train line and less than a hundred metres from a station. Indoor data was checked for the same peaks in order to determine if these could be a result of an equipment malfunction and corresponding peaks were visible in the indoor data set although with an expected smoothing.

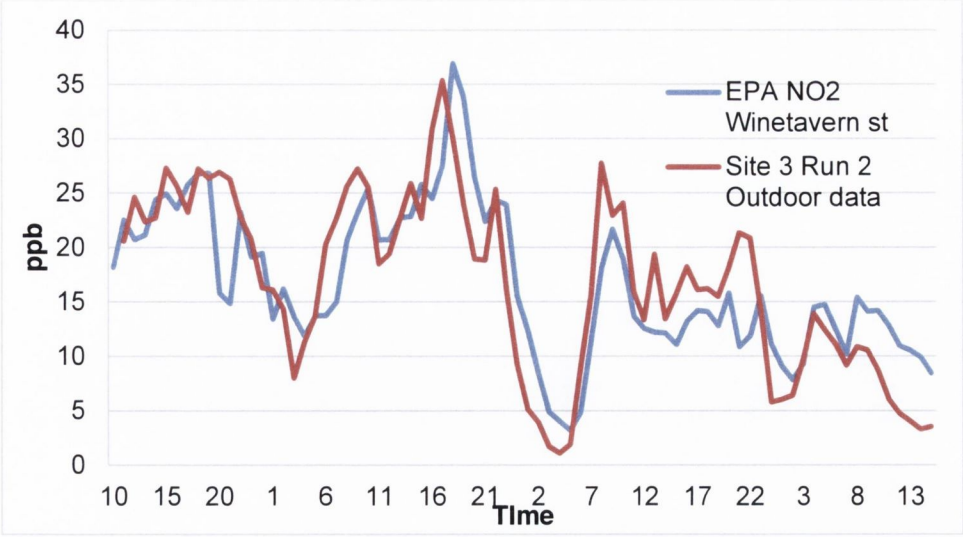


Figure 4.39 NO_2 concentrations - Site 3 run 2 versus EPA/DCC data

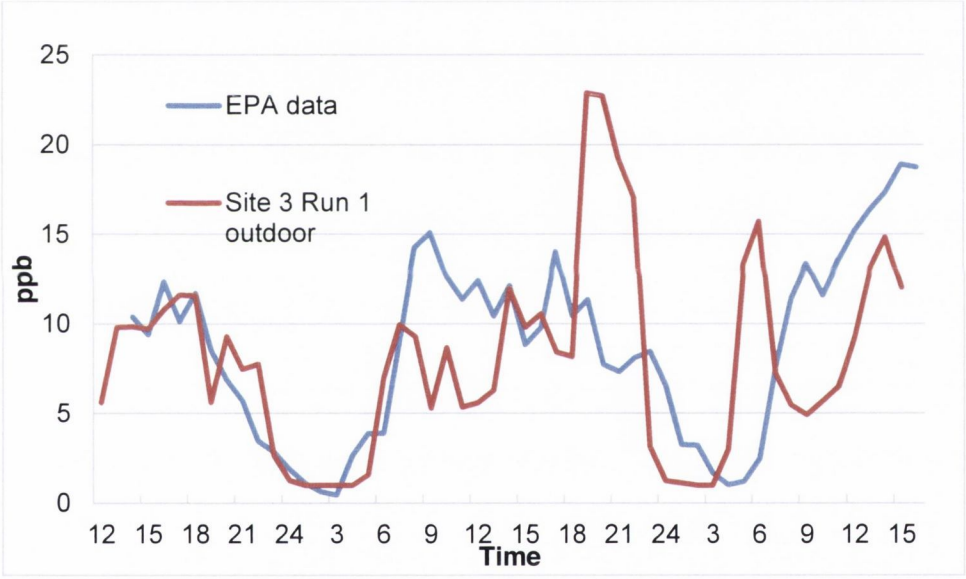


Figure 4.40 NO_2 concentrations - Site 3 run 1 versus EPA/DCC data

Site 5 as seen in Figure 4.41 shows a good correlation to Coleraine Street data but with some smoothing of peaks and overall lower concentrations. A 2 sample T-Test shows an estimate for the difference between data sets of 1.98 ppb and a 95% confident interval of (4.11 ,-0.15) and a P Value of 0.068. Site 5 is located further from the heavy traffic zones in which Winetavern Street is located and therefore the lower concentrations are expected during the hours when traffic is creating a local source of NO_2.

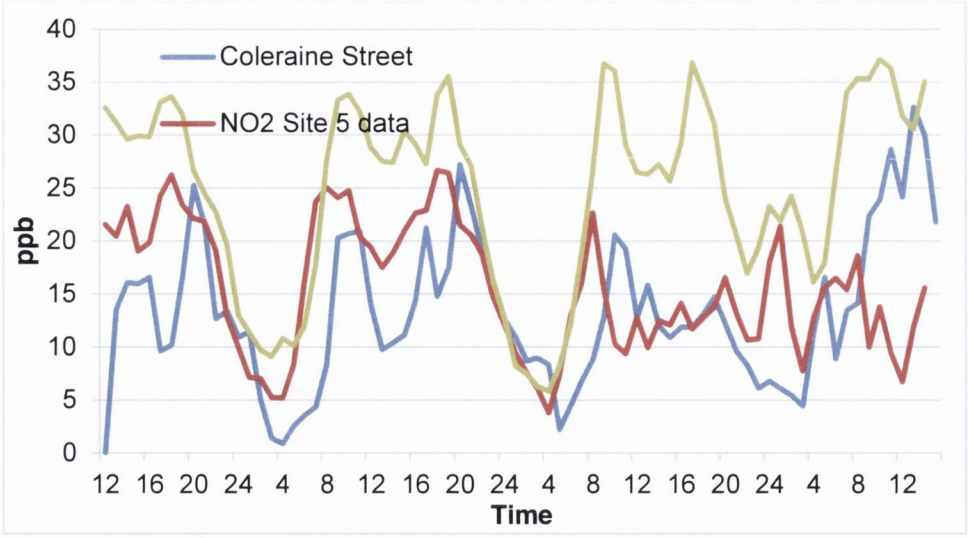


Figure 4.41 NO_2 concentrations - Site 5 versus EPA/DCC data

Figure 4.42 compares Site 7 outdoor data with the two EPA/DCC monitoring sites, showing a poor correlation between the 3 data sets. The pattern shown in the 3 locations differs significantly. Winetavern and Coleraine Street show an estimate of the difference to be 8.85 ppb in a 2 sample T-Test with a T value of 8.30 while, Coleraine Street and outdoor data at Site 7 give an estimate for the difference of 17.24 ppb and a T Value of 11.91) especially when it is compared to the high correlations seen at other sites (including Figure 4.38 for Site 2 run 2 versus EPA/DC data). The data from Site 7 shows a strong diurnal pattern while the two EPA/DCC Sites show a weaker (Winetavern Street) or no (Coleraine Street) pattern. During the monitoring period the Coleraine Street monitor reported several periods of 'no data', this may indicate the equipment had failures and could explain the unusually low data set. High levels of traffic on Pearse Street for the week in which monitoring took place explains the high peaks seen at Site 7.

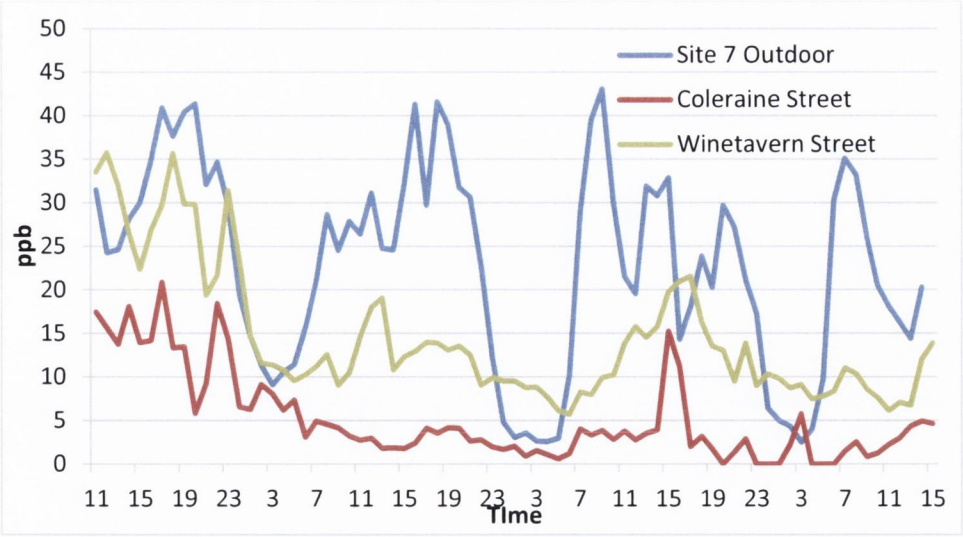


Figure 4.42 NO_2 concentrations - Site 7 versus EPA/DCC data

When all sites are reviewed a strong relationship between EPA/DCC monitored data can be viewed. Real time data allows better comparisons to be made than with $PM_{2.5}$ and at many sites this proves valuable as averaged concentrations may seem different but when plotted it can be seen that very similar trends are followed at various locations across the city. Such an instance occurs in

Figure 4.42 where Winetavern Street produces lower peaks during the day due to local traffic sources than the data from Site 10 run 1, but it is clear there is still a strong correlation between the two data sets with a R^2 of 0.686.

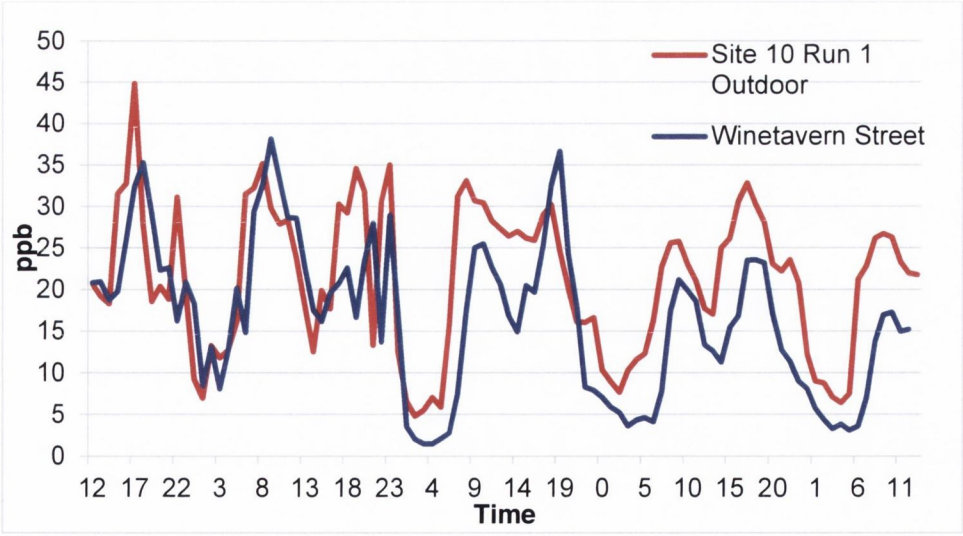


Figure 4.43 NO_2 concentrations - Site 10 run 1 versus EPA/DCC data

4.2.6. Background NO_2 at night

An interesting feature from the data at many sites was indoor background concentrations overnight for NO_2 of 10 to 12 ppb particularly for the mechanically ventilated sites, even when outdoor concentrations were much lower. At night, outdoor NO_2 concentrations drop significantly to levels close to 0 ppb but this was not seen for inside of most of the buildings studied in this research as shown in Figure 4.44. These background concentrations may be due to the reduced air changes per hour overnight which prevent concentrations which were higher during the day being replaced with cleaner air. Naturally ventilated buildings are often less sealed in order to allow natural air changes and this may explain why the background concentration was not as consistent within these buildings. Sinks for NO_2 that were present during the day such as UV light (supplied through artificial lighting or via windows/skylights) and heterogeneous reactions (Nazaroff and Cass, 1986)) would not have been present overnight, and therefore while the conditions outdoors were conducive to reductions in the NO_2 concentrations the same was not seen indoors.

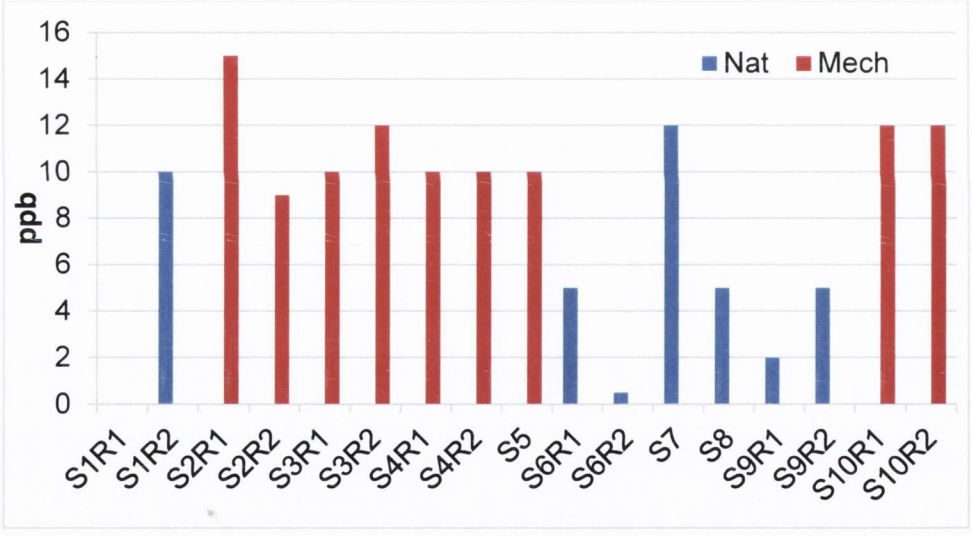


Figure 4.44 Average NO_2 background night-time Indoor concentrations

4.3. Influence of meteorological factors on Indoor/outdoor relationship

In order to find the influence of meteorological factors on the relationship between indoor and outdoor air quality it was decided to carry out best subset regressions using the statistical software package *Minitab*. Best subset regressions consider all possible combinations of predictors to find the best set in order to predict a variable. In this case they are being used to show the meteorological conditions which influenced the indoor concentrations of pollutants at individual sites. For the regressions the available free

predictors were temperature, relative humidity, pressure, wind speed, wind direction, global radiation, stability class and rainfall. A fixed predictor of the outdoor concentrations was also included but this was automatically included in each subset. When choosing the predictors to use it was decided to use the combination of predictors which gave an R^2 above which the addition of extra predictors did not significantly increase. For instance for Site 4 run 2 for $PM_{2.5}$, the best subset of predictors included three free variables (rainfall, temperature and relative humidity) to give a R^2 of 43.5 %. The addition of all 5 other free predictors only generated an R^2 of 46.4 %. Therefore it can be concluded that rainfall, temperature and relative humidity are the most important of the meteorological conditions to consider when reviewing Site 4 run 2 with respect to $PM_{2.5}$.

In general NO_2 showed much higher R^2 and required less predictors within each regression to achieve these high R^2, see Table 4.4 and Table 4.5. Barometric level pressure and relative humidity were predictors which occurred in the best subset for both NO_2 and $PM_{2.5}$ with temperature and wind speed also being commonly used predictors. Site 6 required the most predictors for both NO_2 and $PM_{2.5}$, requiring 6 predictors for both pollutants.

4.3.1. Best subset regression predictors for NO_2

Site 6 run 1 was the only site which found an R^2 below 50 %, with an R^2 = 35.7 %. From reviewing the predictors there is an indication that naturally ventilated buildings required input from a greater number of predictors compared to mechanically ventilated buildings. On average naturally ventilated buildings required 4.14 predictors while mechanically ventilated only required 2.75. From amongst the naturally ventilated buildings the office buildings required more predictors and had lower R^2 values, 60.45 % compared to 68.86 % respectively. Pressure and wind speed were the two factors which were used in the regressions of the most sites with rainfall only being required for prediction at 2 sites. The site which shows the greatest R^2 is Site 2 run 2 which also only requires 1 predictor, relative humidity. The high R^2 is mainly due to the very high R^2 between indoor and outdoor concentrations (79.5 %), with relative humidity contributing the final 11 % to the R^2.

Reviewing one of the lower correlations of 57.4 % at Site 8 and breaking it down, it was found that relative humidity had an R^2 = 45.1% while outdoor concentrations only returned an R^2 = 0.01 %. If temperature, pressure, wind speed and wind direction are used to predict indoor concentrations an R^2 = 57.4 % can be reached. Site 6 returned one of the lowest and highest R^2 values for NO_2, Relative humidity is a high predictor

for indoor concentrations during both runs at Site 6 contributing 41 % to the R^2 during run 2 and 20.1 % during run 1.

Table 4.4 Best subsets regressions predictors for NO_2

	Temp	RH	Press	Wind SPD	Wind Dir	GlobRad	StabClass	Rain	R^2
S1R2	x	x				x			78.6
S2R2		x							90.5
S3R1	x		x	x					81.9
S3R2		x	x	x	x				76.8
S4R1			x	x			x		72.6
S4R2			x	x	x		x		50.5
S5R1				x	x				81.5
S6R1	x	x	x	x		x		x	35.7
S6R2		x		x	x		x		72.0
S7R1			x	x		x			70.6
S8R1	x		x	x					57.4
S9R1	x					x	x	x	66.9
S9R2	x	x	x	x	x	x			67.2
S10R1		x			x				62.0
S10R2	x		x		x				73.5

4.3.2. Best subset regression predictors for $PM_{2.5}$.

Similar to the NO_2 results, the naturally ventilated sites required more predictors than mechanically ventilated sites to provide the best subset, 4.14 and 3.37 respectively. The average R^2 was close for both mechanically ventilated sites (28.7 %) and naturally ventilated sites (29.3 %) although both were less than 30 %, indicating that outdoor concentrations combined with meteorological factors were poor predictors of fluctuations of indoor concentrations of $PM_{2.5}$. The highest R^2 found was 46.2 %, which is a reasonable to poor prediction and only 10 % higher than the worst NO_2 prediction. Temperature and relative humidity were the predictors which were present highest

number of best subsets regressions as shown in Table 4.5, with stability class and wind direction being the two predictors found in the least subsets. The sites which showed the highest R^2 were those which required the least predictors, such as Site 9 or Site 2.

Reviewing in more detail at Site 6 weather data was found to have little influence. Regressions for run 1 found the highest R^2 = 25.3 % when temperature, wind speed, global radiation, relative humidity and outdoor concentrations were used as predictors of indoor concentrations. During run 2 relative humidity, pressure, wind speed and stability class were found to be the best indicators of outdoor concentrations. Their prediction is very weak with R^2 = 14.6 %, showing that indoor fluctuations of $PM_{2.5}$ are influenced very little by outdoor concentrations and weather conditions.

Table 4.5 Best subsets regressions predictors for $PM_{2.5}$

	Temp	RH	Press	Wind SPD	Wind Dir	GlobRad	StabClass	Rain	R^2
S1R2	x	x		x		x			11.7
S2R2	x	x	X						30.5
S3R1		x	X	x	x		x		26.6
S3R2	x	x				x	x		31.7
S4R1	x			x	x				28.5
S4R2	x	x						x	43.5
S5R1	x	x				x		x	42.2
S6R1	x	x	X	x		x		x	25.3
S6R2		x	X	x			x		14.6
S7R1	x	x	X					x	46.2
S8R1	x	x	X			x			41.1
S9R1	x	x	X						43.8
S9R2	x				x		x	x	22.5
S10R1		x	X						11.1
S10R2			X	x	x				15.6

4.4. Conclusions

The initial analysis of the monitoring data at the 10 sites showed a wide range of variability between many of the sites. The plots in Section 4.2.2 showed a time series of each of the runs for both $PM_{2.5}$ and NO_2, with NO_2 generally producing a reasonably predicable diurnal pattern. $PM_{2.5}$ on the other hand tended to vary around a similar mean value both indoors and outdoors. There was a greater presence of a diurnal cycle for $PM_{2.5}$ outdoors with indoor concentrations proving less likely to reduce during non-working hours than outdoor concentrations. Indoor NO_2 concentrations did show a diurnal cycle but mechanically ventilated buildings tended to maintain a baseline level close to 10 ppb which they did not drop below even if outdoor concentrations tended towards 0.

Results showed that the correction for use of the nephelometer rather than the gravimetric $PM_{2.5}$ monitoring device only worked sensibly up to 60 $\mu g\ m^{-3}$ and above this it caused data concentrations to increase rapidly. Concentrations of this level were unusual but did occur at Sites 4 and 7, in which case the correction factor was not applied to concentrations above 60 $\mu g\ m^{-3}$ as it would skew the data more significantly than if it was applied.

Indoor concentrations of $PM_{2.5}$ tended to be higher and NO_2 lower at naturally ventilated sites. The lowest indoor concentrations of $PM_{2.5}$ were seen at Sites 5 and 10, both mechanically ventilated sites, although it should be noted that this may have been due to low outdoor concentrations rather than a strong filtration performance of the filtration system. An analysis of the indoor/outdoor ratios in Chapter 5 will investigate this further.

The naturally ventilated office Site 9 showed indoor $PM_{2.5}$ concentrations which were noticeably higher than outdoors, both for street and roof level outdoor concentrations. The concentrations decreased during the second monitoring run when a window within the room was opened in order to increase the air movement. Increasing the number of air changes however caused an increase in NO_2 concentrations, possibly due to a shorter time available for heterogeneous reactions on surfaces within the room. Site 6, a naturally ventilated office site, showed the lowest indoor concentrations of NO_2. While outdoor patterns were followed the indoor concentrations they were reduced significantly indicating a sink for NO_2 at the site. After investigation of possible sinks in the building it was decided that heterogeneous reactions were the likely cause of the low indoor concentrations. Damp conditions in the building would have extenuated such reactions; this will be discussed further throughout this thesis.

5. Analysis of Indoor/Outdoor Relationships

5.1. Introduction

The relationship between indoor and outdoor pollutant concentrations requires analysis using a variety of methods to gain a clear understanding of the processes the pollutants are undergoing. During this chapter this will be investigated by first reviewing the indoor/outdoor relationships of pollutants with a view to understanding how this relationship changes between mechanically ventilated and naturally ventilated buildings as well as during working and non-working hours. In the previous chapter the initial analysis showed a possible lag between outdoor fluctuations and the corresponding change in indoor data. In order to understand this, cross-correlations have been carried out in Section 5.3. To further understand NO_2 behaviour, the ratio of NO/NO_2 was assessed both indoors and outdoors at each site, in order to determine whether NO is being converted to NO_2 or vice versa as it enters the building from outside.

Once the relationships have been analysed, the final section of this chapter examines the pollutant dosage at the individual sites to a theoretical employee using known breathing rates for a sitting male. This allows a comparison to be made between the 10 buildings as to the most detrimental workplace for an employee's health with respect to NO_2 and $PM_{2.5}$.

5.2. Indoor/Outdoor relationships

5.2.1. Introduction

Indoor to outdoor relationships (I/O) are the indoor concentrations divided by the outdoor concentrations, see Equation 5.1.

$$\frac{I}{O} = \left(\frac{\sum_1^n C_i}{n}\right) \div \left(\frac{\sum_1^n C_o}{n}\right) = \frac{\overline{C_i}}{\overline{C_o}} \qquad \text{Equation 5.1}$$

Where:

C_i = Indoor concentration at a certain time step

C_o = Outdoor concentration at a certain time step

n = number of time steps

From a health perspective, a value below 1 is preferable, indicating that indoor concentrations are below outdoor concentrations. The I/O ratios were calculated using several different averaging periods and methods, but using I/O for the entire data series averaged for each run (rather than finding the I/O for each time interval and then averaging) resulted in the most sensible results i.e. they fitted both what other studies (Phillips et al., 1993, Wallace, 1996, Ní Riain et al., 2003) had found and what visual interpretation of the results indicated. Calculating I/O ratios for individual time steps, and finding the average, gave much higher results as lag times were not being accounted for using this method. The summary of I/O ratios shown in Figure 5.1 and Table 5.1 have been calculated using the total run average for indoor over outdoor including both day and night time values. The correction for Relative Humidity (RH) increases the I/O ratio significantly at all sites. Values of outdoor concentrations before correction for RH are higher, especially at sites where the RH was considerably above 60%. Indoor concentrations are not corrected, as RH rarely increases above 60% indoors and previous literature stated that this correction was only required outdoors(Ramachandran et al., 2003). After correction the concentration outdoors decreases and indoors remains the same, therefore, increasing the I/O ratio. In fact, at the six sites where indoor RH was measured constantly, no exceedances of 60 % were recorded. At sites where RH was not constantly measured, a check on RH was done several times a day which also never recorded RH above 60 %.

One disadvantage to using such ratios is they give no indication of the concentrations of pollutants, i.e. a high ratio does not necessarily mean a high indoor concentrations; it could indicate very low outdoor concentrations with slightly higher indoor ones. However, it does allow comparisons to be made between all sites equally, as it gives the percentage reduction of outdoor concentrations.

From the results below it can be seen that some sites give different results, with low I/O ratios for $PM_{2.5}$ and have little NO_2 reduction and vice versa. This may be due to sources indoors or filtration systems which remove particulates but not gaseous pollutants.

Table 5.1 I/O ratios - Total run averages

Site	$PM_{2.5}$	$PM_{2.5}$ RH	NO_2
S1R1	0.99	1.35	1.15
S1R2	0.83	0.58	1.04
S2R1	0.44	0.50	0.73
S2R2	0.70	1.02	1.11
S3R1	0.64	0.94	1.86
S3R2	0.48	1.00	1.13
S4R1	1.02	2.55	0.57
S4R2 Ground	2.24	4.13	1.02
S4R2 Roof	0.76	1.59	-
S5R1	0.59	1.28	1.03
S6R1	0.63	1.06	0.19
S6R2	0.56	0.92	0.05
S7R1	0.88	1.41	0.86
S8R1	0.45	0.85	0.63
S9R1	3.81	6.29	0.40
S9R2	1.44	2.64	1.12
S10R1	1.06	2.04	0.97
S10R2	1.16	2.72	1.51

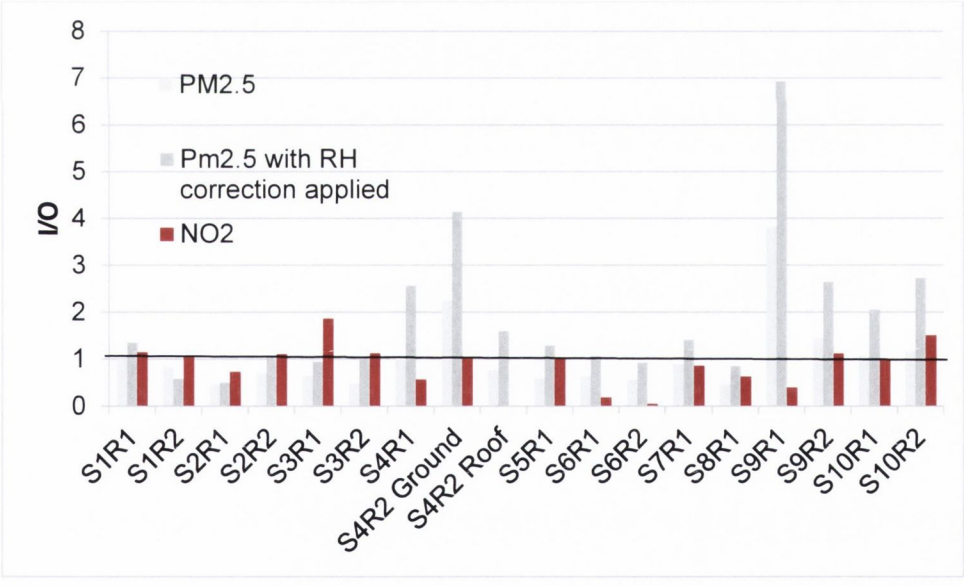


Figure 5.1 I/O ratios for $PM_{2.5}$ with RH correction, $PM_{2.5}$ and NO_2

5.2.2. Sites with I/O ratios significantly greater than 1

Fourteen I/O ratios were found to be greater than 1.3; two of these fourteen being for NO_2 and a much larger proportion (9/14) for $PM_{2.5}$ which had been corrected for RH. Five of these nine elevated $PM_{2.5}$ runs (Site 1 run 2, Site 4 run 1,Site 4 run 2 (roof), Site 10 run 1 and Site 10 run 2) did not have I/O

ratios significantly above 1 before the correction was applied. Two of the three different sites (Sites 10 and Site 4) were mechanically ventilated, both with new systems in place within the past ten years.

The 2 sites with I/O ratios greater than 1 for NO_2 were Site 3 run 1 and Site 10 run 2, where outdoor data was collected from roof level for both of these runs, i.e. near the ventilation intake. As the outdoor data collection location was at roof level, concentrations were lower than they would have been at street level which is one of the reasons why such systems are designed to draw in from the roof level. Both sites had ventilation systems in place with panel and bag filtration but neither ventilation system was designed to treat NO_2 e.g. with an electrostatic precipitator.

A slight elevation of 1.13 in I/O can also be seen for Site 3 Run 2 (when outdoor monitors were moved to street level) for NO_2, indicating a possible source within the building. If the ratios are divided into day and night for this run, the ratios change very little with night time showing a slightly more elevated ratio at 1.95 compared to the day time values of 1.80. Day and night time are chosen as the hours the building ventilation system is working, which were 7 am to 7 pm for this particular site. For run 2 a similar reduction in the I/O was found with day time being 1.10 and night time 1.21. Figure 5.2 shows the continuous time series plot of the I/O ratios for run 1 and 2 where highly elevated ratios can be seen for part of the non-working hours and it is these spikes which pull up the non-working hour ratios. This I/O above 1 points towards a attributed indoor source for NO_2 which grows in importance at night due to the decreasing value of outdoor concentrations. The reduction in the I/O between runs can be contributed to a reduction in the outdoor concentrations between roof and street level, with indoor concentrations staying relatively constant.

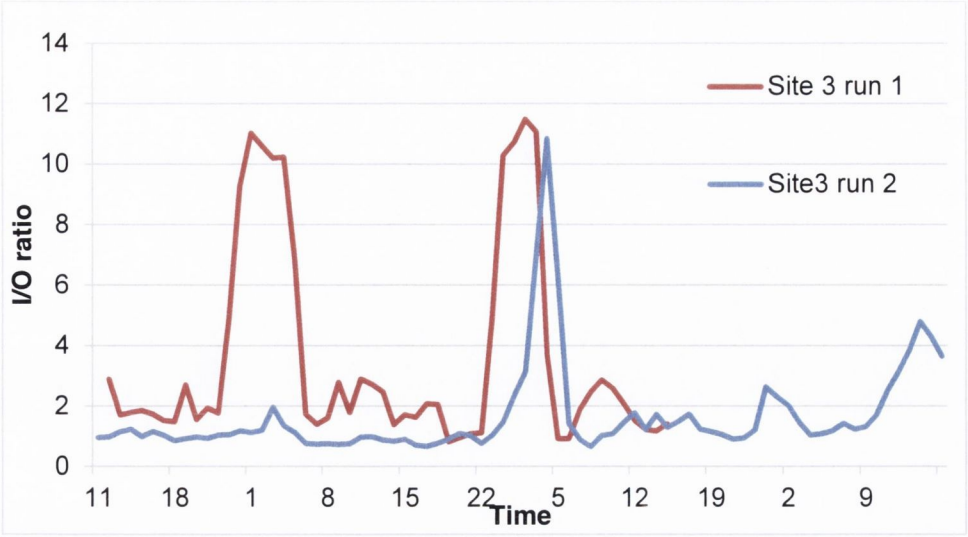


Figure 5.2 Indoor/Outdoor ratio NO_2 for Site 3 run 1 and 2

The other mechanically ventilated building with higher indoor concentrations compared to roof level was Site 10 run 2 with an I/O ratio of 1.51 for NO_2. It should be noted that the $PM_{2.5}$ concentrations were also higher indoors compared to outdoors with an I/O of 2.72 with the RH correction applied and 1.16 without it. The second run of monitoring saw long spells of precipitation with the lowest RH recorded at 69 % with a large proportion of the week experiencing RH above 80 %. Temperature, RH and pressure were also monitored at 5 minute intervals indoors throughout the two runs and the RH averaged at 38.19 % with no spikes above 55 %.

If the NO_2 ratios are broken down into working and non-working hours for Site 10 run 2, it is found that the day time I/O ratio is 1.59 and night time ratio is 1.45 indicating that the source present for NO_2 is stronger during the day and weakens at night. The I/O ratios are plotted for run 1 and 2 in Figure 5.3 which saw sharp spikes in run 2 during non-working hours indicating considerably reduced outdoor concentrations or spikes in indoor concentrations.

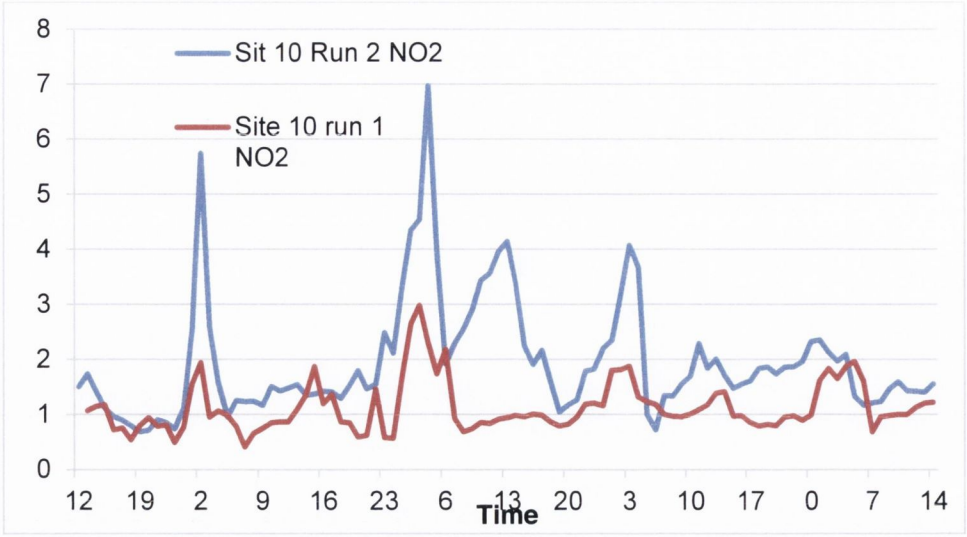


Figure 5.3 Indoor/Outdoor ratio NO_2 for Site 10 run 1 and 2

This building (a mechanically ventilated office which was refurbished in 2001) has no outstanding sources for NO_2, apart from printers and photocopiers, none of which was located on the floor in which monitoring took place. However, from the fact that the ratios are closer to unity (0.97) during run 1, this might indicate that street level pollution is a strong influence on the NO_2 concentrations for this building, especially as they follow similar patterns, as seen in Chapter 4. At this site the ventilation system runs 24 hours per day but during the daytime staff move into and out of the building allowing a higher air exchange with street level air. Investigation into the proportion of NO_2 in NO_x would indicate if this theory is valid, and this will be discussed below in Section 5.4. A closer relationship is also present for $PM_{2.5}$ during run 1 compared to run 2. During run 1 the baseline of the peaks is frequently at concentrations close to outdoor levels, the presence of a large number of pronounced peaks in indoor data causes the high I/O ratio. If no RH correction is applied the ratio is 1.06 and with a ratio applied the ratio rises to 2.04. These ratios should be significantly less than 1 as outdoor data has been monitored on a heavily trafficked street and reductions should have occurred by passing supply air though panel and bag filters, as well as those between ground and roof level.

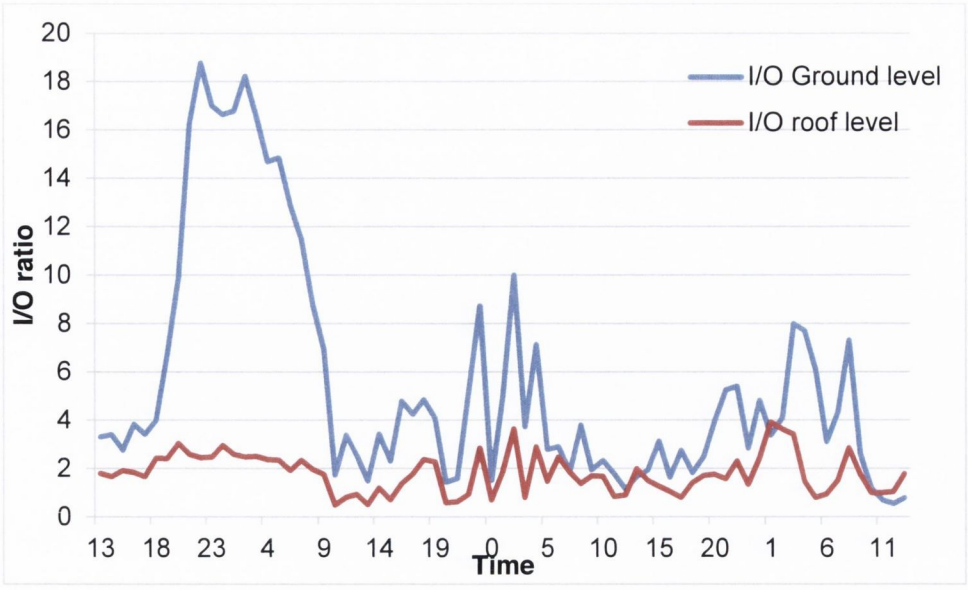


Figure 5.4 I/O ratios Site 4 Run 2 $PM_{2.5}$

Site 4 run 2 show one of the highest I/O ratio for $PM_{2.5}$ due to the unusually high concentrations on day two, as shown on Figure 5.4. If day two is excluded from data the I/O reduces to 2.07 with RH correction which is in a similar range to run 1 with an I/O ratio of 2.55. Although reduced, these ratios are still substantially above 1. In Section 4.2.4 where the elevated $PM_{2.5}$ concentrations were discussed, it was noted that no street level increase was seen but that roof level $PM_{2.5}$ concentrations were significantly elevated for a time during the run. Roof level concentrations were taken at the air inlet of the ventilation system and as the air was drawn into the ventilation system some reduction in $PM_{2.5}$ can be seen. This is a normal event as often street level concentrations would see sharp spikes due to traffic or other ground level sources e.g. road-works. As discussed before, the DCC/EPA data also recorded these spikes in data above normal ambient concentrations. If the I/O ratio from roof level concentrations is used, this gives an I/O of 1.59 with the RH correction. While this is still elevated at one and a half times the indoor concentration on average, it is significantly lower than using ground level concentrations, which gave an I/O of 4.13. Figure 5.5 shows that indoor data has considerable spikes from the evening of the first day of monitoring until the end of the second day. After this it settles to an I/O ratio of just above 1 when outdoor data is taken at roof level. As mentioned in Chapter 3, this building is used as an exhibition space where exhibitions change and construction work and movement of large items of equipment often occurs.

The space also has a large number of guests moving around the space which would cause high levels of re-suspension of particles left over from the construction of previous exhibitions. Site 4 also contains a small café in which food is prepared which could act as an indoor source of $PM_{2.5}$ and influence the increased ratios. This café operates from 8 am to 8 pm so while this could be a cause of the spikes, it is unlikely to have caused the first major spike as it was not open at that time. The first spike indoors and at roof level occurs with a 15 minute time delay indoors although if this data is corrected for relative humidity, the spike outdoors disappears as it coincides with a peak in outdoor relative humidity (Figure 5.6). Unfortunately no indoor relative humidity data is available for this run, which may have provided evidence that the spikes indoors were due to an indoor spike in humidity. The second major spike occurs when the ventilation unit was reengaged at 8 am and alongside a secondary spike in relative humidity outdoors.

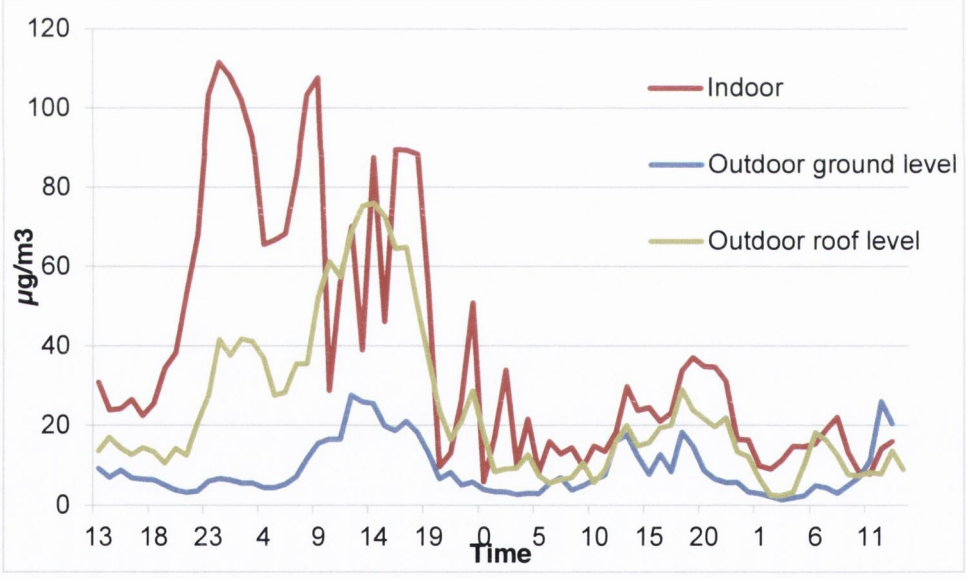


Figure 5.5 Site 4 run 2 $PM_{2.5}$

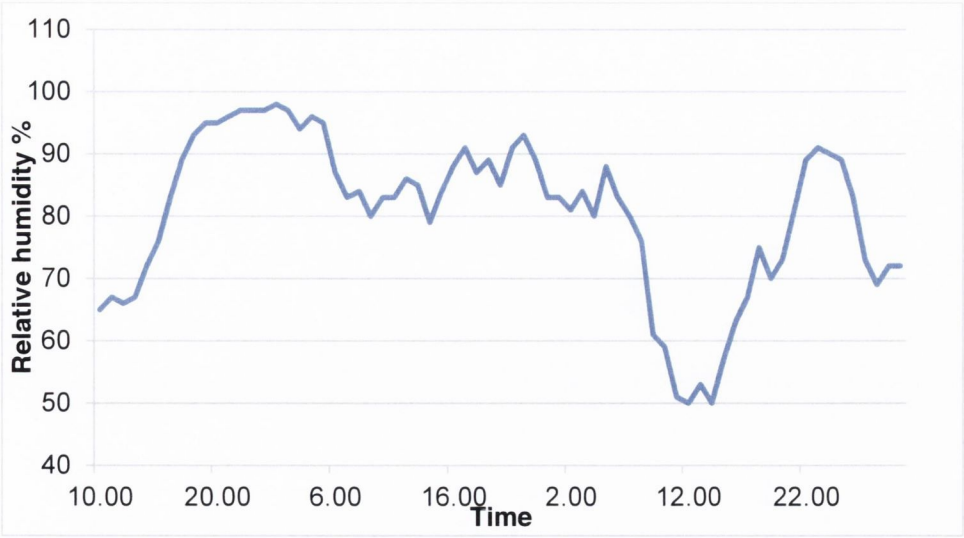


Figure 5.6 Site 4 run 2 outdoor relative humidity

The highest I/Os for $PM_{2.5}$ were recorded at Site 9 (a naturally ventilated office built in the late 1960s) where I/O ratios were elevated at both run 1, where outdoor monitors were at roof level, and run 2, where outdoor monitors were at ground level. An I/O ratio of 6.92, or 3.81 when RH is not corrected, was found when comparing concentrations on the roof and indoors during run 1. As well as a high I/O ratio, run 1 has a low correlation (0.39) between indoor and outdoor. Figure 5.7 shows the real time I/O ratio for Site 9 run 1 with the significant difference between the two monitoring locations clear. The plot also shows the increases in the ratio at the end of the week due to reduced outdoor concentrations. The office where monitoring was carried out indoors contained no source of $PM_{2.5}$ but as mentioned previously the room next door contained an elevator mechanism which may have been the source of $PM_{2.5}$ due to re-suspension and generation of particles from wear and tear.

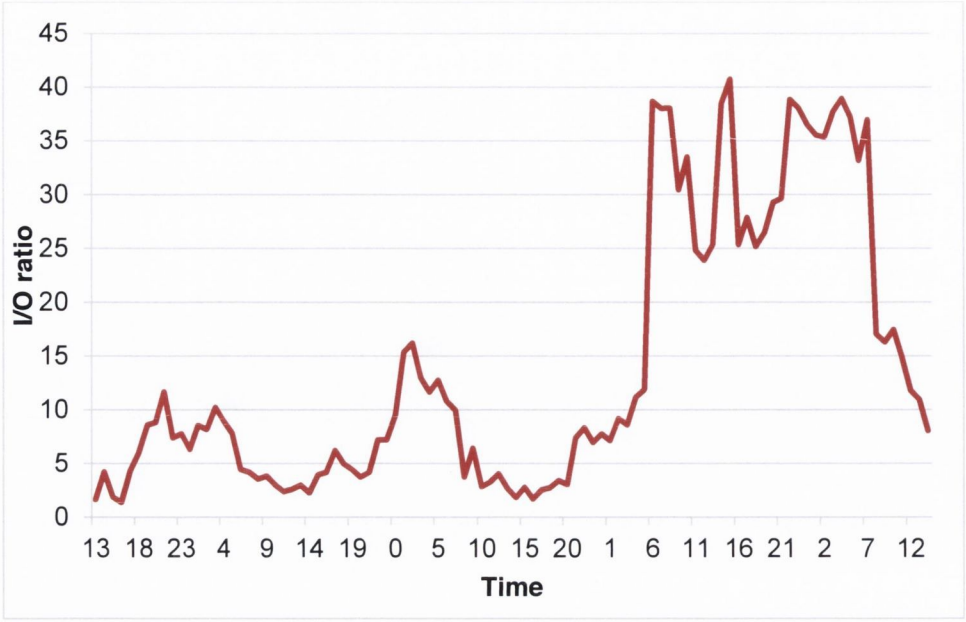


Figure 5.7 I/O ratios Site 9 run 1 $PM_{2.5}$

For the duration of run 1 the window to the office was shut which would reduce the air changes per hour within the office and hence influence the relationship between indoor and outdoor. This window was opened during run 2 resulting in increased air changes and greater fluxes in the data recorded. Outdoor concentrations were measured at the front door to the building during this run. Figure 5.8 shows both runs of data plotted on a single graph, indoor and outdoor data showing similar ranges with indoor concentrations considerably higher than outdoor for the two runs. The second run also saw greatly elevated indoor concentrations compared to the street level outside with I/O ratios of 2.64 when RH was taken into account, although this reduces to 1.44 if the RH correction is not applied.

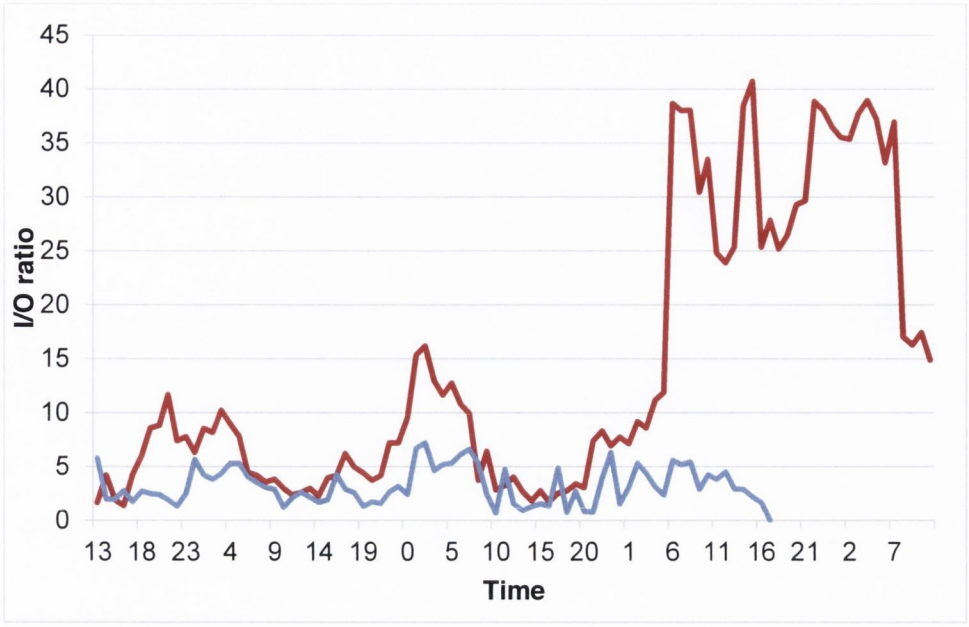


Figure 5.8 I/O ratios Site 9 run 1 & 2 $PM_{2.5}$

5.2.3. Sites with I/O significantly less than 1

As discussed in Section 4.2.5 Site 6 (a naturally ventilated office which was built over 100 years ago) showed highly significant reductions in NO_2 (as shown in Figure 5.9) throughout the two runs alongside reasonably good ratio in $PM_{2.5}$. This office had no system in place to reduce NO_2 although, due to the significant reductions it is suspected that something present in the building was causing the degradation of NO_2 most likely via heterogeneous reactions. Interviews with occupants and maintenance staff have been carried out in order to find the cause of the reductions. Previous work by Nazaroff and Cass (1986) found that different furnishings can significantly degrade NO_2 with further degradations occurring when RH is high indoors. These materials include carpets and glass which were present in Site 6.

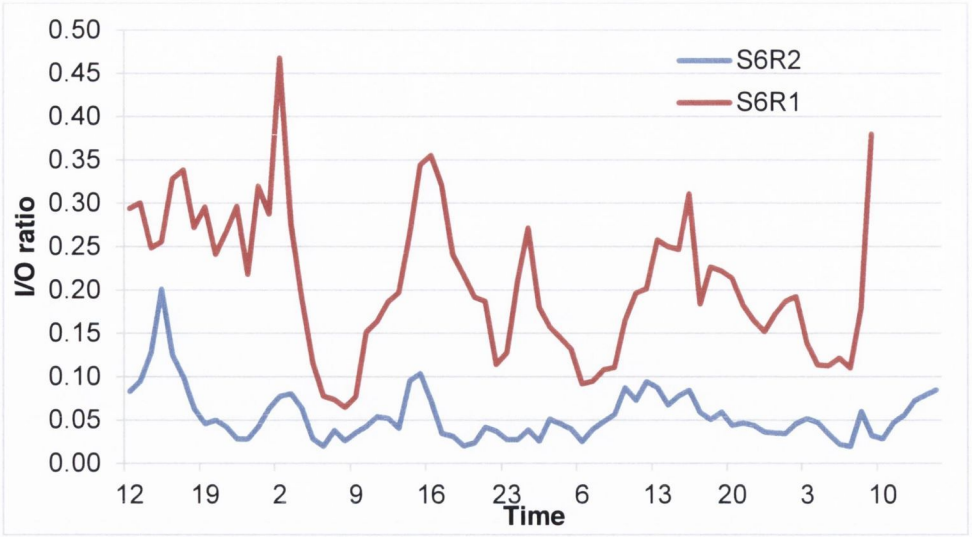


Figure 5.9I/O ratios Site 6 run 1 and 2

The reduction in I/O ratio between run 1 and 2 can be explained by amplified solar radiation which is known to increase heterogeneous reactions. The difference in radiation between run 1 and run 2 is shown in Figure 5.10, this data was provided by Met Eireann.

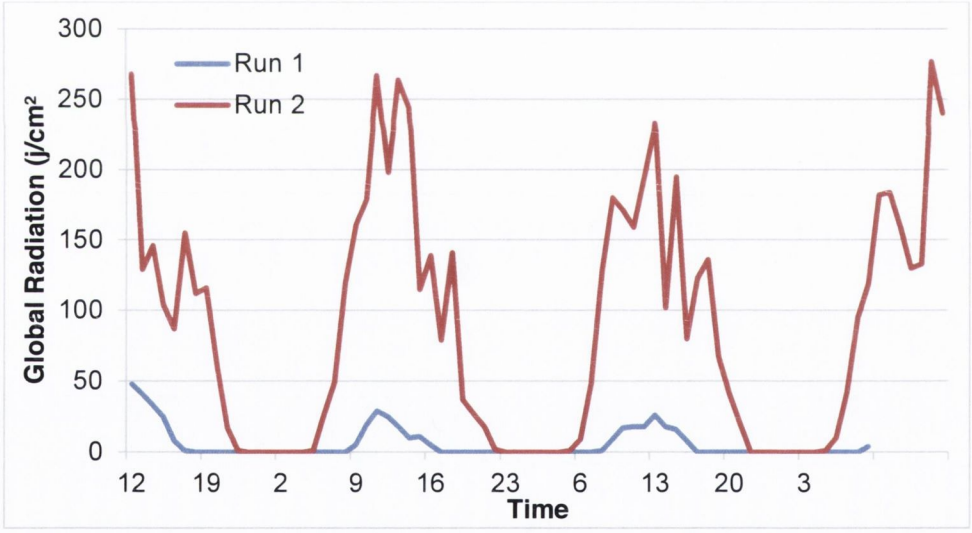


Figure 5.10 Global Radiation at Site 6 run 1 and 2

Site 2 run 1 gave good reductions for both NO_2 and $PM_{2.5}$ with ratios of 0.73 and 0.50 respectively. These ratios would possibly increase more if night time data was included but due to constraints set down by the building's occupier at the time of modelling this was not possible. It has been found that during the night time, concentrations outdoors at many sites reduce to a greater extent compared to indoors due to a lack of air changes indoors, thereby increasing the I/O ratio. This is investigated later in Section 5.2.4. Monitoring outdoors during run 1 occurred at street level and would have

contained a large amount of local sources due to a heavily trafficked road. However, in order to test the ventilation system's ability to remove pollutants run 2's results must be reviewed in Figure 5.11 showing the I/O ratio over the entire run.

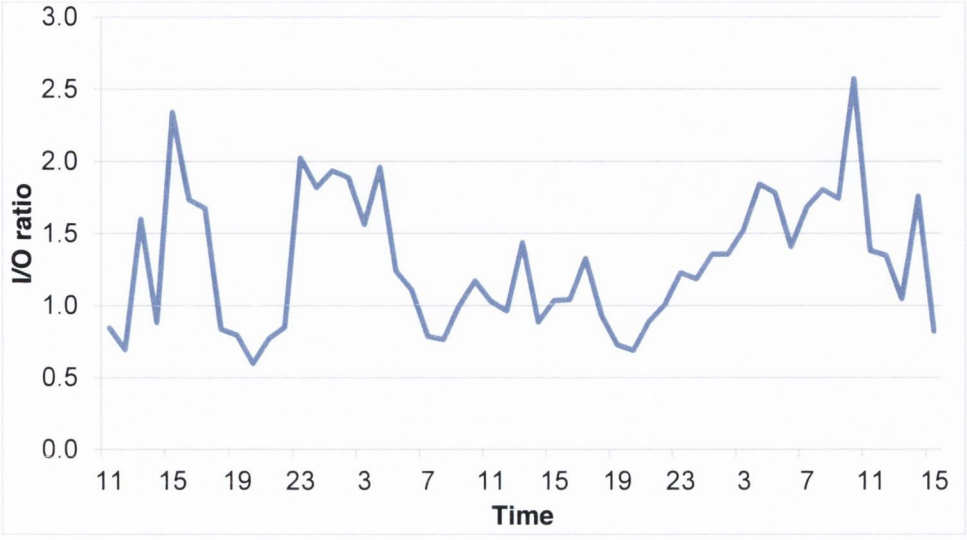


Figure 5.11 I/O ratio $PM_{2.5}$ Site 2 run 2

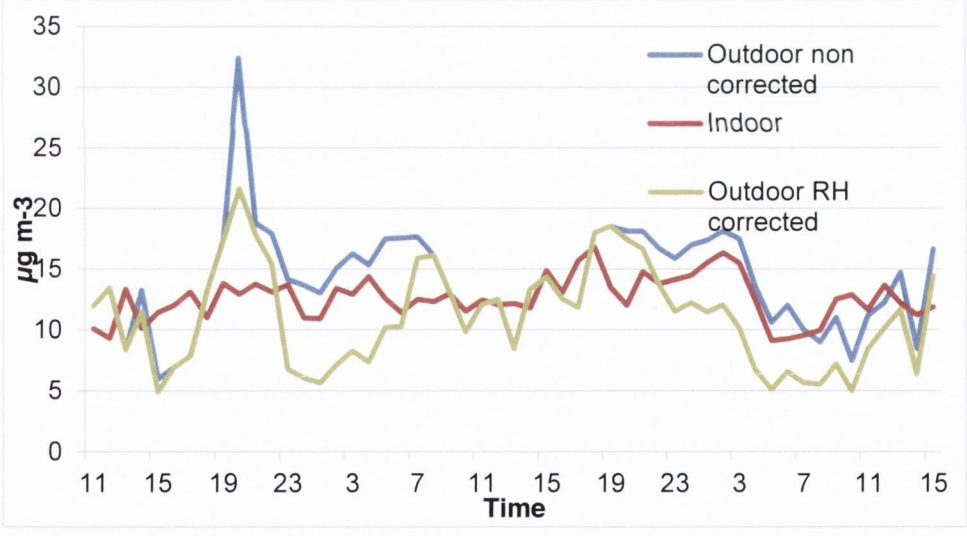


Figure 5.12 Indoor and outdoor $PM_{2.5}$ concentrations Site 2 run 2

During run 2 the outdoor monitoring occurred at roof level beside the air intake, the location of which is shown in Figure 5.13 marked by a circle. I/O ratios increased to 1.025 for $PM_{2.5}$ with RH correction, and 1.11 for NO_2, with peaks both during the working day and overnight. Overnight spikes in the I/O ratio are common due to greater decreases in outdoor concentrations compared to indoors. This is what caused the working hours spikes in the I/O ratio. The reductions in outdoor concentrations with no associated reductions indoors can be seen in Figure 5.12. The corrected

data for RH caused the noteworthy spikes at night, as it reduced outdoor concentrations from above indoor to below indoor concentrations. Day time spikes are not caused by outdoor data being reduced due to relative humidity, as corrected and non-corrected outdoor data are closely related at these times. These may simply have been caused by outdoor reductions in $PM_{2.5}$ concentrations. The intake for the ventilation system located on the far side of the building to the road is partially shielded from the road by the room which contains the ducting. The white unit which can be seen in the picture is the coolant system which was added in 2006 and used to reduce temperature of intake air for warm summer months as staff had complained of rooms being too warm. The room where monitoring occurred was a canteen equipped with a gas cooker and although it was out of term time (and therefore less busy), the canteen was open for business during monitoring. The combination of the cooking source and a low number of air changes per hour due to infiltration of street level pollutants could easily yield I/O ratios above 1. The canteen at the monitoring site stretched the entire width of the building with a number of poorly sealed windows at the back and front of the building which allowed pollutants to enter the building through infiltration.

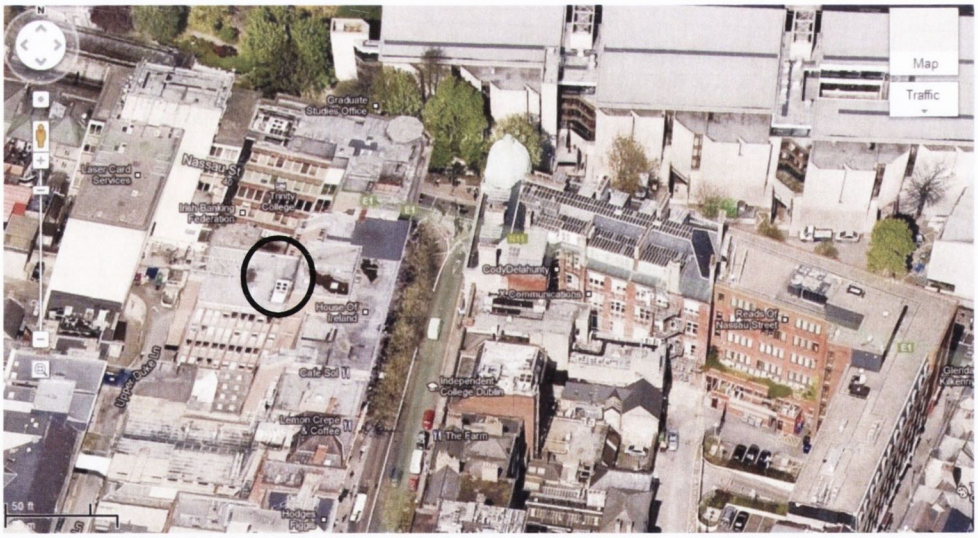


Figure 5.13 Location of air intake at Site 2

Site 4 (a mechanically ventilated building which was opened in 2007) produced very different I/O ratios for NO_2 compared to $PM_{2.5}$. The NO_2 I/O ratio across run 1 was 0.57 compared to 1.02 for run 2. During both runs a strong connection to the outdoor trends can be seen with similar patterns showing a level of smoothing and a short time lag (Figure 5.14). The ratio

is much higher for run 2 which may be due to seasonal changes in data, although reviewing Figure 5.14 shows that whilst outdoor data was significantly decreased for time periods (e.g. day 3) the pattern of the data indoors shows a greater overall increase in run 2. The time in which this increase is present indicates a strong indoor source. A strong connection can be seen between indoors and outdoors, which is partially evident on day 3 during run 2 when a sharp dip occurs outdoors at roughly 9 am.

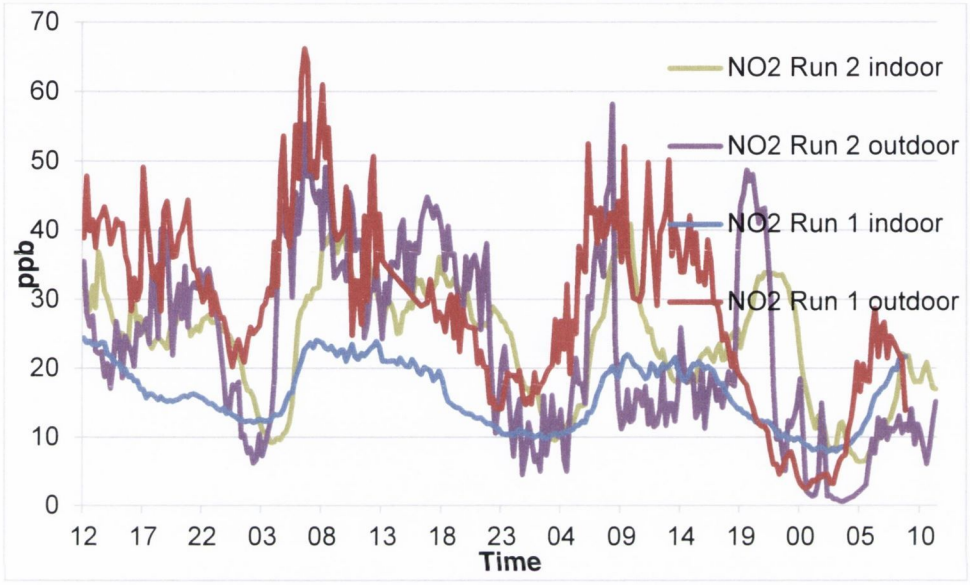


Figure 5.14 Site 4 run 1 and run 2 NO_2

The final noteworthy low I/O ratio is seen at NO_2 at Site 9 where a ratio of 0.40 was seen for run 1 when outdoor monitors were at roof level, although it should be noted that no ventilation system is in place at this site and therefore roof level concentrations are only useful to compare with air which can infiltrate through the office's poorly sealed windows. However, this comparison still produces one of the lowest I/O ratios. During run 2 the window in the office was open significantly increasing the I/O ratio to 1.12, with an increase in the average indoor concentration by 6 ppb (Figure 5.15). Outdoor monitoring during run 2 was carried out at street level just outside the door to the building and seemed to show little correlation to the indoor data collected. It did however show a similar pattern to the EPA/DCC data recorded at the Rathmines station. A best subsets regression was carried out showing that an R^2 = 67.2 % of indoor data concentrations can be explained by the variables: relative humidity, wind speed, wind direction, global radiation, temperature and outdoor data. Only 1.4 % of the indoor

concentrations can be explained by outdoor concentrations, if a regression is calculated with relative humidity as the only predictor of indoor concentrations R^2 increases to 28.6 %. The roof level data taken during run 1 produces provides a much better indication of the indoor concentrations (R^2 = 26.7 %), which it could be assumed would have been increased if the office window was also open during run 1 due to a higher number of air changes per hour. Meteorological variables had a lower influence on indoor air quality during run 1 than with run 2 with the highest R^2= 59.7 % when all available meteorological variables are used in a regression to predict indoor concentrations.

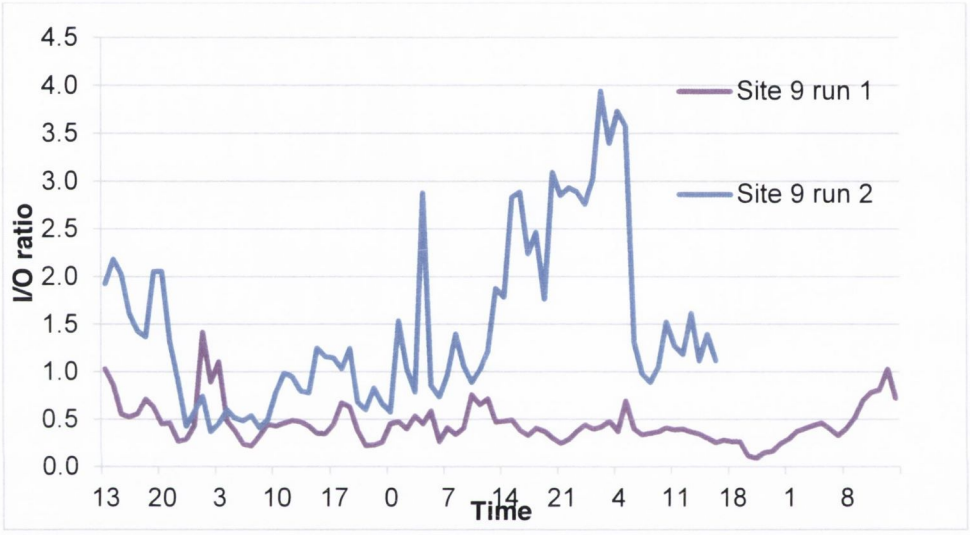


Figure 5.15 I/O ratio NO_2 Site 9 run 1 and 2

5.2.4. I/O ratios during working and non-working hours

The ratio of indoor to outdoor concentrations increased during non-working hours for many sites. For this reason an investigation into the difference of I/O ratios between working and non-working hours was carried out. The working hours and non-working hour's ratios for both studied pollutants are contained within Table 5.2.

Table 5.2 I/O ratios for working and non-working hours

I/O ratios	Working hours		Non-working hours	
	$PM_{2.5}$	NO_2	$PM_{2.5}$	NO_2
S1R2	1.72	1.14	1.27	0.52
S2R1	0.50	0.73	-	-
S2R2	1.26	1.25	0.90	0.83
S3R1	0.72	1.80	1.47	1.95
S3R2	0.86	1.04	1.24	1.19
S4R1	2.12	0.55	3.48	0.51
S4R2	2.81	1.05	8.26	1.02
S4R2 roof	1.29	-	2.09	-
S5R1	1.13	0.93	1.37	1.13
S6R1	0.77	0.27	1.36	0.16
S6R2	0.79	0.18	1.00	0.04
S7R1	1.66	0.81	1.14	0.92
S8R1	0.72	0.82	0.89	0.47
S9R1	4.69	0.49	9.22	0.49
S9R2	1.96	1.13	3.23	1.11
S10R1	1.36	1.02	2.98	0.94
S10R2	1.73	1.60	3.60	1.45

In order to compare the difference between working and non-working hour's ratios at each site, two column plots were carried out placing the working and non-working hour's data side by side in Figure 5.16 and Figure 5.17. The most striking feature of these plots is the I/O ratio for Site 4 run 2 at ground level and Site 9 run, both for $PM_{2.5}$. The I/O ratio for Site 4 of 8.26 was due to increased indoor concentrations which have previously been discussed. At Site 9 the increased ratio of 9.22 during non-working hours is due to outdoor concentrations reducing while indoor concentrations increasing. This further extenuates the elevated I/O ratio of 4.69 seen during working hours.

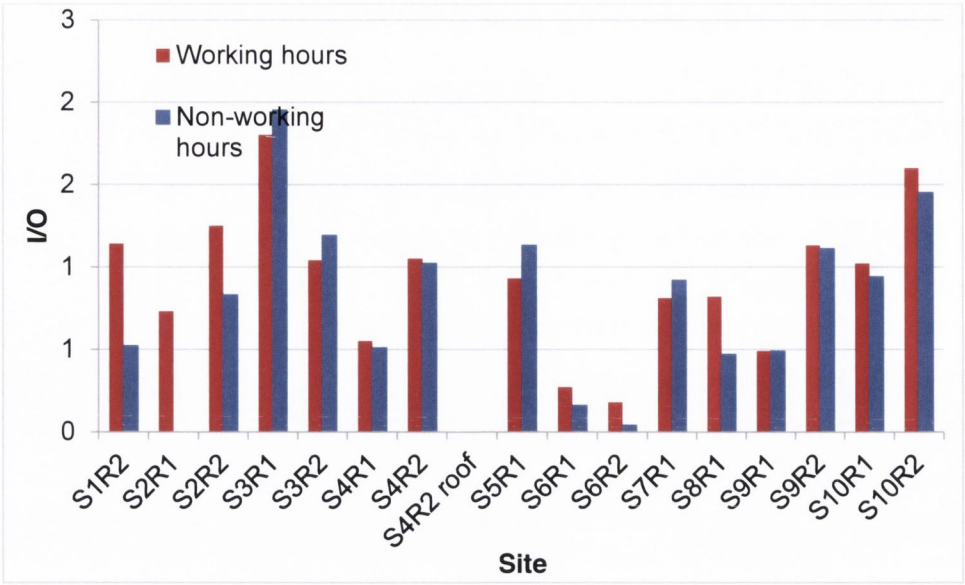


Figure 5.16 NO_2 I/O ratios working and non-working hours

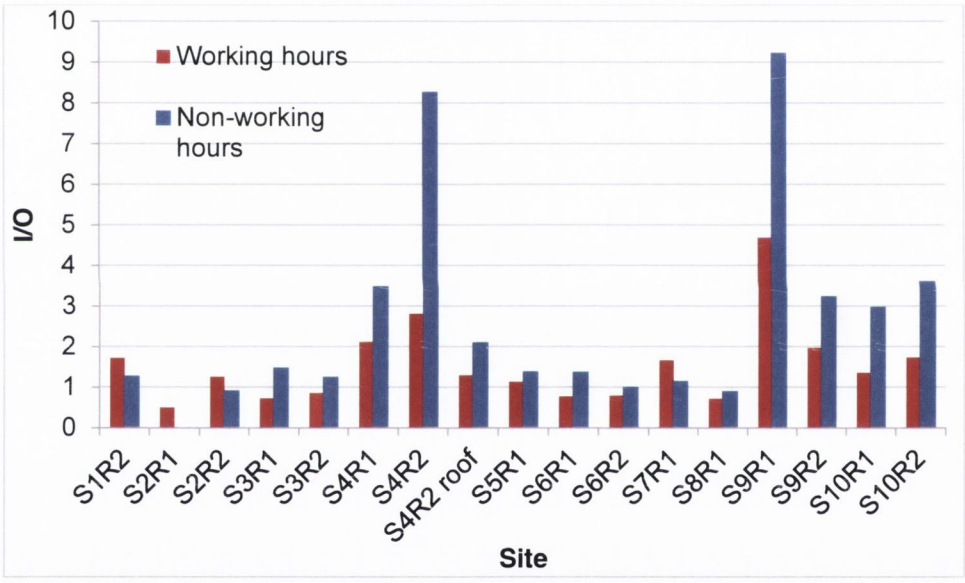


Figure 5.17 NO_2 I/O ratios working and non-working hours

10 of the 16 runs in Figure 5.17 show I/O ratios of $PM_{2.5}$ which are higher during non-working hours, compared to only 4 out of 16 for NO_2 as shown in Figure 5.16. Evidence is seen at many sites of a baseline level of NO_2 during non-working hours close to 10 ppb, while concentrations outdoors reduce to near zero. This contradicts what is seen in the I/O ratios, where only 4 out of 16 runs found average non-working hours concentrations indoors to be higher than outdoors. On investigation the lower ratios for NO_2 may be caused by the initial spike in NO_2 concentrations which occur at sunrise, this influences indoor concentrations, but usually with a slight

lag as the offices and shops have not opened so air changes are lower than during working hours.

As an example Site 10 run 1 is investigated to see if this is the case, with a plot of only non-working hours seen in Figure 5.18. On nights 2, 3 and 4, indoor concentrations were higher than outdoors for several hours, roughly midnight to 4 am. This is due to reductions outdoors which indoor concentrations do not react proportionally to and once the baseline indoor concentration is reached (12 ppb for this site) indoor concentrations fail to drop further. A very short time lag is seen at this site for the sharp spike in NO_2 which occurs in the morning with sunrise. Note: this site was monitored in January so sunrise occurred significantly later than during summer months. For Site 10 run 1 concentrations from the closing of the building to midnight keep the I/O ratio lower than expected for non-working hours.

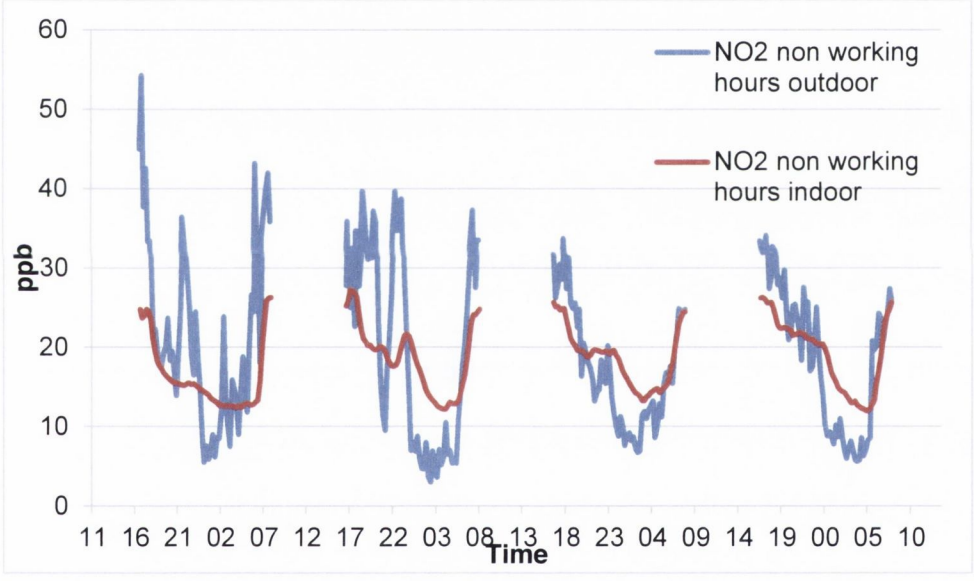


Figure 5.18 Indoor and outdoor NO_2 Site 10 run 1 non-working hours

3 sites show particularly higher NO_2 I/O ratios during working hours compared to non-working hours: Site 1 run 2, Site 2 run 2 and Site 8 run 1. Site 2 has an indoor source of a gas cooker which, combined with outdoor concentrations being measured at roof level for run 2, explains the higher ratio during working hours, when the gas cooker was in use. When the time series for Site 1 run 2 was reviewed in Section 4.2.2 indoor concentrations were greater than outdoor concentrations for 2 of the days monitored with the other 2 days showing an I/O ratio of unitiy. As the opening hours of this business are 10 am to 5 pm, members of staff are not generally present for

the worst effects of morning and evening rush hours on outdoor concentrations, which are higher than indoor concentrations at these times. The final site showing a considerably higher I/O ratio during working hours compared to non-working hours is Site 8. This site shows outdoor data with several sharp spikes but also reductions to just under indoor concentrations and overall very noisy data compared to other NO_2 data plotted. The noise in the data may affect the I/O ratio as lags between peaks indoors and outdoors are not taken into account during these calculations. Note, lag times will be discussed in the next Section 5.2.5.

Reviewing the differences of working and non-working hours' ratios for $PM_{2.5,}$ three sites are outstanding: Site 4 run 2, Site 9 run 1 and 2 and Site10 run 1 and 2. All were noteworthy due to significantly higher ratios during non-working hours compared to working hours. At Site 9 the increased I/O ratios during run 1 and 2 for working hours is clear yet this ratio further increases during non-working hours. This diurnal pattern creates a greater difference between indoor and outdoor concentrations during non-working hours therefore increasing the I/O ratio. This site previously noted an indoor source of $PM_{2.5}$ and very low concentrations of outdoor $PM_{2.5,}$

Site 10 showed ratios doubling over non-working hours compared to working hours. This is caused by substantial peaks recorded indoors in the evening after working hours. No associated peaks were found outdoors indicating that this increase may be due to an indoor source rather than increased outdoor traffic.

In summary it can be seen from the analysis of I/O ratios that $PM_{2.5}$ showed more exceedances of the I/O ratio key value of 1unitiy, above which the ratio implies that average indoor concentrations are higher than average outdoor concentrations. Greatest I/O for NO_2 were found when monitoring was carried out at the ventilation intake and compared with indoor results which indicated either an indoor source for NO_2 or that the influence of street level concentrations is important even in buildings with mechanical ventilation systems. This is evident at both Site 10 and Site 3, which are both recently constructed mechanically ventilated offices.

One of the major finds when reviewing individual time step I/O's was the considerably increased ratios overnight compared to during the day. This was due to concentrations outdoors decreasing to a greater extent outdoors compared to indoors. These increases were not evident in the averaged

working hours and non-working hours I/O ratios as concentrations just after closing and just before opening were often higher outdoors. The peaks in individual time steps for I/O ratios usually occurred within the hours of 12 am and 6 am, therefore only occurring over a portion of the non-working hours I/O ratios.

Some of the highest I/O ratios were seen for Site 4 run 2 $PM_{2.5}$ (a recently built mechanically ventilated building); this was due to sharp spikes being recorded indoors and at roof level but no such spike recorded at ground level. This one monitoring run was the only opportunity to record at all 3 locations simultaneously which was fortunate in this circumstance as it indicates the source of the $PM_{2.5}$ spike was possibly due to an airborne roof level source rather than a street level source such as traffic. While Site 4 run 2 showed high peaks, Site 9 showed consistently higher indoor concentrations of $PM_{2.5}$ compared to outdoors.

Site 6, a naturally ventilated office showed significant reductions in the I/O ratio for NO_2, which is suspected to be due to heterogeneous reactions. Interestingly, several of the naturally ventilated older buildings saw good reductions for indoor concentrations compared to outdoors.

5.2.5. I/O corrections using logs and normalisation

Overnight outdoor concentrations of NO_2 and $PM_{2.5}$ both reduce to a greater extent than indoor concentrations; this creates a spike in I/O ratios. If the outdoor concentrations reduce below 1, the intensity of these peaks further increases and while 0.1 ppb is ten times less than 1 ppb it is not as significant from a dosage of pollutant point of view as 10 ppb versus 100 ppb. In order to deal with these spikes in the I/O ratios it was decided to carry out normalisation of the data set in order to see if this would reduce the significance of these peaks. Normalisation is used to correct for systematic differences between samples which do not represent true variation between samples. The indoor and outdoor data sets were then normalised for each 15 minute time step. The normalised value is calculated using the mean and standard deviation of the run as shown in Equation 5.2. The newly normalised indoor concentration was then divided by the normalised outdoor concentration in order to calculate the new ratio. Examples of the original I/O ratios and the normalised data sets are plotted and shown in Figure 5.19 to Figure 5.22.

Normalisation is achieved by use of equation Equation 5.2;

$$Normalised\ concentration = \frac{Concentration - mean\ concentration}{Standard\ deviation} \quad \text{Equation 5.2}$$

It was decided to also include a log ratio for comparison as a further potential method to account for distortion on I/O ratios due to low overnight concentrations. This log ratio was simply achieved by finding the log to the base 10 of individual time steps for both indoor and outdoor concentrations and then finding the new I/O ratio. This log I/O ratio was then plotted alongside the normalised and original I/O ratio in each plot.

A selection of sites was chosen to compare the three methods to compute the I/O ratios. For each of the plots the original I/O ratio and the logged I/O ratio were represented on the primary y-axis while the normalised I/O ratio is represented on the secondary y-axis. This was necessary because of scaling issues, for instance in Figure 5.19 which shows $PM_{2.5}$ data for Site 1 run 2, the scale of the primary y –axis is from 0 to 4.5 while the secondary axis used for the normalised ratio ranged from -35 to 10.

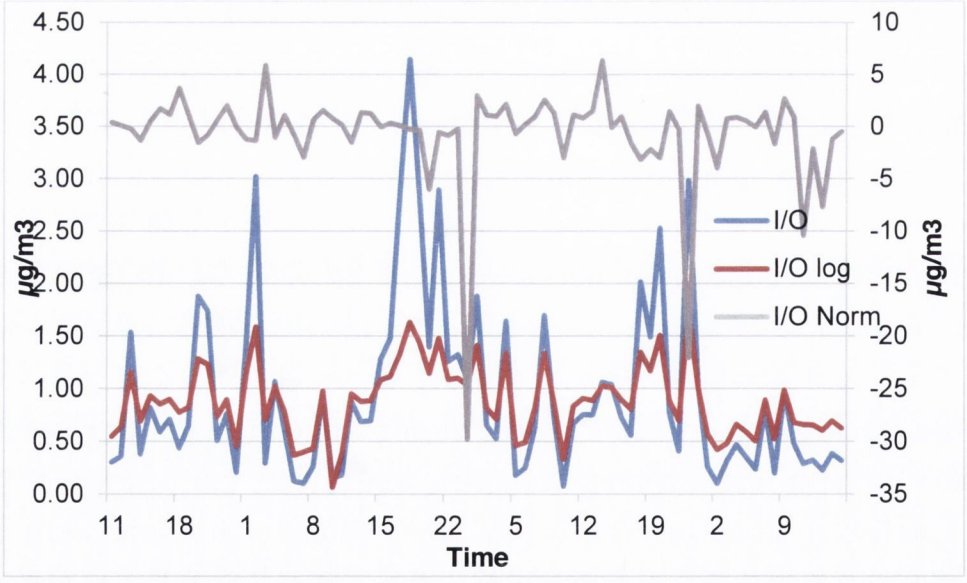


Figure 5.19 I/O ratio $PM_{2.5}$ Site 1 run 2 (Normalised on secondary axis)

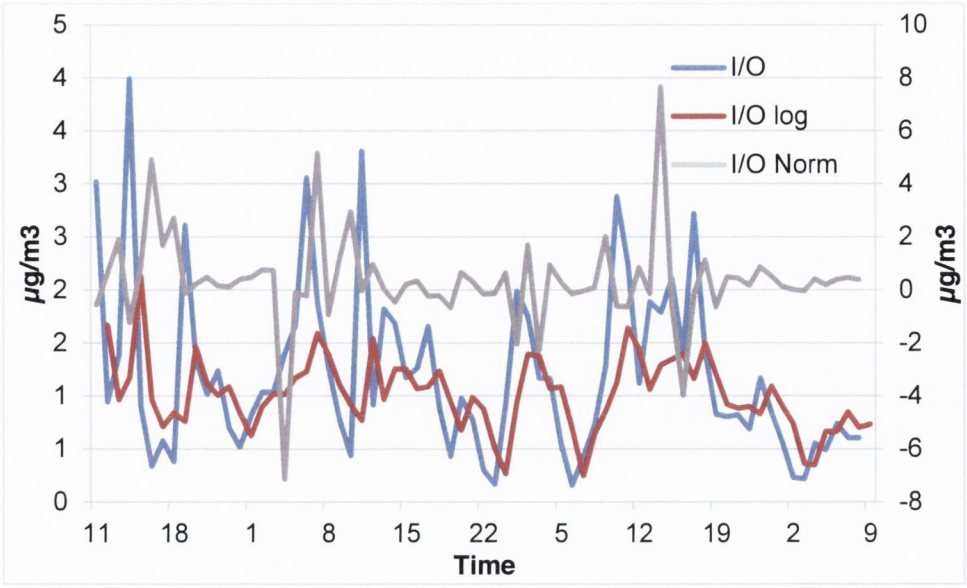


Figure 5.20 I/O ratio $PM_{2.5}$ Site 3 run 2 (Normalised on secondary axis)

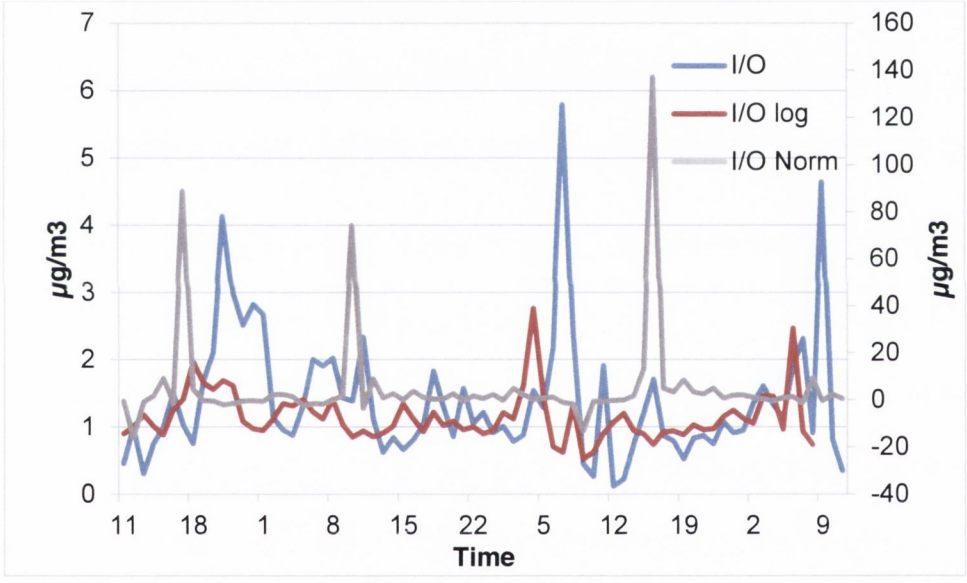


Figure 5.21 I/O ratio $PM_{2.5}$ Site 5 run 1 (Normalised on secondary axis)

The normalised I/O ratios showed much greater variance than the logged or unchanged I/O ratios, with peaks and troughs in the time series which are not intuitive to the data set. For instance, for the NO_2 I/O ratios at Site 7 run 1, (Figure 5.22), both the original I/O ratio and logged I/O ratio show peaks on the 2nd and 3rd nights due to indoor concentrations exceeding indoor concentrations, but no change is seen in the normalised I/O ratio to represent this. Spikes are seen at other times such as just before and after 8 am on the 2nd day, which were not caused by significant differences

indoors or outdoors but rather due to either data set showing peaks considerably above or below the mean.

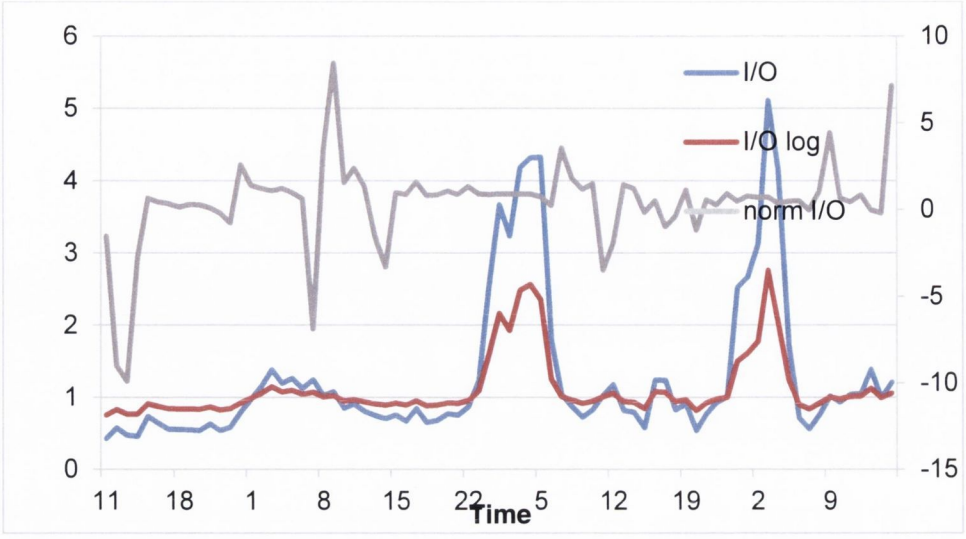


Figure 5.22 I/O ratio NO_2 Site 7 run 1 (Normalised on secondary axis)

A negative I/O indicates that normalised indoor or outdoor data was below the mean value, with a large I/O ratio, either negative or positive, indicating a greater variance of indoor concentration away from this mean value than outdoor concentrations.

While the normalised I/O ratios do provide important information regarding the data sets, they do not indicate clearly if a divergence of indoor and outdoor data takes place as was required by this ratio and therefore it was decided not to pursue the use of them. The logged I/O ratio does dampen the desired peaks with some of the most extreme values, which occur due to outdoor concentrations below 1. However, when outdoor concentrations at night reduced to below 1 ppb or μg m^{-3}, depending on the pollutant, the ratio rapidly increased. This was undesirable as once concentrations went into this range they were almost negligible but caused a significant increase in the ratio, distorting results.

Table 5.3 and Table 5.4 contain the average run I/O ratios for original, normalised and log data. For a large proportion of the sites I/O ratios for the original and logged data are similar but the normalised ratios are considerably different. Logged ratios were found to be closer to 1 than original I/O ratios as peaks were reduced. Figure 5.23 and Figure 5.24 and BB show histograms of the data contained within Table 5.3 and Table 5.4, These figures show the prevalence of I/O ratios of original and logged data compared to the more extreme values, both negative and positively found in

normalised data. Normalised values were calculated to remove the peaks, however, time series plots of the ratios and average normalised I/O ratios over the run showed this was not achieved. Logged ratios did however give stronger predictions if I/O ratios were to be predicted for individual steps rather than using the average of a series. This was because they removed the leveraging factor of values under 1 or extreme peaks in the data set.
It was decided however not to use the log ratios when carrying out work on I/O ratios because the practice is not common in other studies. Therefore, for comparative purposes with other work it was decided to use the original ratios but with a recommendation for future users of individual time step I/O ratios to consider the use of a logged ratio.

Table 5.3 Normalised, Logged and Original I/O ratios for NO_2

	I/O	I/O Log	I/O Normalised
S1R2	1.3	1.26	1.39
S2R2	1.15	1.05	0.01
S3R1	3.57	2.28	1.7
S3R2	1.66	1.54	0.41
S4R1	0.72	0.89	0.77
S4R2	1.53	1.11	0.67
S5R1	1.2	1.07	3.3
S6R1	0.21	0.5	-0.18
S6R2	0.05	0.06	0.15
S7R1	1.27	1.11	0.41
S8R1	0.75	0.87	0.63
S9R1	0.44	0.52	0.32
S9R2	1.47	1.24	-1.24
S10R1	1.13	1.04	1.88
S10R2	1.95	1.33	-0.45

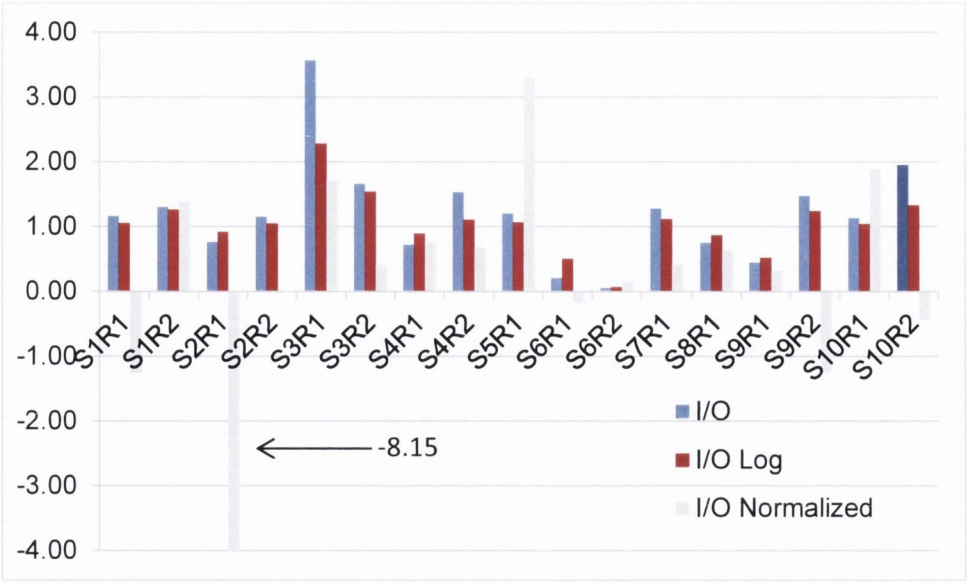


Figure 5.23 NO_2 I/O ratios

Table 5.4 Normalised, Logged and Original I/O ratios for $PM_{2.5}$

	I/O	I/O Log	I/O Normalised
S1R2	0.94	0.88	-0.74
S2R2	0.98	0.92	-0.82
S3R1	1.29	0.97	2.46
S3R2	1.21	1.02	0.34
S4R1	3.80	1.63	0.08
S4R2	5.69	1.95	0.29
S4R2 Roof	1.80	1.21	-0.48
S5R1	1.50	1.14	0.40
S6R1	1.29	1.07	-2.09
S6R2	1.00	0.98	0.55
S7R1	2.20	1.25	1.08
S8R1	1.37	1.13	4.37
S9R1	9.45	2.35	-0.67
S9R2	3.24	1.63	-1.28
S10R1	2.88	1.53	-0.63
S10R2	3.03	1.85	0.38

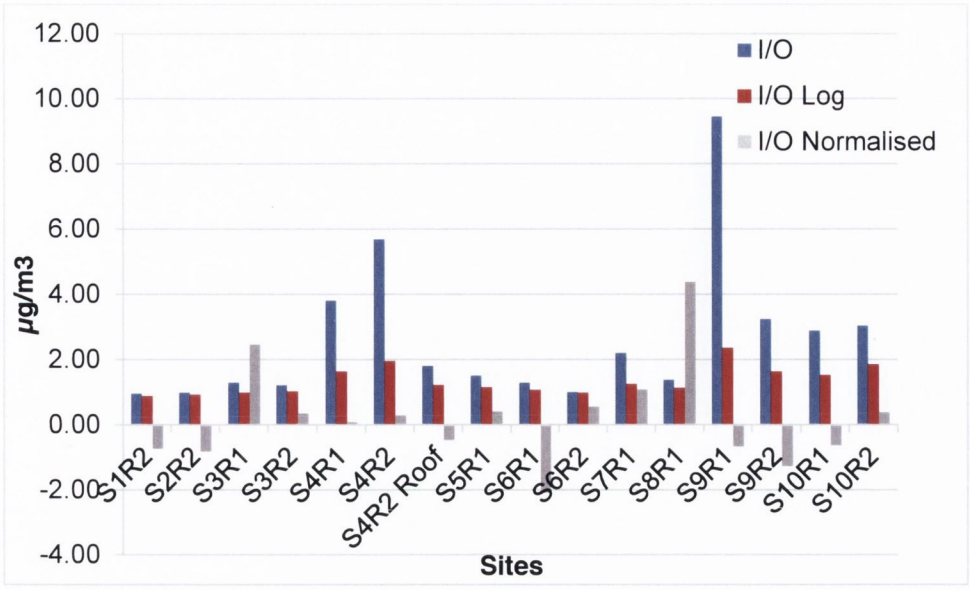


Figure 5.24 $PM_{2.5}$ I/O ratios

5.3. Lag times

In order to calculate whether there was any lag time between variations in pollutant concentrations measured indoors and outdoors (which could therefore indicate the source, speed and direction of the air pollution) a cross correlation method used previously by Eisner et al.(2009) has been employed. The statistical software package called *Minitab* was used to carry out the calculations. Cross correlation (XCORR) estimates a lagged correlation between two time series i.e. the indoor concentrations and outdoor concentrations, by shifting one series relative to the other and calculating the changes in correlation between the two systems in time. Minitab's XCORR function calculated the cross correlation sequence via

$$r_{c_i c_o}(m) = E\{C_{i_{n+m}} C_{o_n}^*\} = E\{C_{i_n} C_{o_{n-m}}^*\} \qquad \text{Equation 5.3}$$

Correlation between two continuous data sets, in this case the indoor and outdoor data, is a measure of how linearly related they are. It is measured using Pearsons 'r' correlation coefficient which range from -1 to +1, a returned value of r =1 showing that the two data sets are perfectly linearly related, an r = -1 indicates inverse correlation, i.e. when indoor concentrations increase outdoor concentrations decrease;

$$r_{C_i C_o} = \frac{\sum_{i=1}^{n}(C_{i_i} - \overline{C_i})(C_{o_i} - \overline{C_o})}{(n-1)s_{C_i}s_{C_o}} \qquad \text{Equation 5.4}$$

Where;

$\overline{C_o}$ = mean of data set C_o

$\overline{C_i}$ = mean of data set C_i

S_{Ci} = standard deviation of data set C_i

S_{co} = standard deviation of data set C_o

N = number of pairs in the data sets

C_o= concentration outdoors

C_i= concentrations indoors

As shown previously, the NO_2 data has less noise compared to the collected $PM_{2.5}$ data and so interactions between indoor and outdoor concentration fluctuations are easier to uncover. In order to reduce $PM_{2.5}$ noise it was decided to use the 15 minute time steps for both data sets even though $PM_{2.5}$ data had been recorded at 1 minute intervals. This also corresponds to the minimum interval available for the NO_2 data which was 15 minutes. A lag of up to 27 steps positively and negatively in time was calculated, i.e. going forward and backwards 6 ¾ hours in order to view a lag for full run samples and up to 15 time steps for shorter sampling periods. The x-axis in all graphs showing XCORR plots contains the lags positive and negative in time, each lag step is 15 minute lag. A positive lag indicates that indoor leads the outdoor concentrations that may be due to unconnected fluctuations occurring both indoors and outdoors which the XCORR numerical method output can be misread as connected since, unless a large source is present indoors, this situation is very unlikely. The data presented below (unless specified otherwise) is for the lags calculated for the complete run, including day and night. A negative XCORR indicates that indoor concentrations are higher than outdoor concentrations at the time of calculation the XCORR. This may be due to high pollutant concentrations trapped indoors while outdoor concentrations drop.

In general, the two different pollutants showed very different behaviour when cross correlated for their entire runs. For the most part NO_2 showed correlations of about 0.65 at a 0 lag with some sites showing much lower and others much higher correlations. On the other hand $PM_{2.5}$ shows average cross correlations at 0 lag to be 0.14. Only three sites showed

correlation above 0.4 for $PM_{2.5}$ at 0 lag, these are Site 4 run 2 (XCORR = 0.54), Site 5 run 1 (XCORR = 0.414) and Site 10 run 2 (XCORR = 0.42).

5.3.1. NO_2 XCORR for entire runs

Table 5.5 contains cross correlations (XCORR) for sites 1 to 10 for the entire run including both working and non-working hours. For each site a 0 lag XCORR value is given stating the non-lagged correlation between the indoor and outdoor data, the optimum lag time in hours and also the correlation of the indoor and outdoor data at this lag. It should be noted that while lag times are in 15 minute intervals, in the following plots of the XCORR values these x–axis units are the number of lags rather than hours or minutes, therefore a lag of 3 equates to 45 minutes (i.e. 3x15 minutes).

Table 5.5 Indoor and Outdoor NO_2 Cross Correlation for entire runs

	XCORR at 0 lag	Optimum lag (Hours)	XCORR at optimum lag
S1R2	0.58	-1.0	0.62
S2R2	0.87	-0.25	0.88
S3R1	0.73	-0.25	0.78
S3R2	0.71	0.0	0.68
S4R1	0.69	-1.75	0.74
S4R2	0.61	-1.5	0.86
S5R1	0.67	-0.5	0.72
S6R1	0.08	-6.75	0.32
S6R2	0.61	-1.0	0.39
S7R1	0.67	-0.5	0.69
S8R1	0.01	-5.25	0.27
S9R1	0.37	-2.75	0.57
S9R2	0.11	-0.25	-0.11
S10R1	0.65	-1.0	0.68
S10R2	0.68	-0.5	0.69

NO_2 shows reasonably strong XCORRs for most sites with smooth patterns which slowly decrease away from the maximum value with time. Some sites show a negative XCORR at the extremities of the explored lag period which lasts for 6 ¾ hours positively and negatively in time away from the 0 lag. Figure 5.25 shows the XCORR pattern for Site 3 run 1, the maximum correlation can be seen close to a lag of 0. Out of 15 runs reviewed (runs with no overnight data such as Site 1 run 1 were not considered in order to

include lags from day and night for initial review), 10 showed strong patterns like the one in Figure 5.25. Some did not show a negative XCORR value at the extremities of the plots including the second run at Site 3.

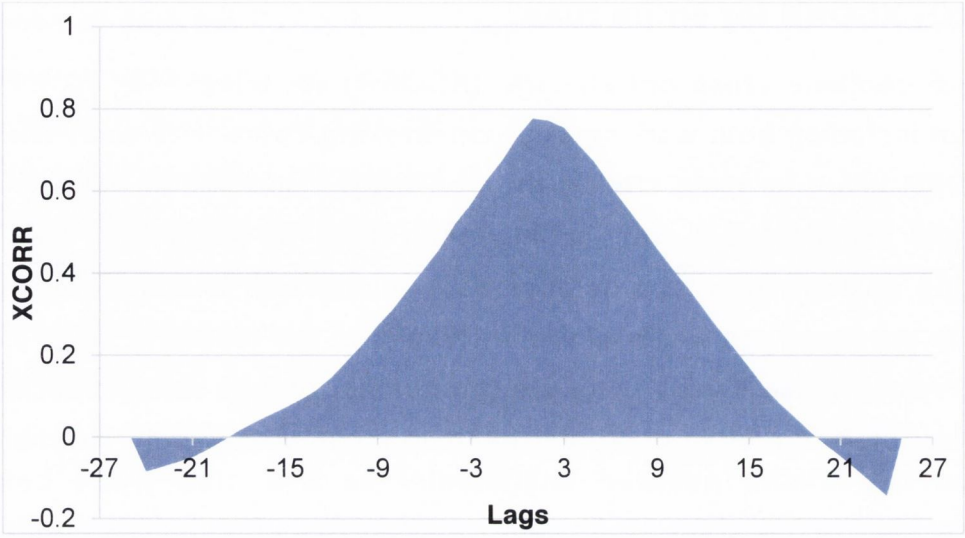


Figure 5.25 NO_2 Site 3 run 1 XCORR plot

Site 10, a recently refurbished mechanically ventilated office, showed reasonable XCORRs of 0.648 and 0.677 at run 1 and run 2 respectively at lag 0. The optimum XCORR were at a lag of 1 hour for run 1 when monitors were at ground level and 30 minutes when monitors were at roof level beside the ventilation intake. This agrees with intuition, the shortest lag at the roof is where the air is being drawn into the building, and a longer lag is present with street level data, as there is an additional lag for the pollutants to rise up from street level to the roof level and then into the building. These lags show strong results with slowly decreasing influence of values moving away from the peak lag, indicating a consistent lag throughout the data, see Figure 5.26 and Figure 5.27

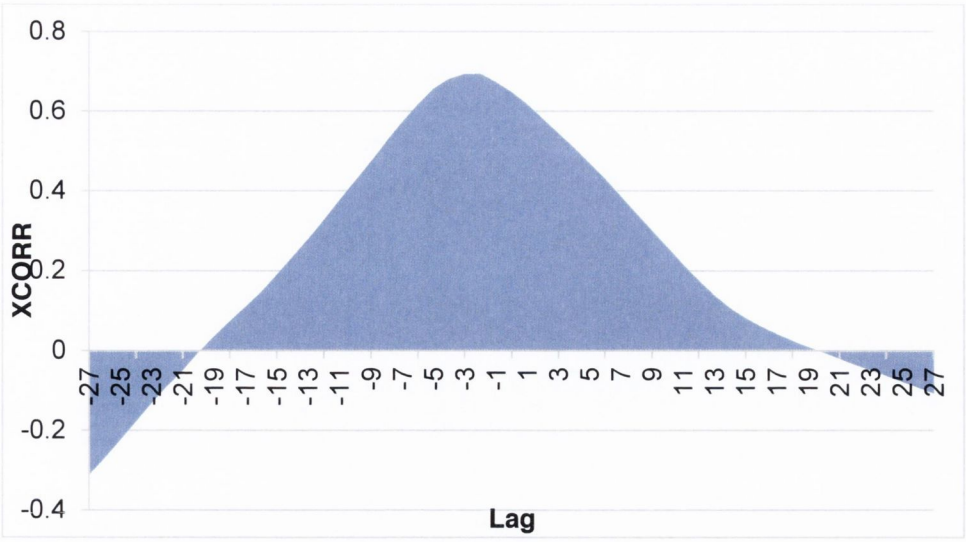


Figure 5.26 NO_2 XCORR values Site 10 run 1

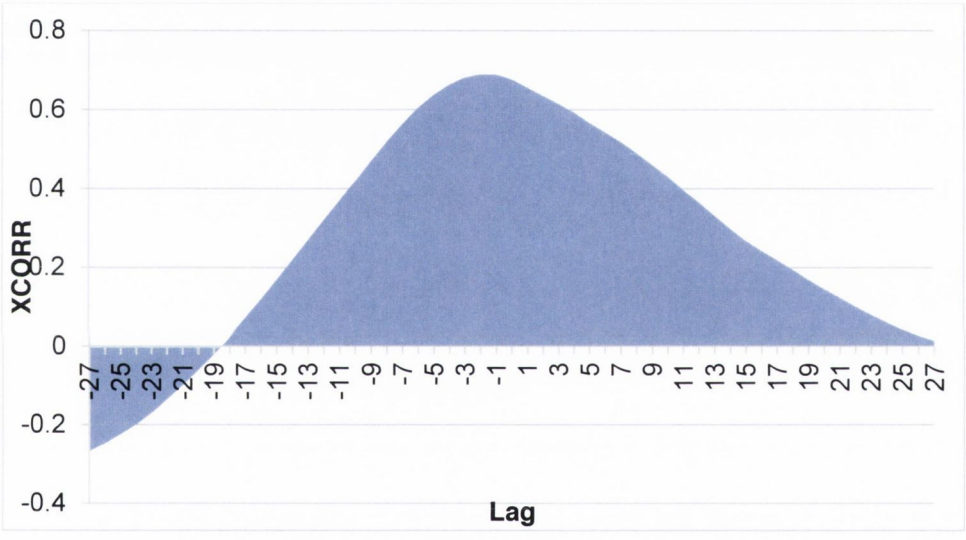


Figure 5.27 NO_2 XCORR values Site 10 run 2

The behaviour pattern of short lags between the indoor responses to outdoor fluctuations for up to an hour is evident for 10 of the 15 sites. The sites with much larger lags i.e. Site 8 and Site 6 run 1 have lower correlations i.e. XCORR 0.273 and 0.315 respectively. Reviewing the plotted indoor and outdoor concentrations (see Section 4.2.2) alongside the XCORR plots (see Figures Figure 5.28 and Figure 5.29) the reason for poor correlation is evident. The diurnal cycles indoors and outdoors at both of these naturally ventilated sites are irregular unlike the rest of the sites which returned high XCORR value. For sections of Site 8 a higher XCORR value could be returned but during other sections of the data little to no connection can be seen between the two plots resulting in the low overall correlation.

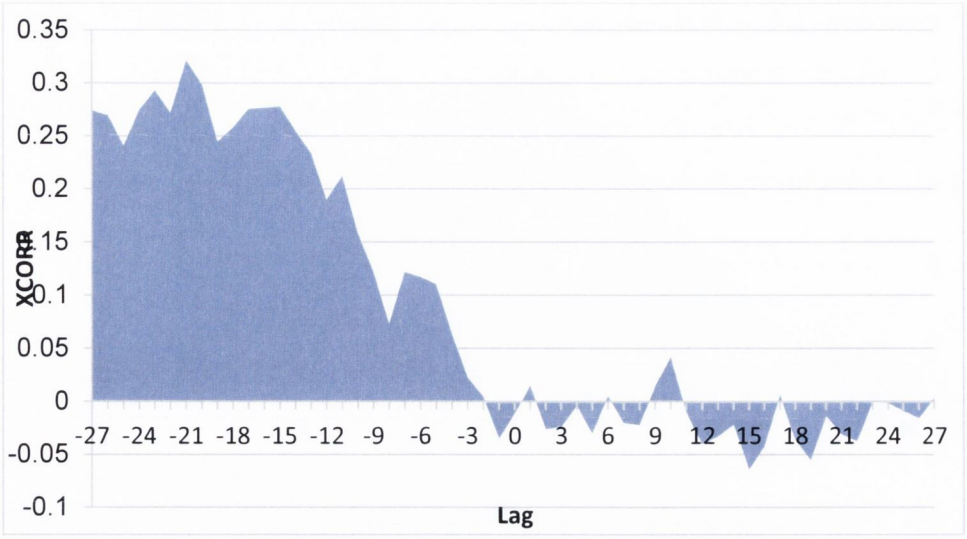


Figure 5.28 NO_2 XCORR values Site 8 run 2

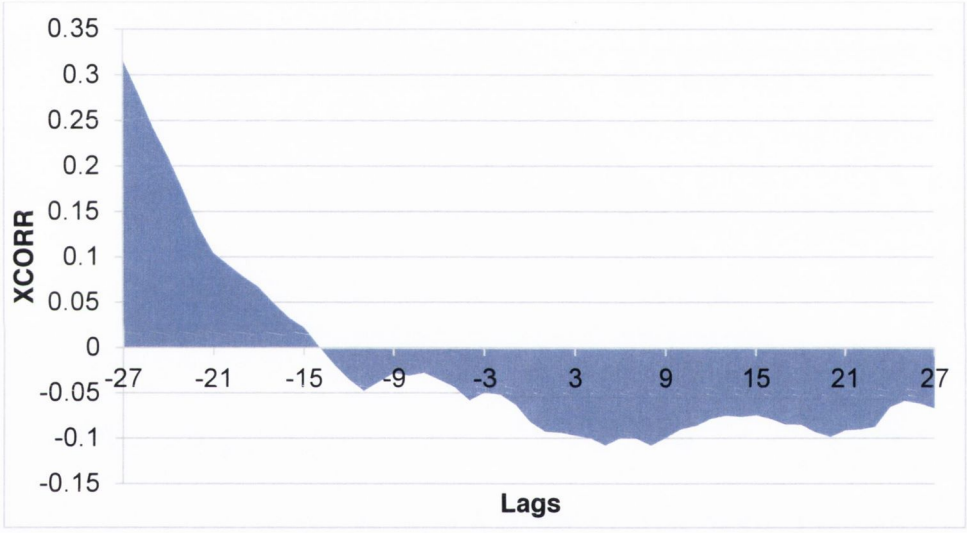


Figure 5.29 NO_2 XCORR values Site 6 run1

The lowest XCORR value for NO_2 was seen for Site 9 run 2 of -0.11 which had a lag of +1 or 15 minutes in the positive direction. The unusual XCORR value was again due to an inconsistent trend between outdoor and indoor over the run. At many sites indoor concentrations are below outdoor concentrations during the day, but as outdoor concentrations reduce overnight the indoor concentrations reach a background indoor level, while outdoor concentrations reduce even further. The pattern viewed during run 2 at Site 9 was not consistent with this due to unusual outdoor behaviour of the gas, but correlated well with EPA/DCC concentrations gathered for the same time period (Figure 5.30).

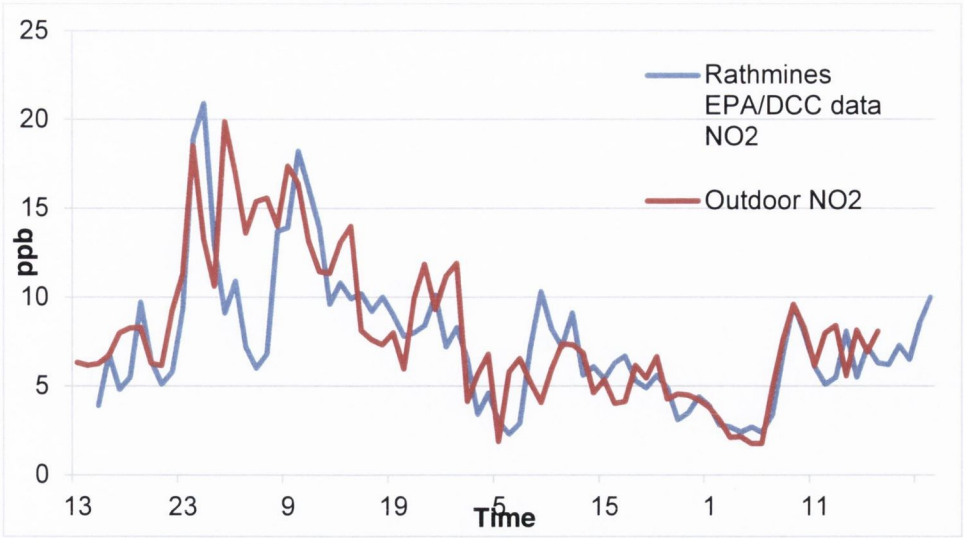


Figure 5.30 Site 9 Run 2 NO_2 versus EPA/DCC data

The data for Site 9 run 1 also shows a clear correlation with this EPA data, be it at reduced values as outdoor monitoring during run 1 was carried out at roof top level. Run 1 for Site 9 gave a much stronger correlation, with the optimum lag at 2 hours 45 minutes. During this run outdoor data was measured at roof level, even though no ventilation system was in place in the building. No windows were open in the office, which was located on the storey below the roof, during this run unlike during run 2. Adding the lag to the data set and reviewing the plot of the amended time series data it is clear the lag is a sensible value as peaks/troughs in outdoor concentrations now result in simultaneous ones in the indoor data, see Figure 5.31.

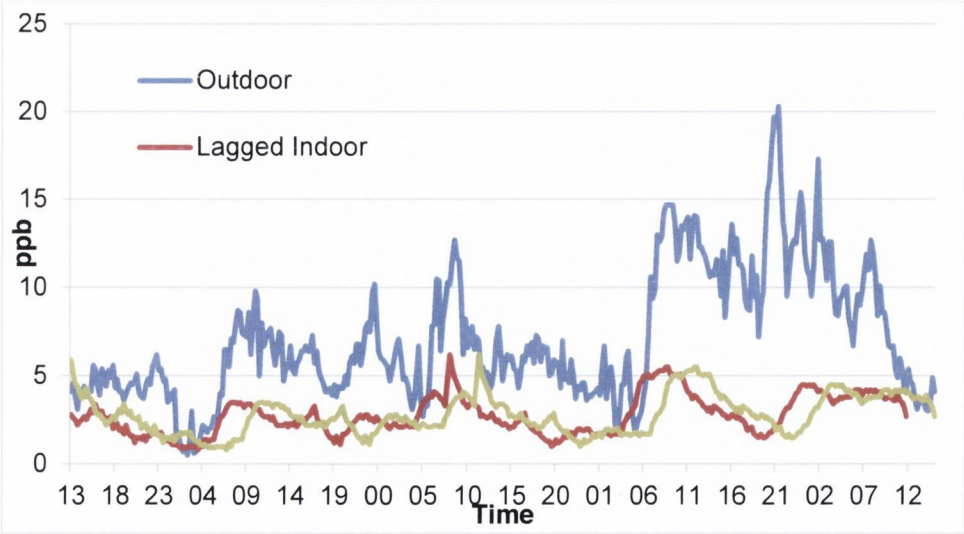


Figure 5.31 NO_2 lagged and unlagged Site 9 run 1

Another site where one run produced a reasonable XCORR value and the other did not is Site 6. Run 1 produced an unusual graph with a negative

XCORR for any lags less than 2 and 1/2 hours, see Figure 5.29. The correlations increased significantly from a lag of 5 hours until the last XCORR was calculated at 6 and 1/2 hours. As with Site 9 run 2 and Site 8 the usual XCORR plot can be linked to a poor connection between indoor and outdoor trends.

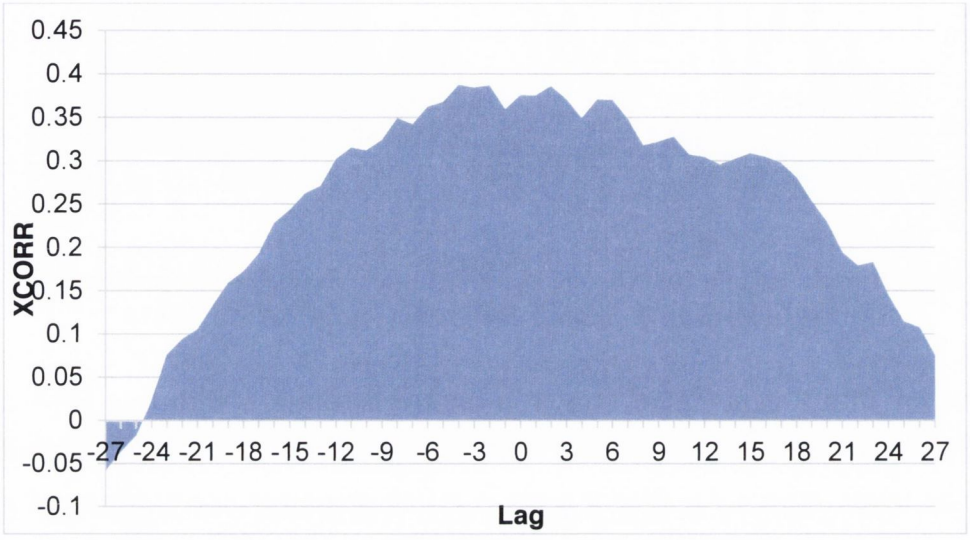


Figure 5.32 NO_2 Site 6 run 2 XCORR

Run 2 at Site 6 produced XCORR values which had a max value at 1 hour but showed low correlation of only 0.387 with XCORR values decreasing linearly away from the max value slowly. This plot pattern indicates that changes which occurred outdoors not at this 1 hour lag might also influence indoor concentrations, but to a lesser degree. However, it is more likely (due to the low r value of 0.387) that outdoors has little influence over the indoors fluctuations which are instead influenced by internally generated sources. The lower XCORR value than expected when looking at the data could be due to the previously discussed very low indoor concentrations compared to outdoors at Site 6 run 2. Visual interpretation of the indoor and outdoor concentrations show clear correlations between increases and decreases but only if a secondary axis is used as the indoor values are a fraction of the outdoor concentrations as seen in Figure 5.33. While indoor trends follow the outdoor trends they do so with much smaller peaks and troughs, leading to the low XCORR between the data sets.

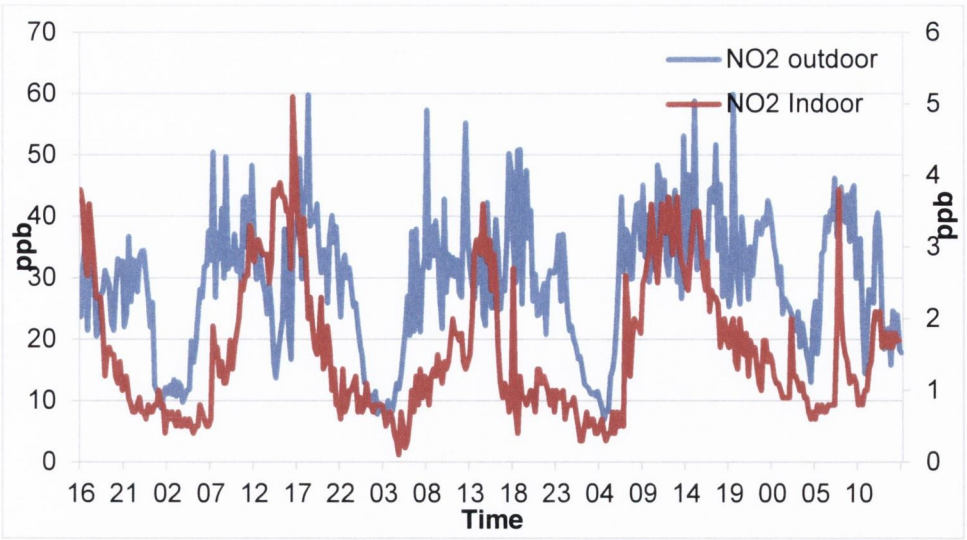


Figure 5.33 NO_2 Site 6 run 2 indoor and outdoor

Figure 5.34 shows the XCORR value for the entire run of Site 4 run 1 which provided a perfectly symmetrical pattern with a 0 lag and XCORR of 1. As monitors are averaged over a 15 minute period a 0 lag is actually a lag of less than 15 minutes. Run 2 at site 4 also showed a high XCORR value of 0.8604 but with a lag of over an hour. This site is a mechanically ventilated gallery space and during monitoring was open to the public. The longer lag during run 1 may be due to the lower temperatures during monitoring which would encourage staff to keep the front door to the building closed.

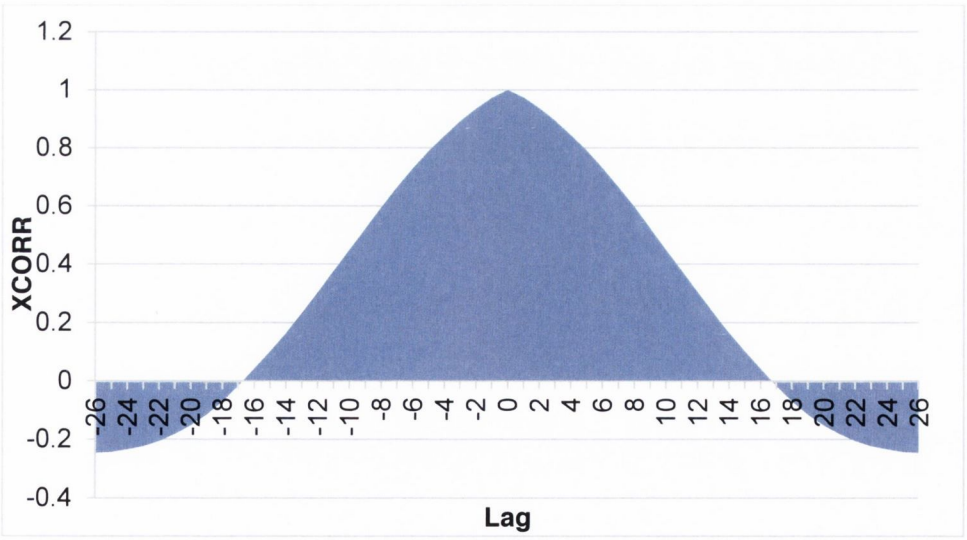


Figure 5.34 NO_2 XCORR Site 4 Run 1

5.3.2. Working hours' time lag for NO_2

Table 5.6 contains XCORR values for NO_2 during working hours only. The XCORR values for non-working hours were also calculated, these are contained in Appendix A. These were also calculated XCORR values are presented for individual days of each run, as non-working time data was removed so there is no longer a continuous data set.

three sites show very good XCORR values across the 4 days of monitoring; these sites are Site 5, Site 4 run 1 and both runs at Site 10. These were all mechanically ventilated buildings which in the case of Sites 4 and 5 were built in the past 5 years and in the case of Site 10 was refurbished and a new ventilation system installed in 2001. These sites also showed high XCORR values when calculated over the entire run as discussed previously in Section 5.3.1. Site 5 shows an averaged XCORR value of 0.811 over the 4 days for working hours, with a lag of 15 minutes or less, but if non-working hours were included as previously calculated, this correlation was reduced to a value of 0.724 at a lag of 30 minutes.

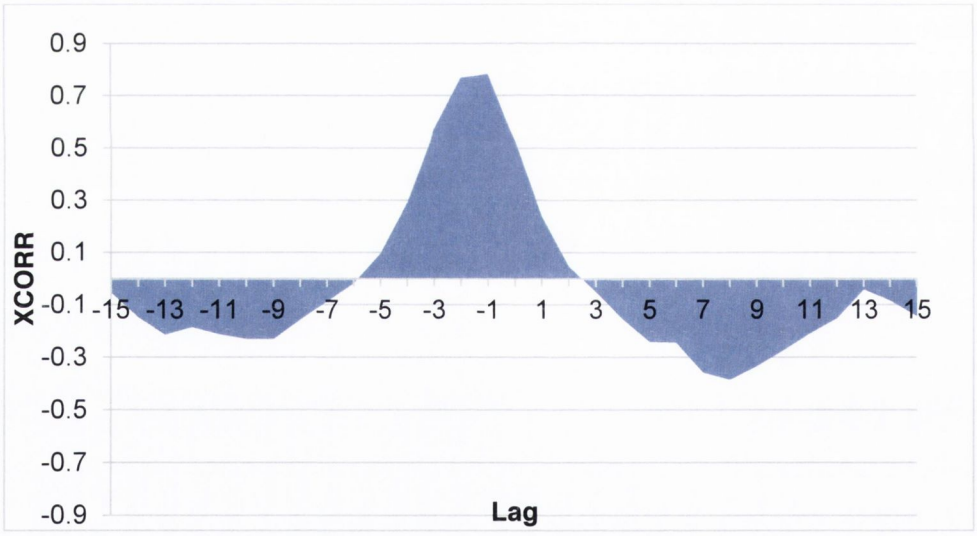


Figure 5.35 NO_2 XCORR - Day 4 Site 5 Run 1

Site 10 shows high XCORR values for both and on all days except on day 3 during run 1, where a value of -0.46 at a much longer lag than shown for all other days of 11/4 hours, see Table 5.6 NO2 XCORR working hours. Overall the highest XCORR values when averaged over the 4 days of monitoring are 0.625 and 0.725 for run 1 and 2 respectively. For each day, except day 3 during run 1, the ground level (run 1) lag ranged between 15 and 30 minutes while the lag at ventilation intake (run 2) ranged between 15 minutes and no lag. This is intuitive as it would be expected that

fluctuations at ground level would take longer to influence outdoors than the fluctuations at roof level where air is being drawn into the ventilation system and directly supplied to the indoor area where monitoring occurs. Site 10 also showed a strong correlation of the influence of outdoor on indoor concentrations when both working and non-working hours are included (as in Section 5.3.1) of 0.680 for run 1 and 0.689 for run 2 with lags of 30 minutes and 1 hour respectively. The longer lag times are probably due to the influence of reduced air changes overnight from the building being shut, although reductions in air changes would not have been as high as other mechanically ventilated buildings as maintenance staff for the building stated that the ventilation system ran 24 hours per day. This is discussed further Appendix A when XCORR are calculated using only night-time hours.

The final site which showed high XCORR values over the individual days was Site 4 during run 1. The XCORR was strongest at 0.597 with a lag of up to half an hour (30 minutes, 15 minutes, 15 minutes and 0 lag for 4 individual days). The first day of monitoring during run 1 was a Tuesday which, according to staff, has fewer customers in the gallery space than other days, therefore the door to the building is open for less time allowing less air to enter from street level. A higher XCORR value was found when non-working hours were included in the calculation of XCORRs of 0.737 with a lag of 1 hour 15 minutes. As mentioned above, this longer lag is likely to be due to the reduced air changes overnight while the building is closed and in this case the ventilation system is switched off. Run 1 was carried out in December 2010 and the results differ from the second run which was carried out in March 2011. Average XCORR values of 0.472 although 2 of these days saw negative correlations indicating higher indoor concentrations than outdoors. The real difference between the two sites is the varying lag time in run 2 which ranges from 30 minutes to 2 hours 15 minutes. This long lag time indicates a high correlation between the indoor and outdoor concentrations. If non-working hours are included in the data set the highest XCORR value increases to 0.851 with a lag of 2 hour 15 minutes indicating that little changes in lag times between working and non-working hours.

Table 5.6 NO_2 XCORR working hours

	Day 1			Day 2		
	XCORR 0 lag	**Optimum lag(hours)**	**XCORR at optimum lag**	**XCORR 0 lag**	**Optimum lag(hours)**	**XCORR at optimum lag**
S1R2	0.19	-0.75	0.32	0.11	0.75	0.5
S2R2	-0.22	2.75	0.56	0.37	-0.25	0.61
S3R1	0.55	-0.25	0.6	0.84	0.0	0.84
S3R2	0.41	-2.5	-0.29	0.74	0.0	0.74
S4R1	0.38	-1.0	0.5	0.64	0.0	0.64
S4R2	-0.381	1.0	-0.51	0.15	-1.5	0.72
S5	0.79	0.0	0.79	0.83	0.0	0.83
S6R1	-0.45	0.0	-0.45	-0.1	-2.0	-0.41
S6R2	0.22	11.25	0.41	-0.17	-2.0	-0.42
S7	0.2	-0.25	0.52	0.3	-0.5	-0.43
S8	-0.12	1.75	0.33	-0.19	-0.25	0.32
S9R1	-0.47	0.0	-0.47	0.06	0.25	-0.23
S9R2	0.04	0.75	0.47	-0.54	-1.5	0.49
S10R1	0.62	-0.25	0.68	0.44	-0.5	0.63
S10R2	0.83	0.0	0.83	0.62	-0.25	0.66
	Day 3			**Day 4**		
	XCORR 0 lag	**Optimum lag(hours)**	**XCORR at optimum lag**	**XCORR 0 lag**	**Optimum lag(hours)**	**XCORR at optimum lag**
S1R2	-0.34	0.0	-0.34	0.11	-1.0	0.6
S2R2	-0.15	-0.5	0.36		n/a	
S3R1	0.38	0.0	0.38		n/a	
S3R2	0.07	1.25	-0.47	-0.15	-1.25	-0.3
S4R1	0.63	0.25	0.7	0.3	-0.25	0.55
S4R2	0.17	-1.5	0.67	-.013	3.75	0.55
S5	0.69	-0.25	0.84	0.53	-0.25	0.78
S6R1	-0.36	-0.25	-0.4	0	-0.5	0.72
S6R2	-0.12	-2.0	0.26	-0.14	-0.5	0.34
S7	0.64	0.5	0.8	0.66	0.0	0.66
S8	-0.01	0.5	-0.33	-0.68	0.5	0.52
S9R1	0.11	-0.75	0.39	0.34	-1.25	0.74
S9R2	-0.25	2.0	-0.34	-0.16	-3.0	0.34
S10R1	-0.14	1.25	-0.46	0.66	-0.5	0.73
S10R2	0.73	0.0	0.73	0.79	0.0	0.79

The sites with the lowest XCORR values for daily runs are Sites 8, 9 and 6 (run 2); these sites were all older naturally ventilated buildings with Site 9 being the newest built facility of the 3, constructed over 40 years ago. Site 8 had a low average working hours XCORR value of 0.375 with a lag time which ranges from 15 minutes to 1 ¾ hours'. Day 4 showed higher XCORR values for Site 8 although this was at a positive lag indicating that indoor

fluctuations occurred before outdoor fluctuations. The difference in day 4 may be due to the shorter monitoring period carried out during this day when monitoring occurred for the morning hours only. Figure 5.36 shows a plot of the XCORR values which remain low ranging from 0.25 to – 0.3 across all lags, indicating little influence of outdoor concentration fluxes on indoor concentrations. The correlation decreases if non-working hours are included as the max XCORR drops to 0.272 with a lag of 5 ½ hours. This site also showed low correlations during the calculation of best subset regressions in the previous chapter with a max prediction of 57.4 %.

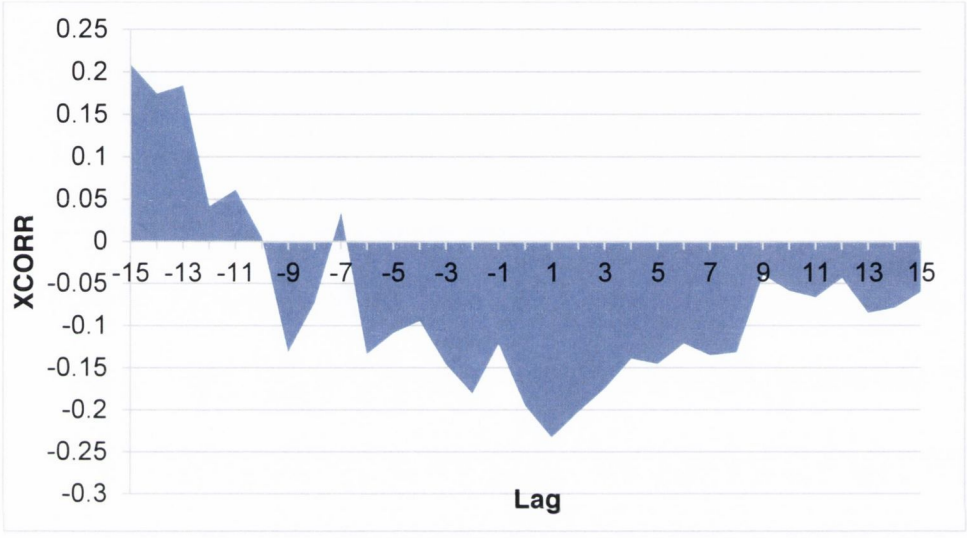


Figure 5.36 NO_2 working hours day 2 XCORR Site 8 run 1

Outdoor concentrations at Site 9 run 2 also displayed little influence on indoor ones, with the average of working hours XCORR values over the four days of monitoring of 0.41. The relationship between indoor and outdoor can be seen in Section 4.2.2 and a plot of one of the days (day 4) of working hour XCORR relationship at different lags in Figure 5.37. Although, they are low correlations the relationships have significantly improved compared to using both working and non-working hours data which saw a XCORR value at a lag of 15 minutes of only -0.11. Therefore, a much greater influence of outdoor fluctuations on indoor fluctuations is seen during the day compared to at night when the building is shut. It should be noted that the window in the office being studied was open throughout run 2 (both working and non-working hours) which would have significantly increased air changes per hour within the room and yet still a low correlation was found. As outdoor data showed such low influence on indoor concentrations (R^2 = 1.3 % p = 0.318) the best subset regressions

carried out in the previous chapter were consulted to investigate if meteorological factors could predict indoor concentrations to a better degree. These showed that the R^2 can be increased to an R^2 = 67.2 % if barometric level pressure, temperature, relative humidity, global radiation, wind speed and wind direction are also included.

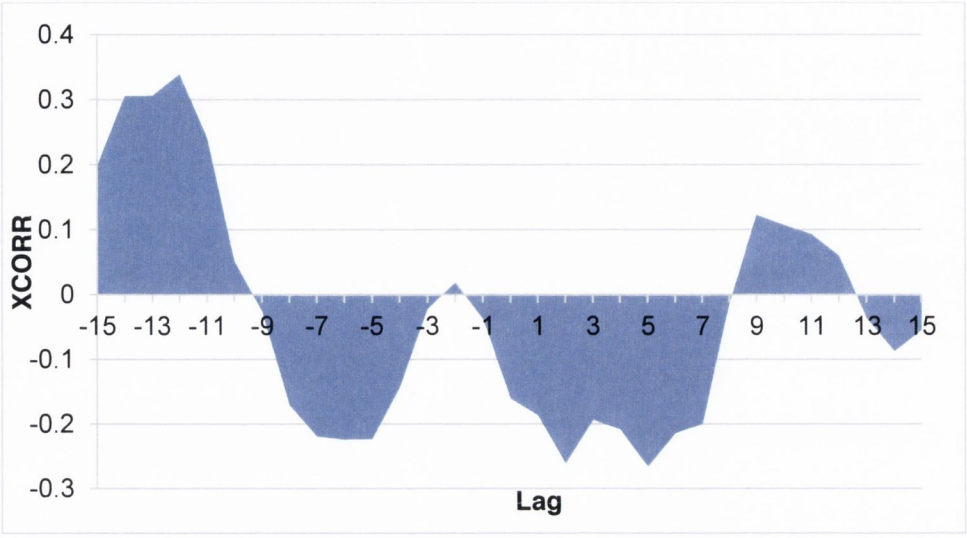


Figure 5.37 NO_2 working hours day 4 XCORR Site 9 run 2

Site 6 returned low XCORR values for both runs when the entire runs were used for the calculations with values of 0.315 and 0.387 with lags of 6 ¾ hours and 1 hour for run 1 and run 2, respectively. The two runs showed very different lag times for each day when calculated for working hours only, while some days showed 30 minute lags, others showed much longer lags of up to 2 hours. On the only day with a high XCORR value (0.72), run 1 day 4, a lag of 15 minutes was seen (Figure 5.38). In order to further investigate the two runs a regression of outdoor predicting indoor concentrations was run for both sites, the results showed run 2 had an R^2 = 20 % (p= 0.344) while run 1 only provided an R^2 = 0.3 % (p = 0.644).

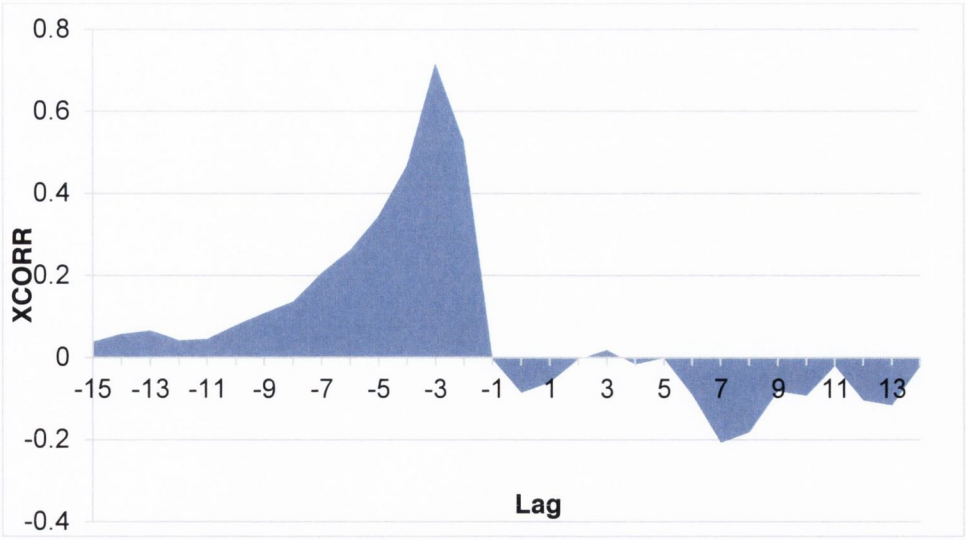


Figure 5.38 NO_2 working hours day 4 XCORR Site 6 run 1

Sites 1, 2, 3 and 7 all showed mixed results. Sites 3 and 7 showed 2 days each of high XCORR values and two other days of slightly lower values. Site 7, a naturally ventilated shop, showed reasonable to low max XCORR values for the first two days of monitoring with values of 0.52 and -0.43 respectively while the 3rd and 4th day saw XCORR values of 0.8 and 0.66. Day 3 which had the highest XCORR values is seen in Figure 5.39 and it shows a strong clear peak. All days of monitoring saw short time lags of between 0 and 30 minutes. Reviewing weather data the major change over these 4 days was a slight increase in temperature from peaks of 12 °C on day 1 to 16 °C on day 2, reduction in pressure from 1007.6 hPa to 998 hPa and reduction in radiation on the 3rd and 4th days.

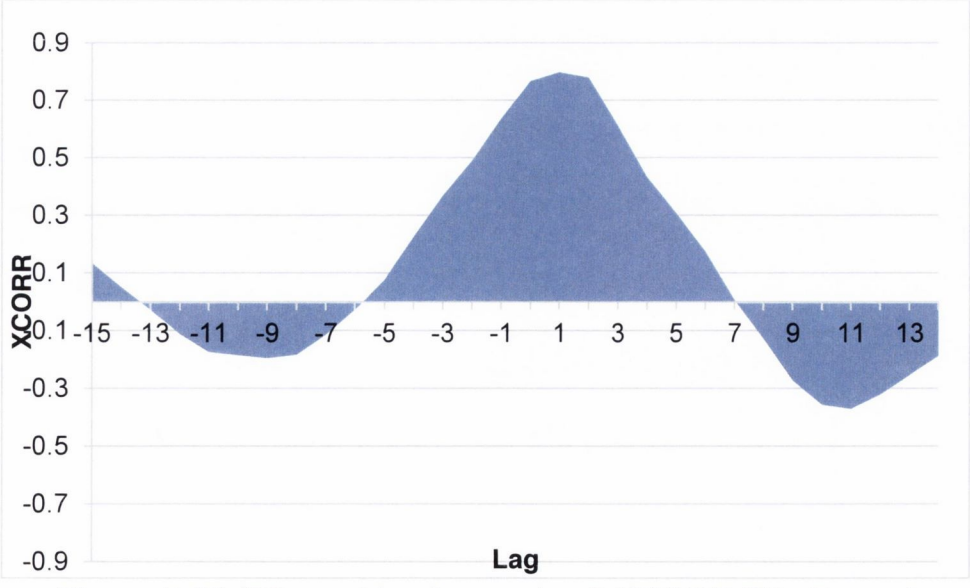


Figure 5.39 NO_2 working hours day 3 XCORR Site 7 run 1

Site 3 (a mechanically ventilated office building) saw a greater connection between indoor and outdoor while the monitors were located at the air intake (run 1) to the building compared to when monitors were located at street level (run 2). There was a longer time lag during run 2 of up to 2 hour 30 minutes compared to the 0 to 15 minute lag time seen in run 1. During the first two days of run 1 there were high XCORR values of 0.60 and 0.84 while on the 3rd day this dropped to 0.38. Due to an issue with electricity supply on the initial day of monitoring, data was unusable so only three days of data on the roof were available for comparison. The high XCORR values are backed up by a high R^2 =64.8 (P = 0) for a regression of indoor versus outdoor concentrations. During run 2 the max XCORR are negative (indicating higher indoor concentrations) for 3 of the 4 days with values of: -0.29, 0.74, -0.47 and -0.30. The only day with a high XCORR was the day with the most sensible time lag. The shortest lag from the three days with the low correlations is 1 ¼ hours while on the day with the high correlation a lag of 0 (i.e. ±15 minutes) was found.

5.3.3. $PM_{2.5}$ XCORR for entire runs

XCORR plots carried out on the $PM_{2.5}$ data are very different from the NO_2 plots discussed above. Many of the sites showed a pattern which indicated that if a peak in outdoor concentration occurs this will lead to a lower than normal indoor concentration several lags later, e.g. a negative correlation. This pattern is shown in Figure 5.40 which plots the XCORR values for Site 3 run 1. While this pattern may make sense for other time series, it does not for $PM_{2.5}$ as there is no reason why an increase outdoors would cause a decrease indoors. Combined with the very low XCORR values (see Figure 5.40) which are generally below 0.2 it can be deduced that for many sites changes in the concentration outdoors appear to have little influence on the indoor concentrations.

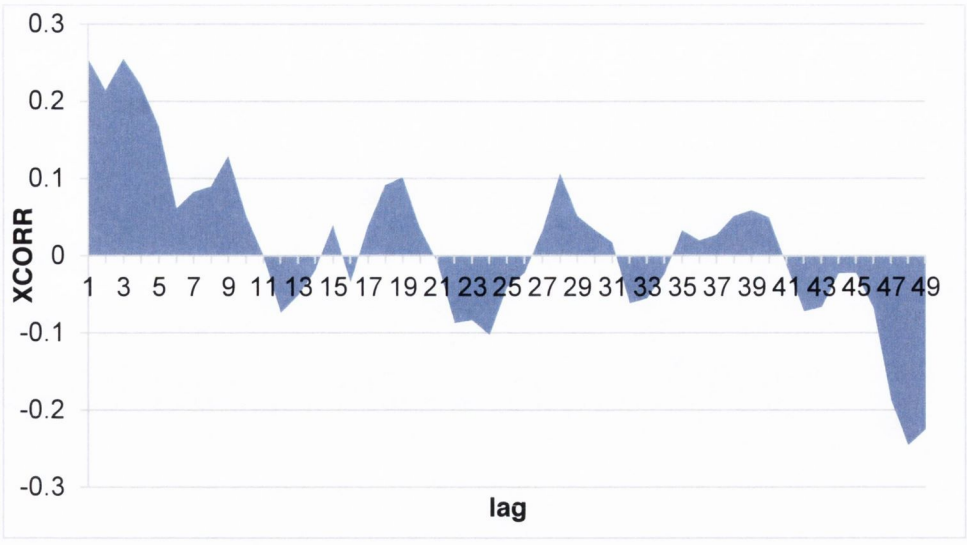


Figure 5.40 $PM_{2.5}$ Site 3 run 1 XCORR plot

As the buildings studied are unoccupied at night the lag times are likely to change as air changes per hour reduce during the night, thereby increasing the lag times of pollutant variance outdoors being picked up indoors. When the data from Site 1 run 2 is broken down into day time only data and XCORR values are calculated for only a day at a time, very high correlations with stronger patterns are present. When this is continued and XCORR values are calculated for night time, high correlations are also revealed. This indicates a very different relationship between indoors and outdoors at night time and during the day when the premises is open for business. Correcting the outdoor $PM_{2.5}$ data for relative humidity (outdoor*) returns marginally better correlations, as shown in Table 5.7 for 0 lags with the highest being for Site 10 run 2 at 0.457. When the XCORR values are plotted the values produce plots which are smoother than those without the correction. These plots still indicate a relationship between indoors and outdoors which changes significantly with higher outdoor concentrations producing lower ones indoors after a lag and vice versa. As mentioned above this inverse relationship is unlikely with $PM_{2.5}$ therefore this result is more likely due to a poor relationship between the two. This is backed up by the low correlations, with localised spikes, in concentrations which are picked up by the monitors. For this reason it was decided to continue the analysis working hours removing the hours while the site is not in use by staff. The lag times were also calculated for non-workings hours with the results contained in Appendix A.

Table 5.7 Indoor and Outdoor $PM_{2.5}$ Cross Correlation

	0 lag	Optimum lag(hours)	XCORR
S1R2	-0.076	-1.25	-0.116
S2R2	0.276	-0.75	0.328
S3R1	-0.040	-4.0	0.129
S3R2	0.138	-1.5	0.274
S4R1	0.103	0.0	0.103
S4R2 Roof	0.651	-0.5	0.673
S4R2 Ground	0.849	-0.25	0.752
S5R1	0.098	-0.25	0.114
S6R1	0.114	-2.25	0.102
S6R2	0.112	-1.25	0.205
S7R1	0.066	0.0	0.066
S8R1	0.090	-2.0	0.128
S9R1	-0.392	-1.25	-0.411
S9R2	-0.004	-0.75	-0.043
S10R1	0.010	-1.5	0.158
S10R2	0.179	-2.5	0.358

5.3.4. $PM_{2.5}$ working hours average XCORR

The XCORR were recalculated for individual days and the results are summarised in Table 5.8. While there was a stronger correlation when XCORR were calculated for only working hours, many sites still showed little or no sign of a correlation between indoor and outdoor or a lag. Sites showed different XCORR patterns on various days which may be due to a variety of reasons such as weather, indoor activity and office/shop doors being opened on certain days and not others. XCORR values had to be calculated for individual days as they were not one continuous data set. This would affect results as the end of one day being followed by the start of the next in the amended data set, although the averaged values over the 4 days of monitoring is contained in Table 5.9.

Table 5.8 Day lag times $PM_{2.5}$

	Day 1			Day 2		
	0 lag	**Optimum lag(hours)**	**XCORR**	**0 lag**	**Optimum lag(hours)**	**XCORR**
S1R2	0.89	0.0	0.89	0.99	0.0	0.99
S2R2	0.57	0.0	0.57	0.25	0.25	0.26
S3R1	0.33	-1.25	0.23	0.10	0.0	0.39
S3R2	0.09	1.75	0.26	0.08	-1.75	0.15
S4R1	0.02	1.5	0.46	0.43	0.5	0.49
S4R2	0.45	-8.25	0.13	0.21	-2.0	0.21
S5	0.27	1.25	0.31	0.45	0.0	-0.45
S6R1	0.06	-0.5	0.17	0.02	-2.0	0.30
S6R2	0.07	1.0	0.29	0.08	-0.25	0.16
S7	0.32	-3.0	0.19	0.66	0.0	0.66
S8	0.19	-3.75	0.45	0.32	-0.25	0.39
S9R1	0.27	1.5	0.44	0.12	-2.0	0.41
S9R2	0.09	-3.5	0.33	0.14	-0.5	0.25
S10R1	0.34	-0.25	0.65	0.05	-0.25	-0.22
S10R2	0.18	0.5	0.48	0.08	1.75	0.21
	Day 3			**Day 4**		
	0 lag	**Optimum lag(hours)**	**XCORR**	**0 lag**	**Optimum lag(hours)**	**XCORR**
S1R2	0.97	0.0	0.97	1.00	0.0	1.00
S2R2	0.30	2.0	0.35	-	-	-
S3R1	0.08	-0.75	0.30	-	-	-
S3R2	0.07	-1.75	0.37	0.06	-1.0	0.29
S4R1	0.18	-0.25	0.18	0.13	-2.0	0.32
S4R2	0.48	-0.5	0.62	-	-	-
S5	0.66	0.0	0.66	0.32	-0.25	0.55
S6R1	1.00	0.0	1.00	0.35	-1.0	0.44
S6R2	0.03	-1.5	0.19	0.05	-0.75	0.48
S7	0.11	0.0	0.11	0.12	-3.75	0.32
S8	0.01	-2.25	0.22	0.13	-0.75	0.47
S9R1	0.13	-3.0	0.24	0.19	0.25	0.26
S9R2	0.16	0.0	0.16	0.11	0	0.11
S10R1	0.29	2.5	0.32	0.28	1.75	0.49
S10R2	0.15	1.0	0.49	0.47	0	0.47

Table 5.9 Averaged $PM_{2.5}$ working hours XCORR over 4 days

Average of 4 days		
0 lag	**Optimum lag(hours)**	**XCORR**
0.96	0.00	0.96
0.18	3.00	0.39
-0.10	-2.50	0.31
0.00	-2.75	0.27
0.11	-0.25	0.36
-0.06	-8.33	0.32
0.20	1.00	0.27
0.33	-3.50	0.48
0.01	-1.50	0.28
0.14	-6.75	0.32
0.07	-7.00	0.38
0.05	-3.25	0.34
0.02	-3.97	-3.32
0.09	2.80	0.11
0.14	3.25	0.41

Site 1 run 2 showed very strong XCORR for a 0 lag for all 4 days, as seen in Figure 5.41. On day 1 and 4 of monitoring i.e. the two days where monitoring would be slightly shorter due to setting up or removing of the monitoring equipment, the XCORR values tended towards 0 faster than the two full days of monitoring. Site 1 is a small naturally ventilated shop which had its doors open for a large proportion of the day due to the warm weather during the week of monitoring, and so a high correlation between indoor and outdoor concentrations would be expected during the daytime.

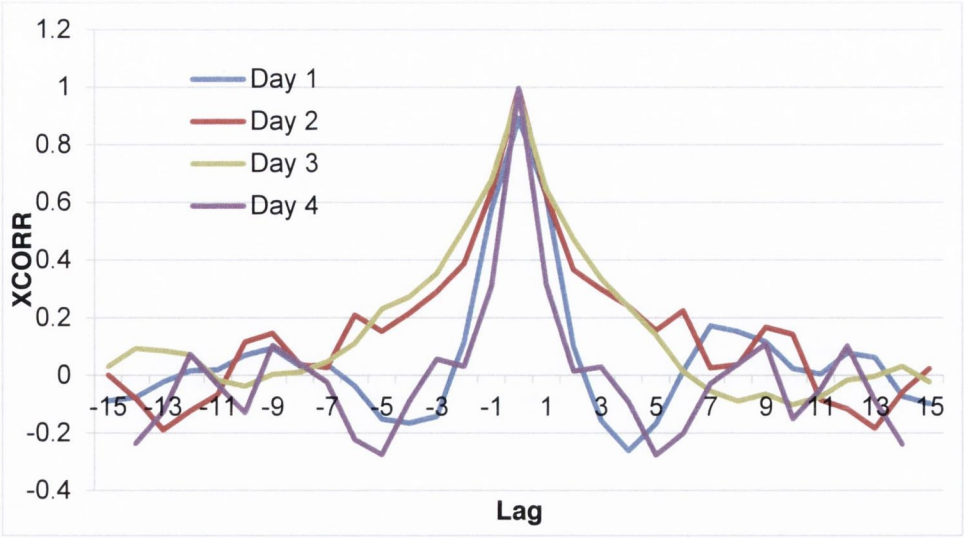


Figure 5.41 $PM_{2.5}$ XCORR plot of $PM_{2.5}$ Site 1 Run 2 working hours

Many sites showed a strong XCORR for certain days during monitoring and none for others. For example, Site 6 showed a poor set of XCORR values with different patterns seen on every day over both runs. While 2 days (run 1 day 3 and run 2 day 4) showed some correlation at lags of 0 and 15 minutes this was not mimicked during other days of monitoring, see Figure 5.42. The site showed a large volume of negative XCORR values indicating that high outdoor concentration caused reductions in indoor concentrations rather than increases. While this may be possible if the site studied was an environment which generated a large source of pollutants, it is unlikely in this environment where there is a large volume traffic source directly outdoors and no major source inside.

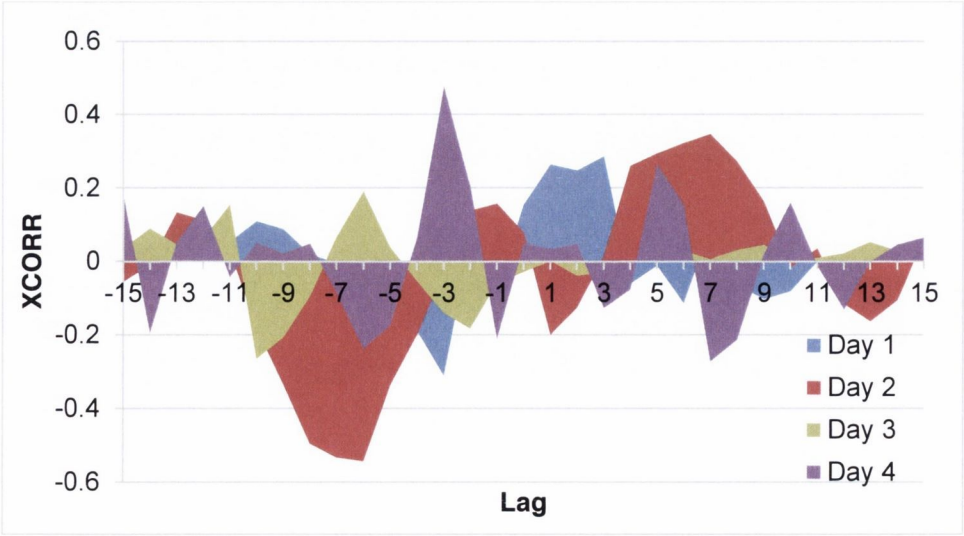


Figure 5.42 Site 6 run 2 $PM_{2.5}$ XCORR

This is a pattern that is seen at many of the sites including Site 2 run 2, Site 3 run 1 and to a certain extent run 2, Sites 7, Site 8 and Site 9. Apart from Site 1 all other non-mechanically ventilated sites have shown a poor pattern for lag times indicating that no clear pattern can be found during the working hours. Within each run, as was seen with run 6, single days can show strong XCORR patterns that indicate a definite lag time with little noise. For instance on day 2 of Site 7, as shown in Figure 5.43, a strong pattern is revealed with slowly decreasing influence as the lags increase in the positive and negative scale away from the highest XCORR value at a 0 lag. The XCORR value at a lag of -1 (or 15 minutes) beforehand was similar. Reviewing weather data it was found that day 2 was a warm sunny day and the door at the back of the shop was opened more this day in order to allow air to circulate and cool the shop, therefore increasing the air changes per hour. On other days when the shop door was kept closed and opened sporadically throughout the day by staff and customers, this may have promoted the irregular lag times. Both indoor and outdoor concentrations were relatively stable on this day with no sharp fluctuations, allowing higher correlations between indoor and outdoor concentrations.

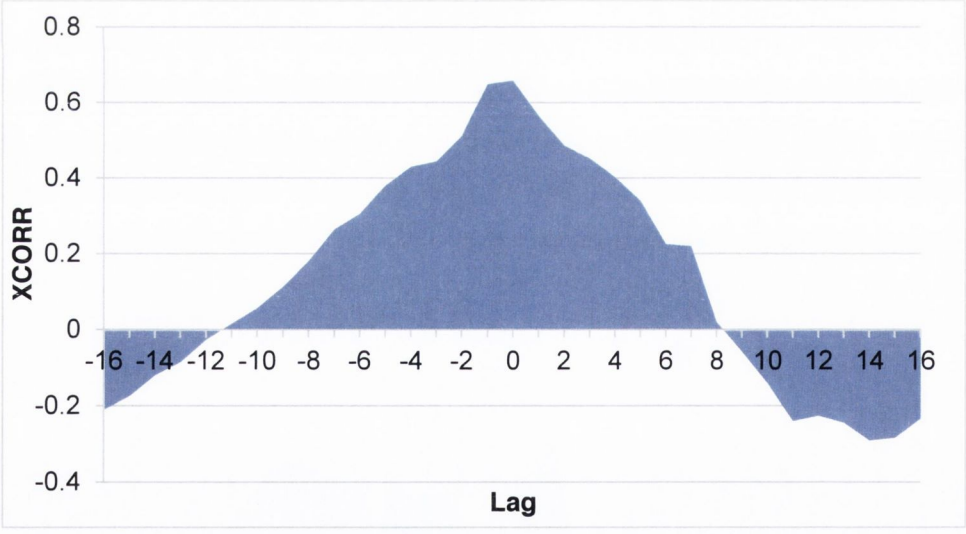


Figure 5.43 $PM_{2.5}$ XCORR Site 7 day 2

Site 5 shows two very different behaviours between days 1 and 2 compared to days 3 and 4. This may be due to the source which was discussed previously that affected the indoor NO concentrations from the end of day one and continued for over a day. Negative XCORR values are seen near the 0 lag for the first 2 days, changing to a positive XCORR for the final 2

days. Negative values indicate that outdoor increases cause outdoor reductions, not increases as instinct would suggest.

Site 4 run 2 (ground) is another site that shows poor or negative XCORR values throughout except for a single day, in this case day 3 (see Figure 5.44).

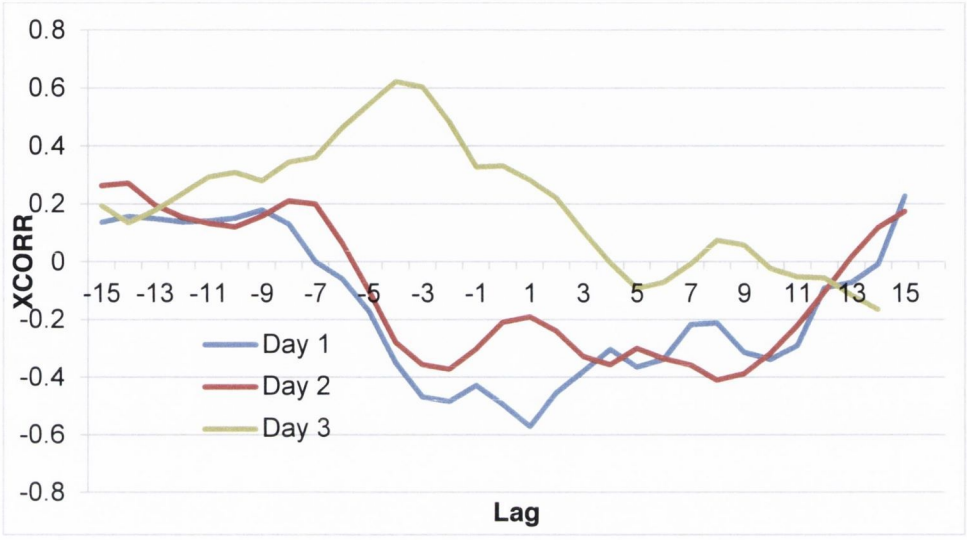


Figure 5.44 XCORR Site 4 run 2 $PM_{2.5}$ days 1, 2 & 3

Site 4 run 1 on the other hand shows strong XCORR for the first two days with a smooth pattern similar to that shown in Figure 5.43 but the XCORR values decrease significantly for day 3. The difference on the final day of monitoring was that rain occurred during the day which may have affected $PM_{2.5}$ concentrations outdoors. This, combined with a sharp change in wind direction which occurred, provided a much lower max XCORR value of only 0.18 for the 3rd day. As some indication of a time lag is available for Site 4, further work was done by carrying out the same XCORR test for 2 sets of the night-time period, from closing until midnight and midnight until opening. This test was carried out for several sites in order to see whether those that showed no stable time lag during the day might show a strong XCORR pattern at night. Reviewing the data, the lags seen for the first half of the night time, when a large decay in outdoor pollutants occurs, a stronger XCORR value can be seen for some sites compared to during the day, yet at others a worse XCORR value can be seen. When regressions are carried out for the entire run, a negligible R^2 is found between indoor and outdoor concentrations, a maximum R^2 = 28.5 % can be found when a best subset regression is carried out which shows pressure, temperature, wind direction as the most important predictors for indoor concentrations.

Site 10 run 2 showed good XCORR values indicating a lag of 45 minutes to 1 hour between the concentrations entering the ventilation system, which operated continuously day and night, and when it was picked up by the indoor monitors. The 4 plots of XCORR for working hours are shown in Figure 5.45. In order to see all 4 days of data, a line plot was chosen over an area plot which is used for other sites.

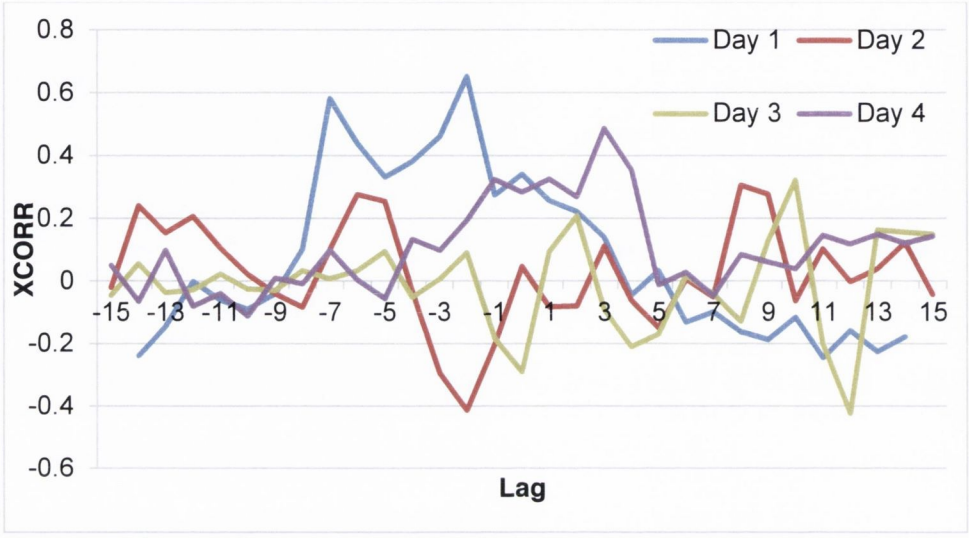


Figure 5.45 Site 10 run 1 XCORR $PM_{2.5}$ working hours

5.3.5. Summary of lag and XCORR values for NO_2 and $PM_{2.5}$

In summary, NO_2 lag times were calculated ranging from 6 hours to a 0 lag, with two thirds of all sites showed lags less than or equal to one hour. Higher correlations and more stable lag patterns were seen for mechanically ventilated sites compared to the naturally ventilated ones. A stable lag pattern indicated a constant lag throughout the day while a noisy one indicated that the lags varied across the day. These occurred more in naturally ventilated buildings, where air changes per hour depended on whether doors were left open. These sites usually were smaller premises where the outside monitor was located closer to the main entrance compared to larger buildings in which monitoring occurred farther away from main entrances. It was important to review at the highest correlation and the pattern of all correlations, around this in order to see if the high correlation was consistent with the pattern or could be simply noise. In order to learn more about the lags, it was decided to break them down into 3 sections: working hours, close of business to 12 am and 12 am to open of business. NO_2 XCORR values increased during both sections of non-

working hours compared to working hours, although lag times also increased. This is logical, as when buildings are closed the air changes per hour decrease but are at a steady rate as doors/windows are not being used. Therefore, while it takes longer for the outdoors to influence the indoor concentration, as air changes are lower, this length of time is consistent throughout non-working hours. The detailed review of the non-working hour lag time relationship for both NO_2 and $PM_{2.5}$ can be found in Appendix A.

$PM_{2.5}$ XCORR values were on the whole much lower than NO_2 with much nosier patterns and less defined lagged times. For working hours, little evidence is present to show that either mechanically ventilated or naturally ventilated sites give longer lag time, with a great deal of variation at even individual sites for different days. During non-working hours the same issues can be seen, with some nights showing a reasonable XCORR value and lags, which fit when the lag is applied to indoor data and plotted against outdoor data, but the other nights showing low correlations and no clear lag.

5.4. NO/NO_2 relationships

The percentage of NO_2 in NO_x can give an indication of the source of the pollutant with a higher proportion of NO_2 being emitted by diesel cars compared to petrol ones and even higher proportions being emitted inside the range of 20-50 km h^{-1}; the current speed limit in Dublin City Centre being 30 km h^{-1}. A combustion source such as a gas cooker indoors would cause the NO_2/NO_x ratio to increase between indoors and outdoors while a sink such as a large number of surfaces which induce heterogeneous reactions could reduce the ratio indoors compared to outdoors. When computing lag times for the 10 sites the pattern remained essentially unchanged when NO values were used for outdoor concentrations while retaining NO_2 values indoor. This held true for all sites with the exception of Site 2 run 2, Site 6 run 2 and Site 9 run 2.

Sites produced very different patterns for the ratio of NO_2/NOx indoors and outdoors as shown on Table 5.10, which might indicate sources or sinks for NO_2 or NO. For some sites the ratios indoors and outdoors were close with high correlation, for instance Site 2 run 2 returned a correlation between

the ratio indoors and outdoors of 0.80 while others showed little or no correlation between indoors and outdoors such as at Site 1 run 2 (Pearsons r = 0.18).

Table 5.10 Average NO_2/NO_x relationships

	In NO_2/NO_x	Out NO_2/NO_x
S1R2	0.28	0.34
S2R2	0.69	0.64
S3R1	0.45	0.51
S3R2	0.53	0.54
S4R1	0.31	0.51
S4R2	0.57	0.66
S5R1	0.56	0.69
S6R1	0.13	0.56
S6R2	0.02	0.4
S7R1	0.56	0.55
S8R1	0.19	0.52
S9R1	0.04	0.69
S9R2	0.25	0.65
S10R1	0.55	0.47
S10R2	0.59	0.61

There was a large degree of variance between the NO_2/NO_x ratios throughout the sites. Site 6 run 2 and Site 9 run 1 saw extremely low NO_2/NO_x ratios of below 0.05 indoors, with Site 6 run 1 also seeing a ratio in the range of 0.05 – 0.25. This indicates that the NO concentration was significantly greater than the NO_2 concentration. If this ratio reduces greatly between outdoors and outdoors, as it does at these two sites, it could indicate that NO_2 was being degraded via a chemical process back to NO or that there was a source of NO present with no O_3 or UV for the conversion to NO_2. Both these sites are old naturally ventilated buildings and the reduction in NO_2 concentrations is beneficial to the health of those working in the offices, as NO_2 is more detrimental to human health than nitrogen in the form of NO.

Figure 5.46 shows the time series of the NO_2/NO_x ratios for Site 6 run 2 illustrating the heavily reduced indoor ratio. The pattern for outdoors has a strong diurnal pattern with a sharp rise in the ratio at 11 pm daily from about 0.3 to about 0.7, reducing then to 0.6 and staying near this level until a sharp drop to a level of 0.2 at 8 am and an increase over the day to 0.4. This pattern is a mirror of the diurnal cycle for NO. As the NO concentration drops overnight due to reduced emissions from traffic sources, the ratio of

NO_2/NO_x increases. Although NO_2 also reduced overnight the proportional drop in NO is greater, which affects the ratio to a larger extent. In the morning when sources due to road traffic and UV from the sun provide the necessary conditions for chemical processes, the NO increases sharply therefore reducing the ratio. A similar outdoor pattern was seen at several other sites including Site 2 run 2, Site 4 run 1, Site 6 run 1, Site 7, Site 8 and Site 9 run 1. However, Site 6 run 2 shows the greatest influence from the outdoor NO pattern.

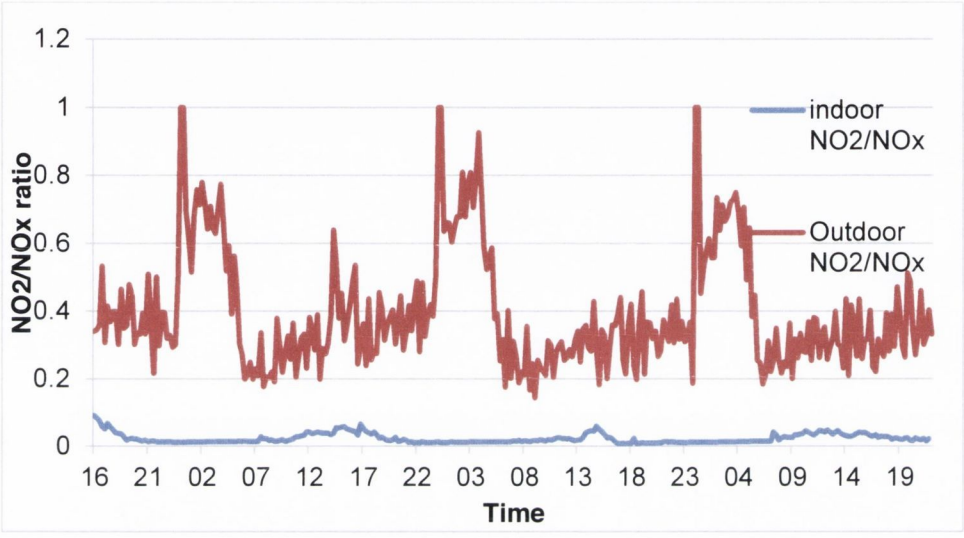


Figure 5.46 NO_2/NO_x ratio Site 6 run 2

5 other sites also saw this pattern (Site 3 run 1 and 2, Site 4 run 2, Site 9, Site 10 run 1 and 2),although not to the same degree. The pattern at these other sites resembles a sine wave rather than the harsh jumps between the low and high regions seen in Site 6 run 2.

Site 8 shows two different patterns for the NO_2/NO_x ratio for indoors and outdoors with outdoor following a similar sinusoidal pattern mentioned above with peaks near midnight and troughs at midday and the opposite sinusoidal pattern indoors. The indoor ratio is in the range of 0.1 – 0.4 while outdoors the range is higher at 0.4 – 0.8. This is due to similar NO_2 and NO concentrations outdoors (a 2 sample T test shows an estimate for the difference of 0.778, T=0.53, P=0.59) while outdoors NO is significantly higher (2 sample T test shows an estimate for the difference of 36.825, T=28.62, P=0.0). As for Site 6 run 2 and Site 9 run 1 there seems to be a conversion of NO_2 to NO inside the building (which, like Sites 6 and 9 is an older naturally ventilated building), more than likely due to heterogeneous reactions on surfaces indoors.

Site 2 run 2 shows a very close pattern for the NO_2/NO_x ratio, as seen in Figure 5.47. As mentioned before this site contained a gas cooker indoors and the effect of this is evident in the plot with the NO_2/NO_x ratio increasing during business hours of the canteen compared to outdoors. Once the canteen closed the indoor ratio progressively returned to the same level of the outdoor ratio.

Figure 5.47 Site 2 run 2 NO_2/NO_x ratio

One other site indicated a similar pattern, with a possible source of NO_2 present during the day. This was Site 7 where the ratio increased, (Figure 5.48) during the day while the outdoor ratio decreased. Initially this ratio indicated an indoor source. Further investigation showed that NO_2 was higher outdoors so the increase in the ratio was more likely caused by a greater reduction in NO concentration compared to the NO_2 concentrations - hence an increase in the ratio. No increase in the NO_2 concentration indoors indicates that the NO has another sink rather than being converted to NO_2.

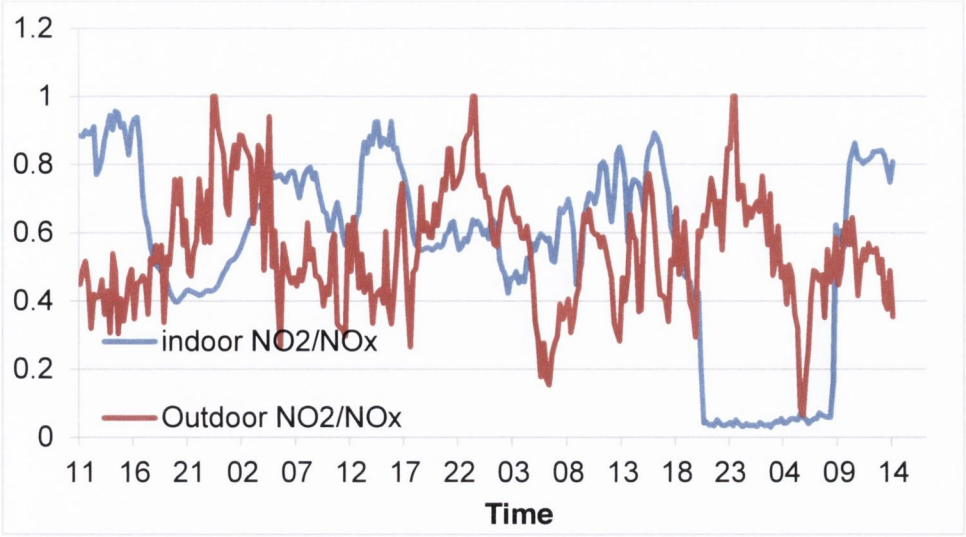


Figure 5.48 Site 7 NO_2/NO_x ratio

On the final night of monitoring indoors at Site 7 a large concentration of NO was emitted from an unknown indoor source, concentrations increasing suddenly at 9 pm and remaining high until the shop was reopened the next morning. The effect of this sharp rise in concentrations of NO is evident in Figure 5.48. No simultaneous or lagged increase occurs for NO_2 although the concentrations that night fluctuated slightly more than the previous nights. Members of staff reported no-one was present out of working hours in the building so the most likely cause of such a spike was thought to be leakage from a canister of N_2O which is used in the process of whipping cream (Site 7 being a catering suppliers shop).

Site 5 saw two notably different patterns throughout the monitoring run (Figure 5.49) with the first portion showing a reduced ratio indoors compared to outdoors and the second showing the ratios return to a similar scale. The outdoor ratio shows considerably more noise than indoors throughout the run. Like the final evening at Site 7 the reason for the unusual behaviour here was probably due to an extended source of NO indoors. The source was first apparent near 5 pm of day one; it reduced overnight but rose again the next morning at 8 am and stayed high until the next day at 8 am when the source seems to have stopped. At Site 7, the catering supplies shop, the indoor source was assumed to be due to a canister of gas leaking but Site 5 is an office and had no explainable source for NO.

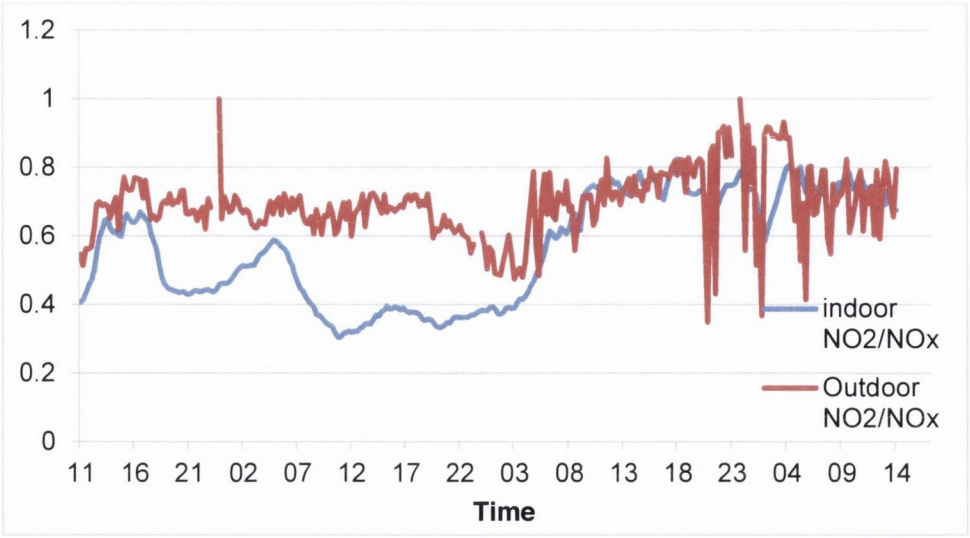


Figure 5.49 Site 5 NO_2/NO_x ratio

A clear lag of 2 hours was seen at Site 10 run 1 between the time series for indoors and outdoors. This lag was reduced to 15 minutes when the outdoor monitors were moved to the roof level beside the air inlet from the ventilation system. Unexplained peaks seen during run 1 in the middle of the night matched similar peaks which occurred both indoors and outdoors during run 2. As the ventilation system runs continuously (24/7) in this building, this may be an indication of roof level sources for these increased ratios. Overall, the ground level ratio (0.47) was lower than roof level (0.61) outdoor ratio indicating a higher percentage of NO in NO_x, caused by the lag on the conversion of NO to NO_2. While primary reactions occur within seconds it can take several minutes for the reaction to occur depending on UV and O_3 availability. This could explain the higher ratios at roof level as the lag during which air travels to the roof from ground gives enough time for these reactions to occur. This theory stands when reviewing the average ratios in Table 5.10 with roof level ratios higher than their ground level counterparts. In addition Site 5 was also measured at roof level and returned a high ratio.

5.5. Typical inhaled dosage of workers in different buildings

Dose is the amount (i.e. mass) of a pollutant e.g.. NO_2 or $PM_{2.5}$ which enters the body over a specific time period. Two time periods were calculated here; dose per average working day and also dose per hour. The mass of pollutant inhaled can be calculated as in Equation 5.5 which estimates the values for the intake of air into the lungs using the concentration, time and ventilation rate of the subject. Before calculating the dose the intake mass of pollutant must first be calculated.

$$I_0 = C_a t \beta \qquad \text{Equation 5.5}$$

(International Commission on Radiological Protection, 1994)

Where:

C_a = Concentration ($\mu g\ m^3$)
t= time (hours)
β = Ventilation rate of subject exposed ($m^3\ h^{-1}$)

Intake mass of NO_2 and $PM_{2.5}$ was calculated per hour and per working day and values for males and females at two different activity levels (using typical breathing rates) are detailed in Table 5.12 and

Table 5.13. The first activity level was for sitting which would be the level used for the average office working throughout the working day. The second activity level which intake mass was calculated for was light exercise, this is more relevant for a shop where staff are moving stock or walking around serving customers all day. The female intake mass are lower than the male due to the reduced β variable. The length of the working day varies for each of the buildings; the average I_o value was calculated for only working hours and then multiplied by the number of hours worked per day in each building.

Table 5.11 β values for males and females

	β	
	Male	Female
Sitting	0.54	0.39
Light exercise	1.5	1.25

Table 5.12 Intake mass of staff per hour during working hours

	NO_2 ($\mu g\ hr^{-1}$)			
	I_0 male sitting	**I_0 male light**	**I_0 female sitting**	**I_0 female light**
Site 1 Run 1	25.78	71.61	18.62	59.68
Site 1 Run 2	23.81	66.15	17.20	55.13
Site 2 Run 1	28.51	79.20	20.59	66.00
Site 2 Run 2	23.80	66.10	17.19	55.08
Site 3 Run 1	16.58	46.05	11.97	38.37
Site 3 Run 2	21.62	60.07	15.62	50.06
Site 4 Run 1	20.45	56.80	14.77	47.34
Site 4 Run 2	28.28	78.56	20.43	65.47
Site 5 Run 1	15.97	44.37	11.53	36.97
Site 6 Run 1	6.59	18.30	4.76	15.25
Site 6 Run 2	2.53	7.02	1.83	5.85
Site 7 Run 1	22.93	63.70	16.56	53.08
Site 8 Run 1	13.27	36.85	9.58	30.71
Site 9 Run 1	3.50	9.73	2.53	8.11
Site 9 Run 2	10.10	28.05	7.29	23.38
Site 10 Run 1	25.81	71.70	18.64	59.75
Site 10 Run 2	25.84	71.78	18.66	59.82
	$PM_{2.5}$ ($\mu g\ hr^{-1}$)			
	I0 male sitting	**I0 male light**	**I0 female sitting**	**I0 female light**
Site 1 Run 1	9.68	9.68	9.68	9.68
Site 1 Run 2	8.33	23.15	6.02	19.29
Site 2 Run 1	8.98	24.93	6.48	20.78
Site 2 Run 2	6.73	18.70	4.86	15.58
Site 3 Run 1	4.97	13.81	3.59	11.51
Site 3 Run 2	5.28	14.67	3.81	12.23
Site 4 Run 1	8.67	24.08	6.26	20.07
Site 4 Run 2	16.01	44.46	11.56	37.05
Site 5 Run 1	5.23	14.52	3.78	12.10
Site 6 Run 1	9.13	25.36	6.59	21.13
Site 6 Run 2	7.46	20.73	5.39	17.28
Site 7 Run 1	14.53	40.35	10.49	33.62
Site 8 Run 1	6.91	19.19	4.99	15.99
Site 9 Run 1	8.96	24.90	6.47	20.75
Site 9 Run 2	7.96	22.12	5.75	18.43
Site 10 Run 1	6.96	19.32	5.02	16.10
Site 10 Run 2	5.24	14.57	3.79	12.14

Table 5.13 Intake mass of staff per working day

	NO_2 (μg working day^{-1})			
	$I_{0\ male\ sitting}$	$I_{0\ male\ light}$	$I_{0\ female\ sitting}$	$I_{0\ female\ light}$
Site 1 Run 1	180.463	501.287	130.335	417.739
Site 1 Run 2	166.698	463.050	120.393	385.875
Site 2 Run 1	199.573	554.369	144.136	461.974
Site 2 Run 2	166.567	462.685	120.298	385.571
Site 3 Run 1	116.037	322.326	83.805	268.605
Site 3 Run 2	151.367	420.463	109.320	350.386
Site 4 Run 1	143.142	397.616	103.380	331.346
Site 4 Run 2	197.977	549.937	142.984	458.281
Site 5 Run 1	111.801	310.558	80.745	258.798
Site 6 Run 1	46.124	128.122	33.312	106.768
Site 6 Run 2	17.695	49.152	12.779	40.960
Site 7 Run 1	160.512	445.867	115.925	371.556
Site 8 Run 1	92.856	257.935	67.063	214.946
Site 9 Run 1	24.513	68.091	17.704	56.743
Site 9 Run 2	70.691	196.364	51.055	163.637
Site 10 Run 1	180.690	501.918	130.499	418.265
Site 10 Run 2	180.888	502.466	130.641	418.721
	$PM_{2.5}$ (μg working day^{-1})			
	$I_{0\ male\ sitting}$	$I_{0\ male\ light}$	$I_{0\ female\ sitting}$	$I_{0\ female\ light}$
Site 1 Run 1	67.774	67.774	67.774	67.774
Site 1 Run 2	58.345	162.069	42.138	135.057
Site 2 Run 1	62.830	174.527	45.377	145.439
Site 2 Run 2	47.129	130.913	34.037	109.094
Site 3 Run 1	34.797	96.657	25.131	80.548
Site 3 Run 2	36.969	102.692	26.700	85.576
Site 4 Run 1	60.692	168.590	43.833	140.492
Site 4 Run 2	112.035	311.209	80.914	259.341
Site 5 Run 1	36.593	101.648	26.429	84.707
Site 6 Run 1	63.909	177.525	46.156	147.937
Site 6 Run 2	52.247	145.131	37.734	120.942
Site 7 Run 1	101.679	282.442	73.435	235.369
Site 8 Run 1	48.363	134.341	34.929	111.951
Site 9 Run 1	62.744	174.290	45.315	145.241
Site 9 Run 2	55.746	154.849	40.261	129.041
Site 10 Run 1	48.694	135.262	35.168	112.718
Site 10 Run 2	36.709	101.971	26.512	84.975

For comparative purposes it has been assumed that all staff are male and the sitting β values are used, for the shops monitored staff are relatively sedentary throughout the working day therefore the light exercise value would be too high. Figure 5.50 and Figure 5.51 plot the average weight of NO_2 and $PM_{2.5}$ that a male, who sits at their desk, at each of the sites breathe in during each working day.

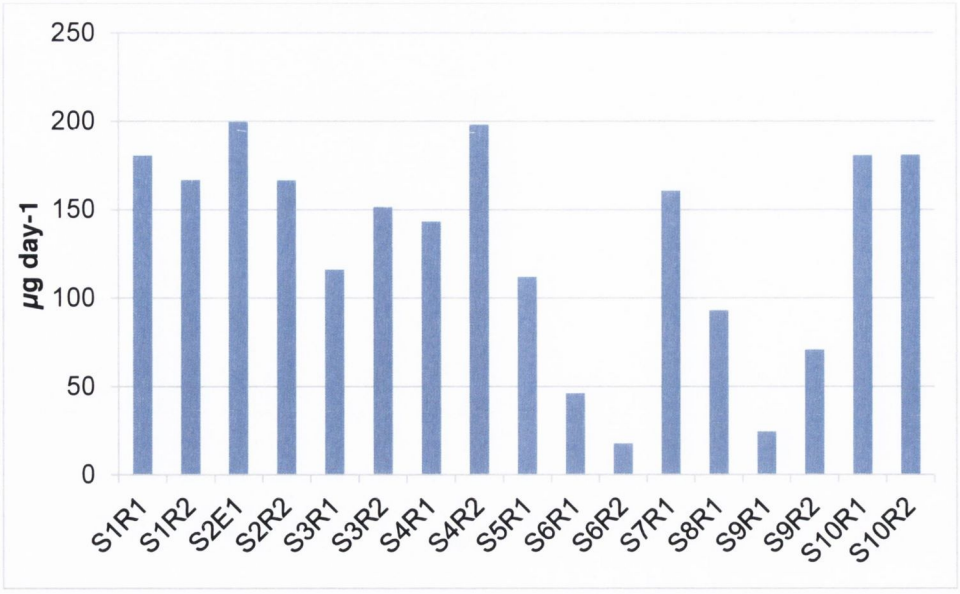


Figure 5.50 Average working hours NO_2 inhaled mass for Male sitting

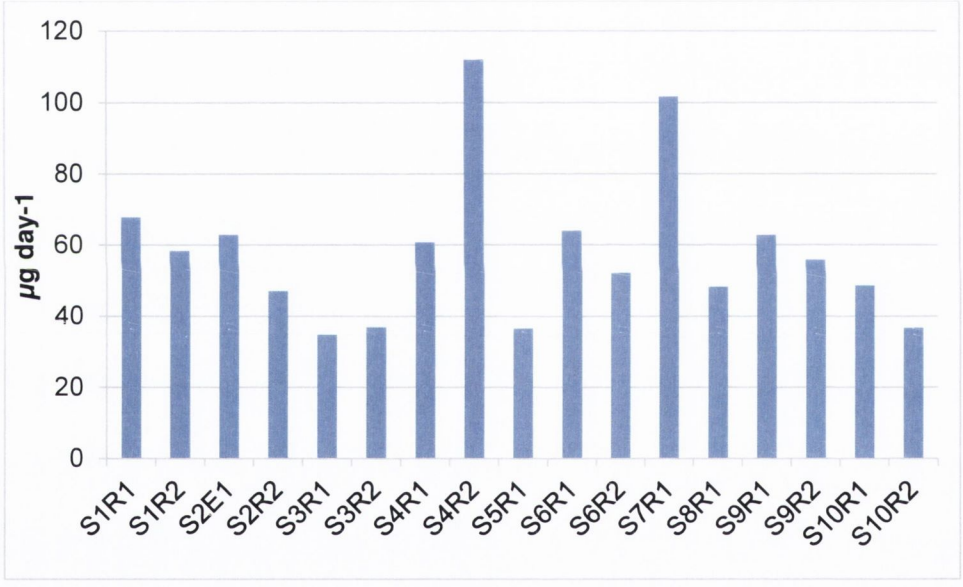


Figure 5.51 Average working hours $PM_{2.5}$ inhaled mass for Male sitting

Previous work by Zuurbier (2010) on exposures of people commuting found $PM_{2.5}$ found a median intake dose ranging from 45.6 µg hr^{-1} for use of an electric bus up to 100.4 µg hr^{-1} for cycling in high traffic. These are considerably higher than the dose which was found for $PM_{2.5}$ per hour for a sitting male. For a male carrying out light exercise while at work, say lifting boxes of stock, the peak intake dosage was found at Site 4 during run 2 at 44.46 µg hr^{-1}which is similar to that found by Zuurbier (2010) for those travelling on an electric bus in their study location of Arnhem, the Netherlands. For a person commuting by cycling their dosage is increased

due to the higher ventilation rate of the person compared to those sitting on a bus.

The highest mass of pollutant inhaled during the working day occurred at Site 4 during run 2 for both $PM_{2.5}$. Site 7 also saw high $PM_{2.5}$ inhaled dosage comparative to other sites. Site 4 run 2 showed some usually high $PM_{2.5}$ concentrations during the monitoring period which have been discussed previously in the chapter. It also had a long working day with the building open from 8 am to 8 pm and some staff working throughout this time. Sites 3, 5 and 10 showed the lowest $PM_{2.5}$ dosage throughout the day at just less than 40 µg; these were all mechanically ventilated offices which had ventilation systems installed in the previous 10 years for Site 10 and 5 years for Sites 3 and 5.

With respect to NO_2, Site 2 during run 1 and Site 4 during run 2 recorded the highest inhaled dosage. Site 2 contained a gas cooker in a room adjoining the monitoring area which acting as an internal source of NO_2 and $PM_{2.5}$. Use of this cooker was reduced during the second run due to students attending the college being on holidays; therefore only staff used the canteen during this monitoring run. While Site 4 had long opening hours (12 hours per day), the indoor concentrations for NO_2 were heightened in run 2 compared to run 1 hence pushing up the exposure. Site 6 and Site 9 run 1 saw considerably lower inhaled dosages to staff in the buildings, these buildings were both naturally ventilated office located in older buildings. Site 9 run 2 and Site 8 also saw reduced NO_2 concentrations compared to other sites, Site 8 being an older naturally ventilated building although used as a small shop.

Sites with longer working days are more likely to experience a higher inhaled dosage than those with short working days due to the shorter duration that they are exposed to the pollutants for. The sites which record the lowest inhaled dosage of $PM_{2.5}$ are mechanically ventilated buildings, Sites 3 and 5. Both these building were constructed in the past 5 years and indoor monitoring took place in offices. These buildings contained filtration systems specially designed to remove such pollutants and therefore lessen exposure to staff. With respect to NO2 naturally ventilated older buildings proved to provide the least exposure to occupants of the building, with Sites 6 and 9 providing a partially low inhaled dosage compared to other sites.

The values calculated in Table 5.12 andTable 5.13 are the inhaled mass dosage of each pollutant; once inhaled only a fraction of particles will stay in the respiratory tract; this fraction is the actual dosage to the individual. Some papers have been found to use the inhaled dose rather than the deposition factor calculated dose (Su et al., 2011). The deposition fraction (DF) of particles remaining in the lungs increases with activity levels, values for DF for rest range 0.14 to 0.8 for $PM_{2.5}$ (Int Panis et al., 2010, Löndahl et al., 2009).

5.6. Comparison of monitoring two indoor locations at Site 3

Site 3 run 1 collected data on the roof and indoors, the panel and bag filters caused no known reduction in NO_2, in fact indoor NO_2 was greater than outdoor NO_2 for a large proportion of monitoring. Background concentrations of NO_2 in site 3 are indicated due to consistently higher indoor levels, with concentrations not reducing below 10 ppb indoors even when outdoor concentrations reduced to negligible levels. While the monitoring took place in offices located in this building, the building's main function is a sports complex. Prior to monitoring in other mechanically ventilated buildings which also displayed these background concentrations, it was decided to carry out further investigations to find the source of the indoor NO_2 concentration. Initially this source was thought to be the UV disinfection system in the sports complex swimming pool. The occupants of the building kindly agreed to a 3rd run of monitoring where the monitors were located in the basement where the UV generator was located and in the same office previously monitored for a 5 day period, the results of which are detailed in Figure 5.52. This monitoring was carried out in early November 2010, while the initial 2 runs were carried out in July 2010.

These investigations showed a Pearsons R^2=0.86 for NO_2 between the office space on the second floor and the plant room on level -2 where the UV generator is housed. The 10ppb office background level was visible during this 3rd study of the office. The background levels are also visible in the plant room at a slightly higher concentration. A strong correlation for NO of R^2=0.92 was also present but here the office had consistently higher NO concentrations. The input air for the office and plant room is drawn in through two different air handling units which are located side by side on

the roof of the building. Due to their close proximity input air should have very similar properties, especially when averaged over 15 minute intervals.

The difference between NO and NO_2 relationships may be due to the presence of the UV water treatment system. The UV generator causes a chemical transformation, converting NO to NO_2 in the presence of Ozone. This effectively reduces the NO concentration and increases the NO_2 concentration in the plant room resulting in lower NO levels than the office but higher concentrations of NO_2. Other studies have tied long term increases of as little as 5.3ppb exposure to NO_2 to 0.5% increases in hospital admissions due to respiratory illnesses (Chaloulakou et al., 2008, Namdeo and Bell, 2005).

While it was initially thought that this may be the contributor to the baseline NO_2 level of roughly 10 ppb that do not reduce overnight, this was later seen in various other buildings which do not contain such apparatus. It can be concluded that distinctly separated areas of this building show strongly correlated fluctuations even when supplied by separate air handling units.

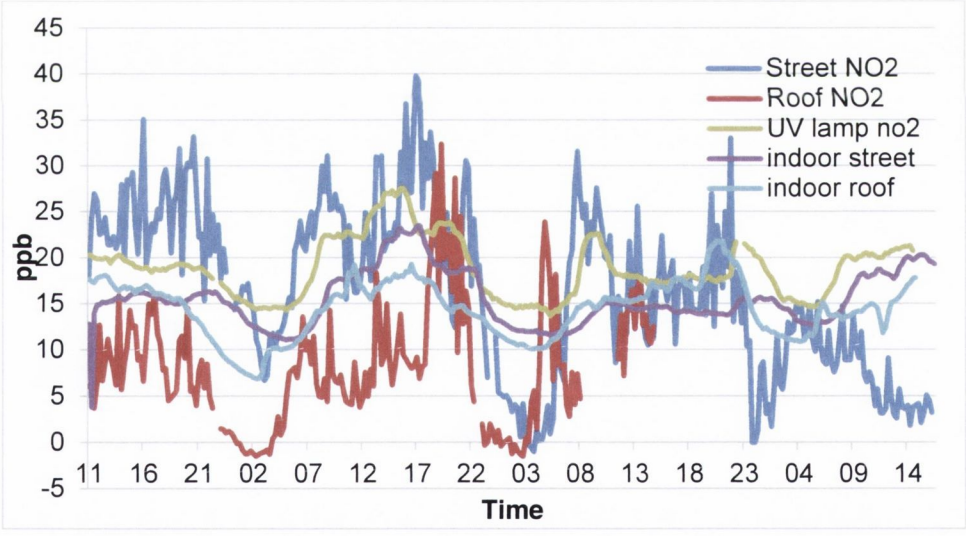


Figure 5.52 Site 3 Run 1 and Run 2 plus comparison basement with UV lamp

5.7. Conclusions

Reviewing the detailed analysis of monitoring results provided a greater insight into the influence of outdoor pollutant concentrations on commercial indoor environments.

The results show that NO_2 generally provide greater correlations between indoor and outdoor, with clear lag times of up to an hour and obvious

diurnal cycles. Results indicate that naturally ventilated office buildings provide a greater reduction in NO_2 compared to mechanically ventilated or naturally ventilated shop, - Site 6 being a prime example of this. The most likely cause of the sink is due to increased heterogeneous reactions on surfaces and the increased presence of moisture in these older buildings which amplifies such reactions. Similar results were obtained at Site 9, where the sink reduced when air changes were increased during run 2 at Site 9 due to less time for heterogeneous reactions to occur indoors. The information gathered from NO/NO_2 ratios further signifies a sink indoors, with the NO/NO_2 ratio notably reduced compared to outdoors. Site 9 also showed an I/O ratio trend which did not follow the usual relationship. Reviewing the time series at the site shows very little interaction between the indoor and outdoor concentrations, which may be due to the influence of the heterogeneous reactions or other unknown influences.

$PM_{2.5}$ concentrations show a much lower correlation between indoors and outdoors, both varying erratically around a mean value. $PM_{2.5}$ does not show the clear lag times that were seen for NO_2, with XCORR showing noisy results and low values. NO_2 ratios on the other hand for most sites show lags between 0-1 hour with mechanically ventilated sites showing a more stable pattern and higher R^2 values. The results do not indicate a difference between mechanically ventilated sites regarding time lag. However, a slightly longer lag was found at mechanically ventilated sites between the indoor and roof level fluctuations than between the ground level concentrations the corresponding indoor fluctuations.

The correction applied to $PM_{2.5}$ for use of the light scattering monitor results causes issues (particularly for the I/O ratios) when concentrations go above 60 $\mu g\ m^{-3}$. $PM_{2.5}$ showed high I/O ratios, with frequent ratios above 1 during working and non-working hours. This occurred for both mechanically ventilated and naturally ventilated buildings. The addition of the correction for relative humidity further increased these ratios as it effectively reduced outdoor concentrations while indoor concentrations remained unchanged.

Only two sites saw I/O ratios for entire runs above 1 for NO_2. These were Site 3 run 1 and Site 10 run 2, both mechanically ventilated office buildings with outdoor concentrations taken at roof level run this run and no significant indoor sources for NO_2. Both of these sites saw the ratio increase overnight, although at Site 10 this was muted due to sharp early morning peaks outdoors before opening of the office. In fact almost all sites saw this relationship where I/O ratios for NO_2 and $PM_{2.5}$ increased overnight due to higher indoor concentrations and outdoor concentrations reducing significantly. The results show that mechanically ventilated buildings have baseline NO_2 concentrations (roughly 10-12 ppb) indoors, levels which will not drop further, even if indoor concentrations tend towards 0. $PM_{2.5}$ concentrations however, do not show the same diurnal reductions indoor compared to the outdoor concentrations, instead remain variable around a mean value throughout the night.

Street level concentrations of NO_2 showed strong influence on the indoor air quality of the mechanically ventilated buildings, with concentrations indoors having higher correlations with these concentrations than with the corresponding roof level concentrations. The purpose of the ventilation system being placed at roof level is that it can draw in air which has lower concentrations of air pollutants; unfortunately this does not seem to be the case with several of the mechanically ventilated buildings monitored in this study. For example, I/O ratios for NO_2 at Site 10 showed a value closer to unity than when outdoor concentrations were measured at ground level than beside the ventilation intake at roof level when I/O ratio values increased to 1.51. It should also be noted that indoor concentrations were measured on the 5th floor of this building and no windows were open. NO/NO_2 ratios also indicated a higher percentage of NO_2 in NO_x at roof level compared to ground level, which is logical as the predominant source of NO_2 in urban areas is vehicles' exhausts. These produce large quantities of NO which will convert to NO_2 upon reaction with O_3. Therefore the kerbside monitors should pick up a higher proportion of NO in NO_x compared to the roof level outdoor monitors as they are further from the source allowing time for conversion of NO to NO_2.

6. Indoor outdoor recursive mass balance model

6.1. Introduction

When approaching occupants of buildings, for possible sites to monitor, it was found that although many had concerns regarding the air pollution concentrations in their work environment, they could not accommodate monitoring equipment being placed in the building due to noise, space, security or health and safety constraints. This enthusiasm for the opportunity to learn about the air quality in their workplace confirmed the need for a model which can be used by those working in such buildings in order to estimate their air pollution exposure while at work, using only information that is openly available and easily accessible.

A generalised recursive mass balance model has been developed in order to carry this out. The model uses a combination of simple inputs provided by the user via *Microsoft Excel*, a format which is commonly used and installed on most workplace computers. Downloading and installing an unfamiliar program may have been a barrier to usage for many end-users, which was opposed to the overriding aim of the model. Detailed individual best fit models have also been developed for each monitoring site, whereby the parameters required for the specific building type has helped to give an insight into the development of the generalised model.

The calculation of indoor air quality requires the characteristics of buildings which influence the infiltration of pollutants from outdoors, the contribution of indoor concentrations due to indoor sources, homogeneous and heterogeneous chemical reactions and the level of pollutants which are removed by transport through interior spaces of the building (Drakou et al., 2000). Characteristics utilized are; air exchange rate, composition of indoor surfaces and indoor pollution sources. These parameters have been used in previous studies where theoretical calculations aim to give a estimate of the air quality of an indoor environment and are discussed individually below in Section 0 (Nazaroff and Cass, 1986).

The data which the user will utilise for inputs is freely available on the EPA website. The NO_2 data utilised for the developed NO_2 model is available in 1 hour time steps as used by the model and in an *Excel* file format. Unfortunately, the EPA uses a gravimetric monitoring method for the collection of $PM_{2.5}$ data and the data is only available at 24 hour average time-steps. This is the reference method set out by the EU and other governing bodies for calculation of PM concentrations but it means that it

is not possible to download $PM_{2.5}$ data for input into the model developed here. For this reason (as well as the generally poor correlations detailed between indoor and outdoor concentrations in Chapters 4 and 5) the model focuses on NO_2 as the pollutant of interest. $PM_{2.5}$ is included in the best fit models for the individual sites for $PM_{2.5}$ but not for the generalised model.

6.2. Scope and Application

The scope of this recursive mass balance model is to predict the average weekly indoor NO_2 and $PM_{2.5}$ exposure of those working in commercial buildings within a 95% confidence interval of the true value. The model's scope includes accounting for indoor fluctuations of NO_2, initially it was hoped to also include short term fluctuations in $PM_{2.5}$, however, given the analysis of the indoor/outdoor relationship for $PM_{2.5}$ in Chapters 4 and 5 it was concluded that this may not be possible. Section 6.8 will discusses if the model is successful in achieving its scope.

The application of this model puts constrains on its inputs and design. It is required to be used by the everyday office or shop employee and therefore software packages to run the model that are widely installed on such computers could only be considered. It also required only inputs which are openly available to the user can be required. No costly monitoring of indoor air quality or testing on the building characteristics such as air exchange rates can be required. It aims to educated interested building occupants to the level of NO_2 and $PM_{2.5}$ exposure, which hopefully will in turn make them consider the health effects of such exposure and how they implement mitigate measures to improve air quality the workplace.

6.3. Model overview

After an extensive literature review, which is detailed in Chapter 2 Sections 9 and 10 it was decided to combine two frequently used modelling techniques in order to achieve these methods are;

(1) Regression: Using the indoor and outdoor concentrations gathered during monitoring of the 10 sites, a regression of indoor concentrations on outdoor concentrations can be conducted. Section 6.6 contains a detailed explanation of how the regression technique provides an infiltration and indoor source factor for each of the buildings. Once individual regressions are carried out the collected data is sorted into parameters which can be used in the final model. This is an important stage as these parameters are not available for Irish

commercial buildings in literature yet the parameters are required by the mass balance stage of the model. A summary of the individual regressions is contained in Section 6.6, with calculations and discussion in Appendix B.

(2) Recursive mass balance: Section 6.4 describes in detail the inputs to the mass balance equation; the output of this equation is the new hourly indoor concentration of a building. The inputs used in the mass balance equation are; the infiltration factor and source calculated by the regression, outdoor concentrations provided by the EPA, inputs provided by the user of the model describing the building and values for parameters collected from literature review. Section 6.7 provides the final choice of parameters. Once inputs are provided they can be inputted into the equations contained in Section 6.5. The section shows the main mass balance equation for both naturally ventilated and mechanically ventilated buildings.

6.4. Model parameters

The model is designed to work across several *Excel* worksheets with calculations occurring in the background in worksheets which are not accessible by the user. Three openly accessible worksheets are provided: one in which a number of questions regarding the building are answered as well as outdoor air quality being input; the second worksheet providing the user with the modelled indoor concentrations; and the third worksheet briefly explaining what these concentrations mean. The parameters and equations used for this model are detailed in this section with a brief review of previously used parameters in other literature.

Inputs change for day and night time. Night time represents the non-working hours of the business when ventilation systems are turned off and doors/windows to the building are shut. The input factors provided by the building occupant dictate which of the values for certain process is chosen, for instance the A/V ratio or deposition rates. "If" statements are used in *Excel* which control which of these is inputted automatically into the equation to calculate indoor concentrations. For most inputs there are three options available (a low, medium and high level) although for some options there is only two i.e. whether there a mechanically ventilation system in place requires a yes or no answer.

6.4.1. Review of parameter choices

The overall model used for NO_2 is shown in Equation 6.1 with all the variables necessary to predict the indoor concentrations of NO_2 using the outdoor data downloaded from the EPA. Chapter 2 Section 10 describe some of the previously used values for the variables required by this model from literature, from which the most appropriate values were derived.

$$C_{indoor} = \frac{\mathrm{p\ a_f\ C_{out}}}{\mathrm{a_f + k}} + \frac{\mathrm{\alpha\ a_f\ C_{out}}}{\mathrm{a_m + k}} + \frac{\mathrm{\alpha\ a_r\ C_{out}}}{\mathrm{a_r + k}} - \sum \mathrm{Deposition} + \mathrm{s} \qquad \text{Equation 6.1}$$

Where:

C_{indoor} = Modelled indoor concentration

C_{out} = Monitored outdoor concentration

a_f = Infiltration air exchange rate

k= Deposition velocity

s = Indoor source

$\sum \text{Deposition}$ = The sum of all deposition or decay factors acting on NO_2

p = penetration factor

α = A factor used to account for the fact that much of the influence of the ventilation system was already accounted for via the regression equation

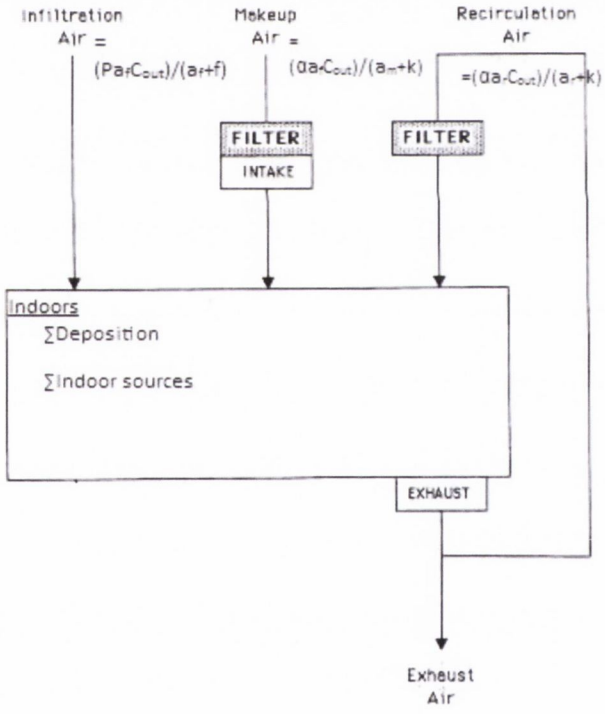
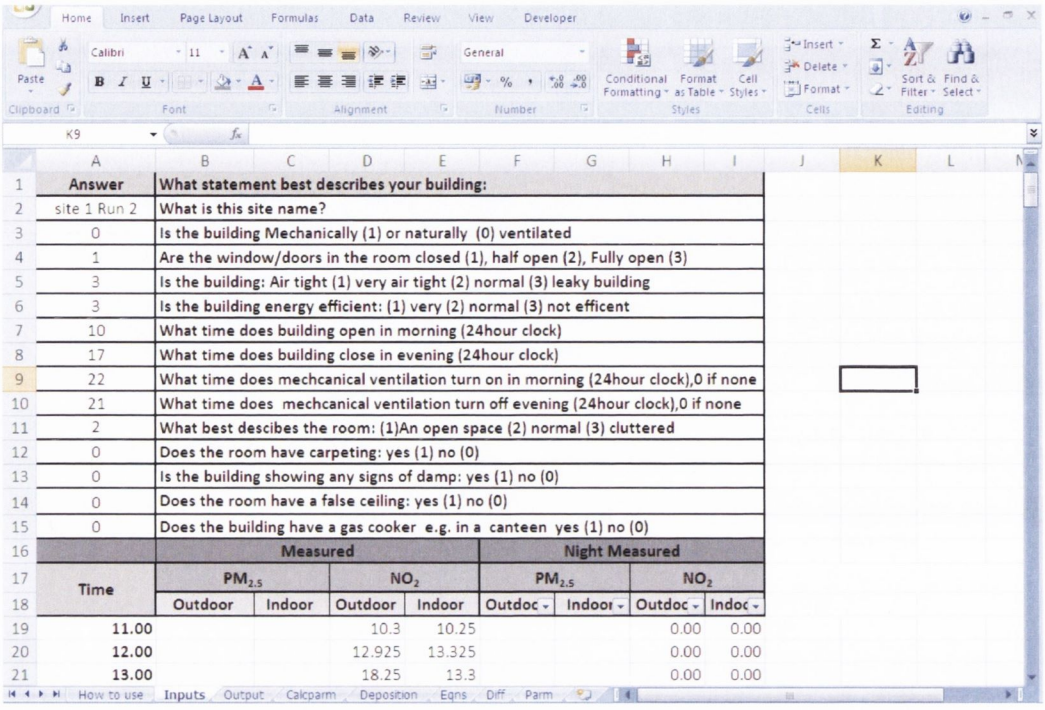


Figure 6.1 Representation of mass balance model theory

6.4.2. Input data provided by building occupant

A series of questions is put forward in order to gain knowledge on the building parameters which are important to the modelling process. It was important that these are questions that could easily be answered by building occupants. Information which was not found to be readily available when carrying out the monitoring phase of this

project was not included, for instance the number of air changes per hour. Each question can be answered by a number input to the adjoining cell; the correct number is indicated in brackets beside the statement.



	A	B	C	D	E	F	G	H	I
1	Answer	What statement best describes your building:							
2	site 1 Run 2	What is this site name?							
3	0	Is the building Mechanically (1) or naturally (0) ventilated							
4	1	Are the window/doors in the room closed (1), half open (2), Fully open (3)							
5	3	Is the building: Air tight (1) very air tight (2) normal (3) leaky building							
6	3	Is the building energy efficient: (1) very (2) normal (3) not efficent							
7	10	What time does building open in morning (24hour clock)							
8	17	What time does building close in evening (24hour clock)							
9	22	What time does mechcanical ventilation turn on in morning (24hour clock),0 if none							
10	21	What time does mechcanical ventilation turn off evening (24hour clock),0 if none							
11	2	What best descibes the room: (1)An open space (2) normal (3) cluttered							
12	0	Does the room have carpeting: yes (1) no (0)							
13	0	Is the building showing any signs of damp: yes (1) no (0)							
14	0	Does the room have a false ceiling: yes (1) no (0)							
15	0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)							
16		Measured				Night Measured			
17	Time	$PM_{2.5}$		NO_2		$PM_{2.5}$		NO_2	
18		Outdoor	Indoor	Outdoor	Indoor	Outdoc	Indoor	Outdoc	Indoc
19	11.00			10.3	10.25			0.00	0.00
20	12.00			12.925	13.325			0.00	0.00
21	13.00			18.25	13.3			0.00	0.00

Figure 6.2 User interface for model

The questions put to building occupants were as follows;

- What is this site name?
- What type of ventilation system is in place; Mechanical (1) natural (0)
- Are the windows/doors closed (1), half open (2), Fully open (3)
- Is the building relatively air tight (1) very airtight (2) medium airtight (3) not airtight
- Is the building energy efficient (1) very (2) med (3) not energy efficient
- What time does building open in morning (24hour clock)
- What time does building close in evening (24hour clock)
- What time does mechanical ventilation turn on in morning (24hour clock)
- What time does mechanical ventilation turn off evening (24hour clock)
- What best describes the room (1) open space (2) normal (3) cluttered with large surface area
- Does the room have carpeting; yes (1) no (0)
- Is the building showing signs of damp? yes (1) no (0)
- Has the building a false ceiling yes (1) no (0)

Each of these questions provides information regarding what parameters to use within the model, the answer allows the model to choose the most suitable parameter and use this information when computing the indoor concentration. Numbers were chosen over text to remove the errors possible with use of capital letters and misspelling.

The first question is to simply name the site. The second tells the model if air is taken in via only natural methods or via a mechanically ventilated system. It should be noted that some shops have small units which are not in use for most of the year; these are not included as mechanically ventilated as these units do little other than act as a natural vent while not in use.

The third question also refers to air changes, if doors or windows are left open a greater number of air changes occurs than if they remain closed. This affects naturally ventilated buildings more as occupants of mechanically ventilated buildings are more likely to have inoperable windows and automatic doors. For members of the public unsure regarding their building air tightness, or other inputs, a short guide will be available for downloading alongside the model. The fourth question refers to the air tightness of the building, whether windows/doors etc are well sealed. If there is an ability for air to enter the building through poor seals, or a number of natural air vents, then the input for this will be a '3,' but if the building is well sealed the user can input a '1', with other buildings falling in between and users input a '2'. The fifth question is used with respect to mechanically ventilated buildings. The more energy efficient the building, the higher the proportion of return air to make up air in the ventilation system.

The next four questions refer to opening times for the building and running times for the ventilation system. The running time for the ventilation system is the question which is most likely to cause issues for building occupants and so Instructions will be given in a guidance document explaining that this question can easily be answered by the buildings maintenance staff. For example, in all the buildings monitored during this study such a person who knew this information was well known to all staff. Conversely, when this person was questioned regarding air changes per hour no information was available. Most buildings were automatically controlled through a building management system (BMS) which kept the building at a set point temperature rather than a set air changes per hour.

The tenth question refers to deposition in the room, the ratio of the surface area in a room which affects the decay rate of pollutants and therefore is a vital component of the modelling process. If rooms have a large surface area of items such as books, computers, stock etc they are more likely to have higher decay rates due to

heterogeneous reactions. The next question regarding carpeting is due to the same issue, as carpeting be it wool, acrylic or synthetic fibres are known to increase heterogeneous reactions. Therefore, the use of carpeting in the building would increase these decay rates. The damp mentioned in question 11 is a factor which can affect the rate of heterogeneous reactions for NO_2 greatly.

The penultimate question is regarding the reactions that occur in dark areas (such as false ceilings) with respect to NO_2. This information helps to build a clearer image of the effect that the building has on outdoor pollutant concentrations as they enter the building. The final question refers to use of a gas cooker which, while less common in commercial buildings than in homes, remains a possible source of NO_2 and $PM_{2.5}$.

Once questions have been answered the user will also be requested to input local air quality information. This can come in two forms either via data from the EPA website or ideally via outdoor monitoring conducted at the door of the building. Chapter 4 showed a strong relationship between monitored ground level concentrations and EPA data sets, as shown for example in Figure 6.3 which compares outdoor EPA data at Winetavern Street to the data collected at Site 3 which is located on Pearse Street, a distance of approximately 1 km apart as the crow flies.

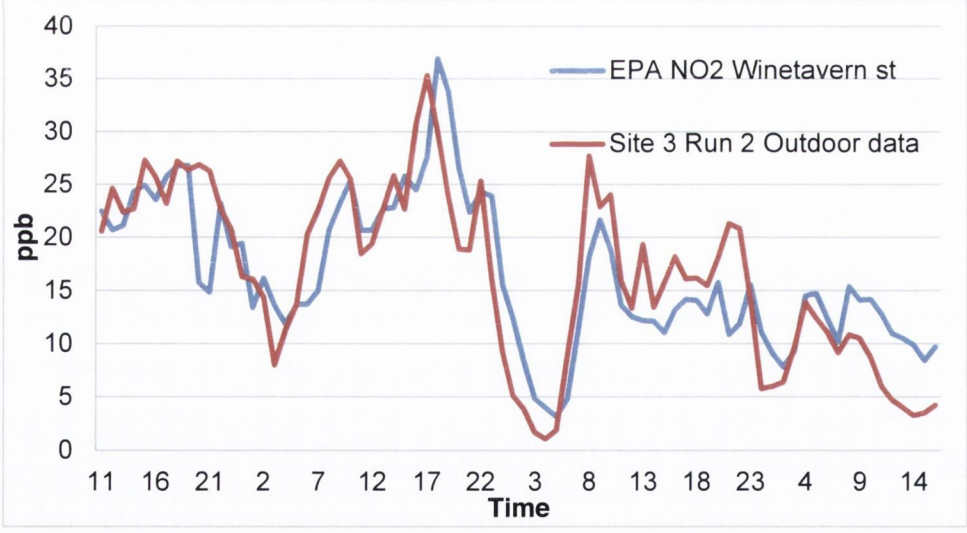


Figure 6.3 Site 3 run 2 NO_2 comparison with EPA data set

EPA data can be accessed at http://erc.epa.ie/safer/ and the appropriate data set downloaded. EPA pollution data is easily downloadable via the *safer* website and the user is then requested to copy and paste the data (which is in the correct hourly format) for the appropriate date, into the input columns as indicated. The downloaded EPA data is also contained within *Excel* files format.

6.5. Model structure

6.5.1. Naturally ventilated buildings

Inputs given by the user, as discussed in 6.4.2 are provided. These inputs include the outdoor data concentrations provided by the EPA or another appropriate source. If the building is naturally ventilated the inputs of return and make-up air are given null input values. After much consideration it was decided to use the building fabric filtration factor (f_{inf}) values calculated for Dublin using the 10 monitored buildings for this study. This removes the need to input values for penetration factor, air exchange from infiltration and decay rates. It was found that indoor concentrations often followed the outdoor trend but with a large amount of smoothing. This is reflected in the returned values for f_{inf} which are on the low side of the reported values discussed in Chapter 2 Section 10. The regression values for f_{inf} tend to be lower for sites where a large amount of noise is recorded outdoors but little is seen indoors. This smooths the data but this causes the mean concentration to fall below the value required; in order to deal with this the regression provides an indoor source value shifting the time series into the correct range.

In order to distinguish between various building types and possible chemical reactions within these buildings, deposition/decay calculations are made. This allows to the model to account for various situations such as carpeting which are known to increase both deposition rates for $PM_{2.5}$ and decay rates for NO_2. Heterogeneous reactions for NO_2 can be a particular influence on concentrations and so for these a generic low value has been included to which extra factors are added if local conditions dictate (for example carpeting and / or damp in building). Sinks for NO_2, due to its reaction with O_3, are also considered. These reactions occur overnight, in ventilation ducting and also in false ceilings or raised floors. These reactions may also occur when the lighting is poor within buildings as the reaction product NO_3 cannot photolytically degrade, and therefore act as a source of NO_2. The chosen rates for this model are laid out in Table 6.1.

Table 6.1 NO_2 decay rates (h^{-1})

Carpeting	1.1
Other flooring	0.11
Dampness	57%
Lack photolysis at night	0.48
Ducting/false ceiling	0.48

All values in Table 6.1 are decay rates in units per hour with the exception of the dampness heterogeneous reaction rate as this fluctuates with concentrations indoors. This is therefore calculated using a percentage reduction of the previous time step's indoor modelled value. These deposition values are only used if the conditions deem it necessary. To account for general deposition the decay rate is calculated via a V_d rate of 0.99 h^{-1} (Yamanaka, 1984) multiplied by averaged A/V values for office/shops, varying depending on questions answered by the used input, multiplied by the indoor concentration calculated for the previous time step as shown in Equation 6.2. The decay rates for use in Equation 6.3 in Table 6.1.

$$C_{in} = f_{inf} C_{out} + source - V_d \left(\frac{A}{V}\right) C_{in(n-1)} - k \qquad \text{Equation 6.2}$$

$$k = \sum capeting + other\ flooring + dampness + photalysis \qquad \text{Equation 6.3}$$

6.5.2. Mechanically ventilated buildings

Mechanically ventilated buildings are dealt with in a similar manner to naturally ventilated buildings with the addition of two extra components; the first accounts for the supply or make-up air being drawn in from the outdoors and the second for the return air being recirculated through the system. When using the regression equation to calculate values for f_{inf} and S it could be argued that some of the ventilation system is already accounted for within the equation. However, the purpose of keeping the rates within the equation is to provide the facility to be able to adjust the model for the times the ventilation system turns on and off. These times may be different to the opening and closing hours of the building and are provided through user inputs. The additional factors to be added in are shown in Equation 6.4,

$$\frac{\alpha a_m C_{out}}{a_{m+k}} + \frac{\alpha a_r C_{in(n-1)}}{a_{r+k}} \qquad \text{Equation 6.4}$$

Where a_m is the air exchange due to the mechanical ventilation system and a_r is the return air exchange rate.

where α is a factor used to account for the fact that much of the influence of the ventilation system was already accounted for via the regression equation.

The air exchange rates for mechanical ventilation used for efficient, normal and non-efficient buildings are listed in Table 6.2 (Hayes, 1991, Fadeyi et al., 2009, AIVC, 1994, Chaloulakou and Mavroidis, 2002). The more efficient sites have a higher number of return air changes per hour and less new air (a_m) brought into the system. The non-efficient sites show a higher proportion of new air and less return air.

Table 6.2 Air exchange rates for mechanical sites (h^{-1})

	Efficient	Normal	Non-efficient
a_m	1.00	2.64	5.00
$a_{m\ night}$	0.20	0.80	1.00
a_r	11.00	8.00	5.50
$a_{r\ night}$	0.40	0.80	0.80

6.5.3. Summary of model structure

Figure 6.4 shows the full final equation used for both naturally ventilated and mechanically ventilated buildings.

Stage 1 - Regression	Stage 2 - Mass Balance	
$C_{in} = f_{inf} C_{out} + S$	*Naturally Ventilated*	$C_{indoor} = \frac{p\, a_f\, C_{out}}{a_f + k} + \frac{\alpha\, a_f\, C_{out}}{a_m + k} + \frac{\alpha\, a_r\, C_{out}}{a_r + k} - \sum \text{Deposition} + s$
	Mechanically Ventilated	$C_{indoor} = \frac{p\, a_f\, C_{out}}{a_f + k} + \frac{\alpha\, a_f\, C_{out}}{a_m + k} + \frac{\alpha\, a_r\, C_{out}}{a_r + k} - \sum \text{Deposition} + s + \frac{\alpha a_m C_{out}}{a_{m+k}} + \frac{\alpha a_r C_{in(n-1)}}{a_{r+k}}$

Figure 6.4 Equation for choice of equation for naturally and mechanically ventilated buildings.

6.6. Choice of final parameters for individual best-fit models

Using information gathered while monitoring each of the 10 buildings, an individual best fit model was developed for each site. It was decided to use only ground level concentrations rather than roof level concentrations to make the results complementary to the EPA data which is collected at this height. This varied the above parameters by trial and error in order to get a best fit to the known indoor concentrations. The information learnt from this was then used in the choice of the final parameters for the more generalised model.

During monitoring at mechanically ventilated sites information on air changes per hour (ach) was requested, but at each of the 10 sites this information was unknown. The building services personnel advised that ventilation strategies were instead calculated by a set point temperature. There is also little information available regarding air exchange rates/air changes per hour and penetration factors for Irish building practices and so it was decided to use the regression equation shown in Equation 6.5 to calculate specific factors for Dublin.

$$C_{in} = f_{inf}\, C_{out} + S \qquad \text{Equation 6.5}$$

Using this regression to calculate f_{inf} removed the need to estimate K, P and ach for infiltration. Linear regressions using outdoor concentrations to predict indoor concentrations for each site were carried out (Hoek et al., 2002, Long et al., 2001). The results found are detailed in Table 6.3 and Table 6.4. Sites 6, 8 and 9, all naturally ventilated sites, show very low infiltration factors for NO_2. This could be expected at Site 6 due to the very low indoor concentrations, but is somewhat surprising for the other sites. For situations like this the figures found for the regression were applied to the model, and adjusted if results were not appropriate or the regression did not represent a realistic f_{inf} or source value. An example of plots of these regressions is also shown in Figure 6.5. By using a F_{inf} this also infers a low air exchange rate and penetration factor but a high K (decay rate). Appendix B contains the individual best fit models for each of the sites.

6.6.1. Choice of final parameters for individual best-fit NO_2 models

Source and infiltration factors were calculated for 3 ranges; during the working day, from close of business until 2am and the final range was 2am until opening of the business. These ranges were chosen to represent the different possible infiltration and source times.

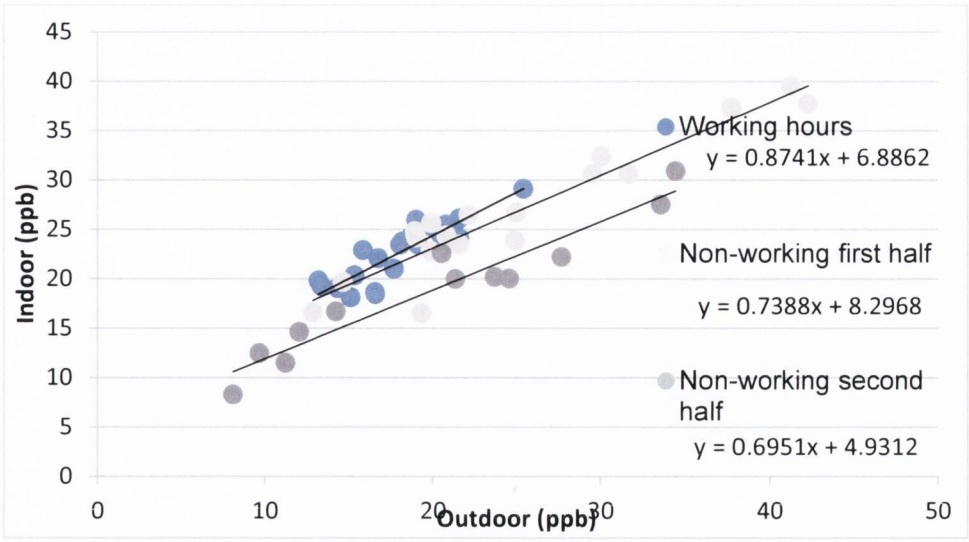


Figure 6.5 Regression of indoor versus outdoor NO_2 concentration Site 2 run 2

Table 6.3 Working hour's infiltration and source for NO_2

	Infiltration factor	Source
S1R2	0.67	9.38
S2R2	0.87	6.89
S3R2	0.32	14.88
S4R1	0.10	17.09
S4R2	0.41	17.11
S5R1	0.66	4.30
S6R1	-0.05	7.53
S6R2	-0.03	3.39
S7R1	0.35	12.82
S8R1	-0.03	13.32
S9R2	-0.09	10.61
S10R1	0.08	23.17

Table 6.4 Close of business to 2 am infiltration and source for NO_2

	Infiltration factor	Source
S1R2	0.46	7.76
S2R2	0.74	8.30
S3R2	0.48	10.48
S4R1	0.19	8.68
S4R2	0.35	16.97
S5R1	0.27	12.76
S6R1	0.08	3.19
S6R2	0.03	0.23
S7R1	0.30	11.38
S8R1	0.13	7.53
S9R2	-0.24	11.39
S10R1	0.22	14.40

Table 6.5 2 am to opening of business infiltration and source for NO_2

	Infiltration factor	Source
S1R2	0.25	9.64
S2R2	0.70	4.93
S3R2	0.20	11.82
S4R1	0.22	6.58
S4R2	0.37	7.50
S5R1	0.13	13.91
S6R1	0.02	3.32
S6R2	0.02	0.39
S7R1	0.40	11.66
S8R1	0.08	5.69
S9R2	0.13	5.53
S10R1	0.29	10.67

Appendix B contains the individual best fit models for each of the sites. For each site the parameters used in the best fit model are explained, the model fit is then statistically analysed using the analysis of variance and 2 sample T- test to determine whether the means are statistically different. Some of the calculated values for f_{inf} and source were adjusted for the best fit models in order to further improve fit. Figure 6.6 and Figure 6.7 show a summary of the comparisons of two parameters (f_{inf} and source) used for each site over the 3 time intervals.

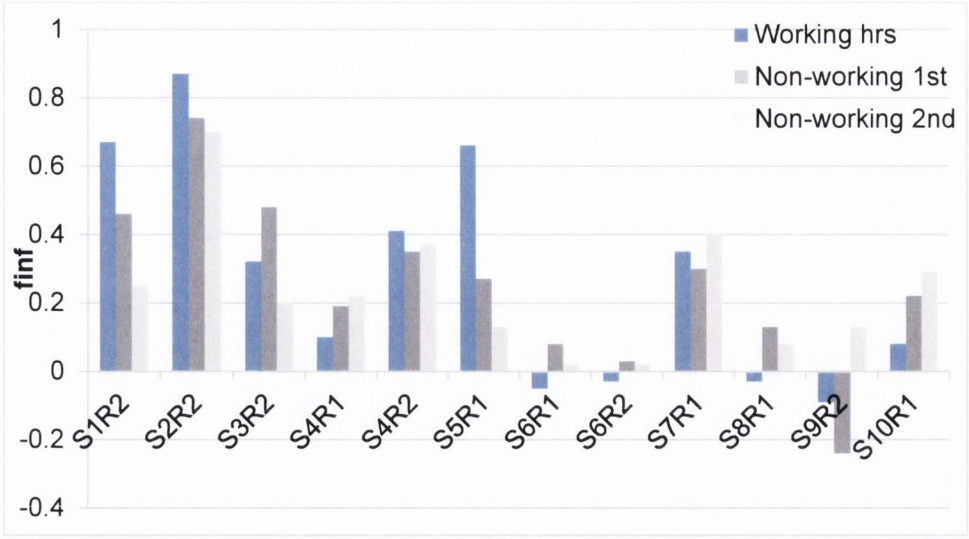


Figure 6.6 Comparison of f_{inf} for each site for the 3 time intervals

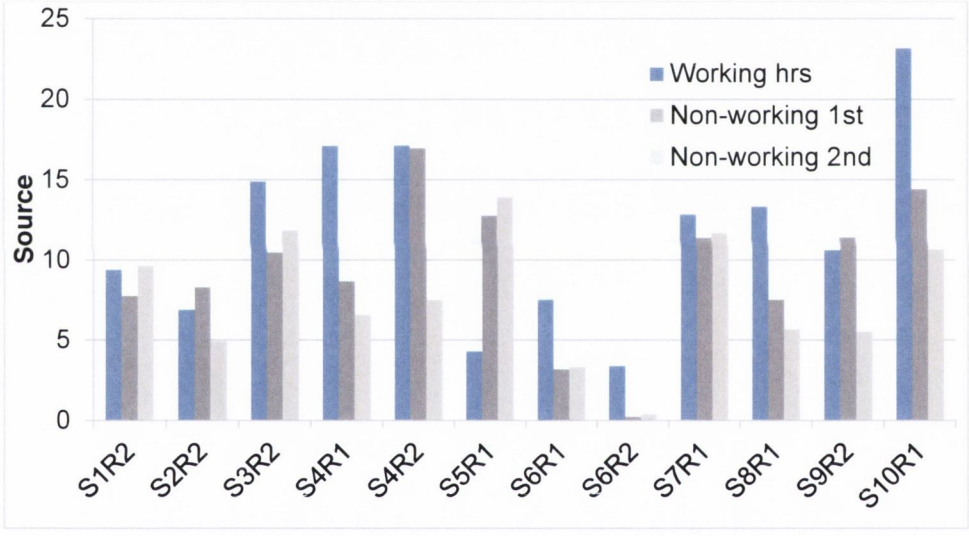


Figure 6.7 Comparison of source for each site for the 3 time intervals

this study to the 14 questions. The individual answers to these questions are contained within Appendix C and a summary is shown in Table 6.7

Table 6.6 shows the questions which provide the necessary information to calculate the indoor concentrations. The Table 6.7 shows the inputs used for each of the buildings monitored for this study to the 14 questions. The individual answers to these questions are contained within Appendix C and a summary is shown in Table 6.7

Table 6.6 Input variables

Question number	What statement best describes your building
1	What is this site name?
2	Is the building Mechanically (1) or naturally (0) ventilated
3	Are the window/doors in the room closed (1), half open (2), Fully open (3)
4	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
5	Is the building energy efficient: (1) very (2) normal (3) not efficient
6	What time does building open in morning (24hour clock)
7	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
9	What time does mechanical ventilation turn off evening (24hour clock),0 if none
10	What best describes the room: (1)An open space (2) normal (3) cluttered
11	Does the room have carpeting: yes (1) no (0)
12	Is the building showing any signs of damp: yes (1) no (0)
13	Does the room have a false ceiling: yes (1) no (0)
14	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Table 6.7 Input variables for each site

Question number	Input parameters for individual sites										
1	S1R 2	S2R 2	S3R 1	S3R 2	S4R 2	S5R 1	S6R 2	S7R 1	S8R 1	S9R 2	S10R 1
2	0	1	1	1	1	1	0	0	0	0	1
3	1	1	1	1	1	1	1	1	1	3	1
4	3	3	2	2	2	1	2	2	2	2	1
5	3	3	2	2	2	1	3	3	3	3	2
6	10	8	8	8	8	8	10	10	8	9	8
7	17	18	18	18	20	17	18	18	19	18	18
8	0	8	8	8	8	8	-	-	-	-	23
9	0	18	18	18	20	17	-	-	-	-	0
10	2	1	3	3	1	1	3	3	2	3	1
11	0	0	1	1	0	1	1	1	1	1	0
12	0	0	0	0	0	0	1	1	0	1	0
13	0	0	1	1	0	0	0	0	0	0	1
14	0	1	0	0	0	0	0	0	0	0	0

6.6.2. Choice of final parameters for individual best-fit $PM_{2.5}$ models

The same procedure, as was carried out for NO_2, was used for $PM_{2.5}$ in order to compute best fit models for $PM_{2.5}$. Unfortunately, as seen in other analyses for $PM_{2.5}$, the indoor and outdoor fluctuations do not correlate strongly. $PM_{2.5}$ data collected for this study tends to vary around a mean value, and this mean value outdoors does not

necessarily affect indoors. This can be seen during overnight reductions outdoors with no such reduction seen indoors. Infiltration (f_{inf}) factors and sources were calculated using the same regression method as with NO_2 in Section 6.6. The results of the regressions are shown in Table 6.8, Table 6.9 and Table 6.10. f_{inf} were partially low for many sites due to reduced fluctuations indoors at these sites. Many sites also showed a negative f_{inf} indicating that as outdoor concentrations increased, indoor concentrations decreased and vice versa. This is likely to be due to the large amount of fluctuations in both sets of data which do not correspond to each other. The values contained within Table 6.8, Table 6.9 and Table 6.10 are not the final values used within the best fit models. These values were inputted to the best fit model but if the indoor modelled valued returned are not representative of indoor data the values are adjusted in order to get a better fit. Appendix B contains the individual best fit models for each of the sites.

Table 6.8 Working hour's infiltration and source for $PM_{2.5}$

	Infiltration factor	Source
S1R2	0.21	12.49
S2R2	0.06	11.57
S3R2	0.69	1.37
S4R1	0.02	16.42
S4R2	2.58	-7.56
S5R1	0.01	9.86
S6R2	0.27	9.76
S7R1	0.78	15.68
S8R1	0.02	12.41
S9R2	-0.02	14.95
S10R1	-0.34	16.74

Table 6.9 Close of business to 2 am infiltration and source for $PM_{2.5}$

	Infiltration factor	Source
S1R2	-0.34	15.97
S2R2	0.10	12.31
S3R2	0.40	6.36
S4R1	0.16	15.98
S4R2	9.93	-17.22
S5R1	0.06	13.25
S6R2	0.06	11.60
S7R1	-0.05	16.00
S8R1	-0.07	11.74
S9R2	-0.18	16.65
S10R1	0.13	14.56

Table 6.10 2am to opening of business infiltration and source for $PM_{2.5}$

	Infiltration factor	Source
S1R2	0.68	8.59
S2R2	0.31	9.34
S3R2	-0.12	9.71
S4R1	-0.09	19.15
S4R2	14.85	-63.12
S5R1	-0.34	13.68
S6R2	0.07	13.68
S7R1	-0.23	18.98
S8R1	0.26	7.97
S9R2	-0.31	18.18
S10R1	-0.13	13.64

Figure 6.8 and Figure 6.9 show a comparison of the f_{inf} and source values calculated from the regression calculations for the 3 time intervals. The second half of non-working hours segment of data shows a large number of the negative correlations mentioned above with several also seen during the first half of non-working hours, during these hours outdoor concentrations show more of a diurnal variation while indoor concentrations tend to continue varying around a mean value, hence the negative relationship. Site 4 run 2 showed notably high f_{inf} and negative source values, these occurred due to the high peaks shown through this run. Due to the effect these peaks had on the regression it was decided to use run 1 for best fit analysis. To avoid repetition of the inputs describing the sites it can be assumed that they are the same as the input tables used for NO_2 in Section 6.6.

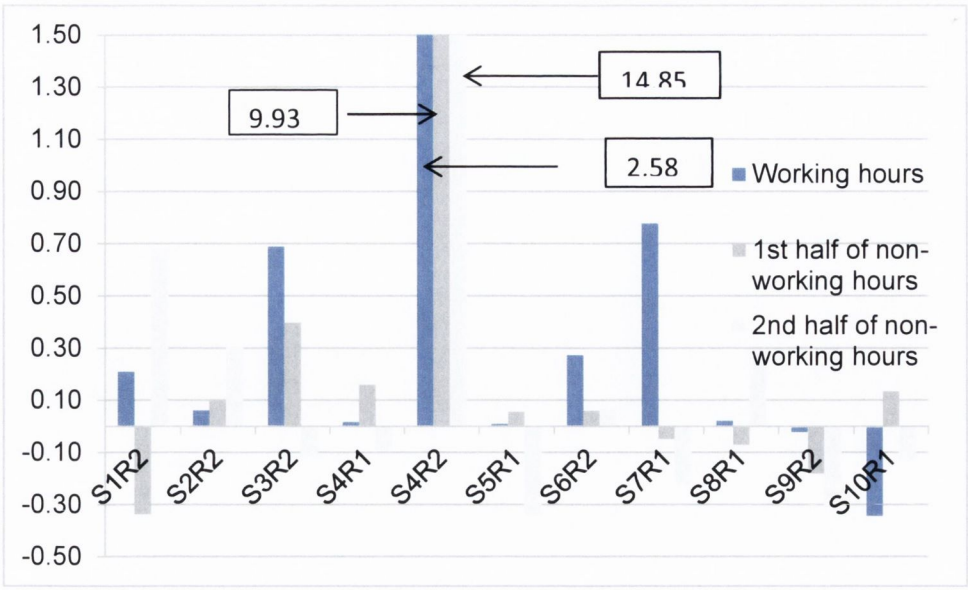


Figure 6.8 Comparison of f_{inf} for each site for the 3 time intervals

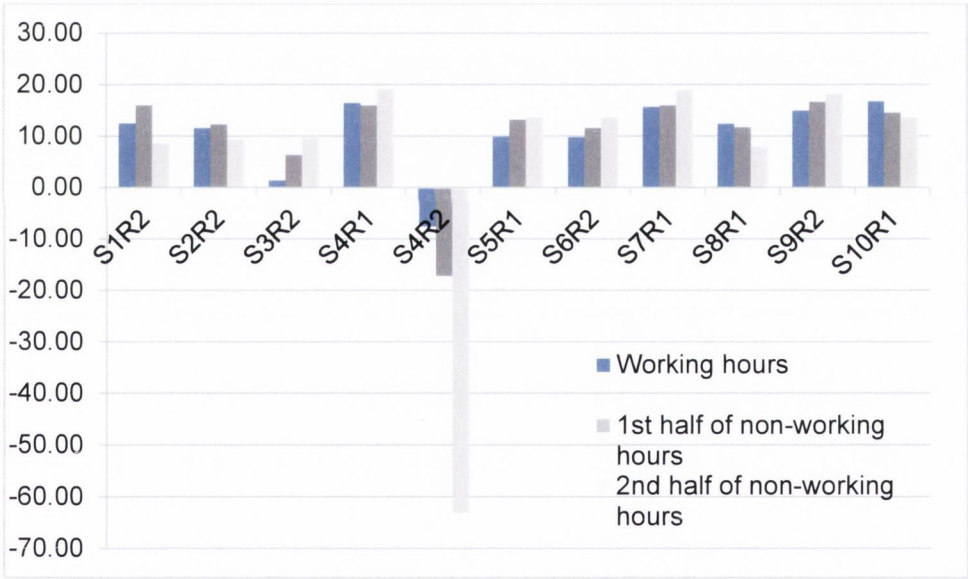


Figure 6.9 Comparison of source for each site for the 3 time intervals

6.6.3. Best fit NO_2 models – Conclusions

The NO_2 best fit and general models showed strong results with reasonable R^2 (average = 63.56 %) but more importantly, for this study at least, the 95 % confidence interval for the estimate of the difference in mean concentrations throughout the run for actual indoor and modelled indoor data contained the H_0=0. This means the exposure of staff to NO_2 at each of the buildings is statistically not different if found using the modelled or using actual indoor data. Some of the f_{inf} used are considerably lower than literature but, as noted previously, this was due to the regressions of indoor versus outdoor data using lower values of f_{inf} in order to smooth data. Indoor data usually showed considerably less short term fluctuations compared to outdoor data and consequently the f_{inf} factors were lower and the source values higher than literature in order to push up the mean values which were reduced during smoothing.

6.6.4. Best $PM_{2.5}$ models – Conclusions

The 10 individual best fit models for $PM_{2.5}$ produce poor prediction values for short term fluctuations of indoor concentrations. This is shown by the very low R^2 values between actual indoor and outdoor concentrations (on average 3.25%) making it difficult to use these uncorrelated outdoor fluctuations to calculate the indoor fluctuations. The best fit models tend to smooth the data producing a modelled fit for indoor concentrations which smoothes out much of the indoor variation but does provide a mean exposure to within the 95 % CI of a 2 sample T-test for 8 out of the 10 sites. The 2 sites which did not achieve difference in mean exposure within the 95 % CI did have estimates of the difference between actual indoor and modelled indoor of 1.096 $\mu g\ m^{-3}$ (Site 4) and 1.56 $\mu g\ m^{-3}$(Site 5). These sites did show some relationship between indoor and outdoor concentrations although this varied throughout the run whereby some days there were increases in outdoors concentrations with no respective change in indoor levels.

6.7. Choice of final parameters for generalised NO_2 model

The best fit models used regression and recursive mass balance techniques in order to fit the modelled data to the true indoor concentrations. This provided an insight to the behaviour of NO_2 for different building characteristics. The parameters used in each of the best fit models have been compiled and categorized depending on the building inputs provided by the user. The best fit models used regressions of indoor and outdoor data to calculate the f_{finf} and source, the only change to the best fit model in the generalised model being that it used predetermined values for f_{inf} and source; all other

parameters and inputs were the same. Indoor data will not generally be available to the user that this model is designed for e.g. rather than monitoring equipment they will be using EPA data, and therefore, while it was a benefit for the best fit models the generalised model must run without such an input time series. The best fit parameters from the 10 sample sites were used to find average values for f_{inf} and source for various building types. In some cases 3 buildings fell into the same category (e.g. Site 10, Site 3 and Site 4) while in others only one site was available to calculate the values. The categories were determined by the air tightness of the building as well as the ventilation strategy, e.g. mechanical or natural ventilation. Table 6.11 shows the chosen factors for the various categories. 1 represents an air tight building with low air changes per hour, 2 represents the normal building and 3 is for a leaky building which has a high number of air changes. There are separate values for each of these categories for naturally ventilated and mechanically ventilated buildings. As with best fit models, these values also change for 3 separate time intervals throughout the day, working hours (day), non-working hours (night 1^{st} half) and early morning before the building opens but concentrations are rapidly changing outdoors (night 2^{nd} half). While strictly not a source and f_{inf} in the traditional sense they were calculated using the regression technique used by Hoek et al. (2008) and Long et al. (2001). To calculate these parameters, the results of these regressions gave the higher source and lower f_{inf} factors than expected but they proved to represent data well and therefore were retained. The f_{inf} are lower than reported in literature for NO_2 as they are also acting as a smoothing parameter as indoor concentrations of the pollutant do not fluctuate to the same extent as the outdoor concentrations. The source factor is necessary to account for the decrease in mean values due to the higher f_{inf}, the combination of using the two gives the required patterns for indoors.

Table 6.11 Chosen f_{inf} and source

	Naturally ventilated			Mechanically ventilated		
	1	2	3	1	2	3
f_{inf} day	0.12	0.32	0.67	0.2	0.36	0.87
source	2	16	16	11	12.5	3
plus cooker	0	0	0	0	0	0
Source	2	16	16	11	12.5	3
f_{inf} night 1st half	0.08	0.28	0.46	0.2	0.3	0.7
source	2	11	10	13	9.58	2
f_{inf} night 2nd half	0.08	0.25	0.4	0.2	0.36	0.73
source	2	12	10	13	11	3

Where: 1= well sealed/ low number of air changes, 2= Normal building, 3 = High number of air changes/ poorly sealed

6.7.1. Results and discussion of generalised model

The outdoor data from the 10 sites was inputted into the model, and the results are found in Table 6.12. All models were found to have 95 % confidence intervals (CI) for the estimate of the difference between actual indoor and modelled indoor concentrations which included H_0=0, indicating that there is no statistical proof that the difference between the two sets of data over the entire run is not equal to 0, with 7 of the 10 Sites showing an estimate of the difference of less than 1 ppb. Regressions carried out using modelled indoor data to predict actual indoor data showed R^2 ranging from 6.1 % up to 72.2 %. The lowest R^2 value was for Site 9, where indoor and outdoor data showed little correlation (R^2 = 1.3 %), with outdoor concentrations rising when indoor concentrations increased and vice versa. A similar result was seen at Site 8 which returned R^2 of 20 %. When using the generalised model it is more difficult to account for such unusual fluctuations while keeping the model applicable for other buildings. Although the R^2 values are low, the data predicts an estimate for the difference between the modelled and indoor concentrations of only 0.23 ppb and therefore the difference in overall exposure is negligible. The difference at Site 8 is even less than this at 0.134 ppb. Site 6 also showed a low correlation, see Figure 6.10, this was due to fluctuations that remained within the modelled data which required further smoothing to match the actual indoor data.

Table 6.12 R^2 and estimate of differences for indoor versus modelled

Site	R^2 %	95% CI for difference	Estimate of difference (ppb)
1	64.5	(-4.86, -0.37)	-2.62
2	69.3	(-2.38, 2.37)	0
3	65.3	(-0.101, 2.755)	1.327
4	70.4	(-0.65, 4.34)	1.85
5	46.7	(-1.267, 0.422)	-0.422
6	33.5	(-0.471, 0.082)	-0.195
7	44.4	(-1.760, 1.629)	-0.066
8	20	(-1.155, 0.888)	-0.134
9	6.1	(-0.965, 0.503)	-0.230
10	72.2	(-1.539, 1.183)	-0.178

The indoor data shows that the concentrations were significantly reduced from the outdoor concentrations at Site 6, as shown in the best fit model for the site in Appendix B. While more smoothing could be used in the best fit model via amending the f_{inf} factor, this is not possible in the generalised model as all sites would not experience the same behaviour. As with the other sites with low R^2 values Site 6 does show a low estimate for the difference of only 0.195, making exposure concentrations insignificantly different compared to the actual measured indoor data.

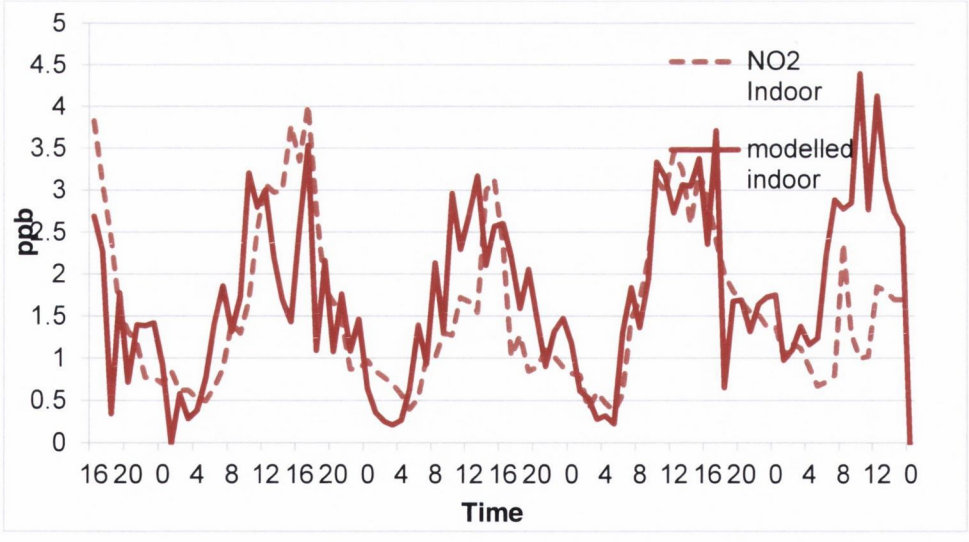


Figure 6.10 Site 6 indoor and modelled concentrations (using generalized model)

As noted above Sites 3, 4 and 10 all fall into the same category as air tight mechanically ventilated office buildings. While some variables differed such as opening hours and the A/V ratio for the rooms, many of the variables used must account for the

fluctuations of indoor data due to outdoor changes in pollutant concentrations. Figure 6.11, Figure 6.12 and Figure 6.13 show the output plots of these with the R^2 and the estimates for the difference previously shown in Table 6.12, with all 3 sites showing a good prediction level.

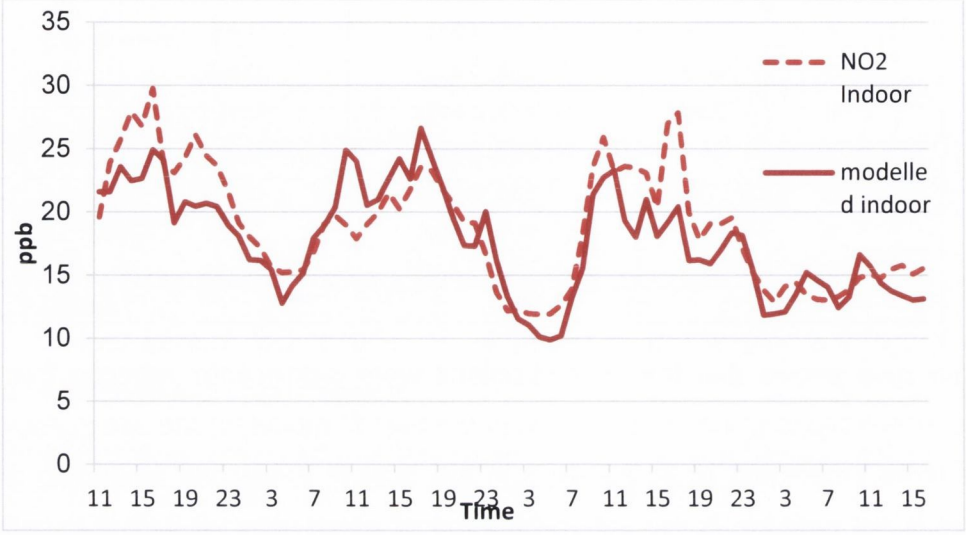


Figure 6.11 Site 3 indoor and modelled concentrations

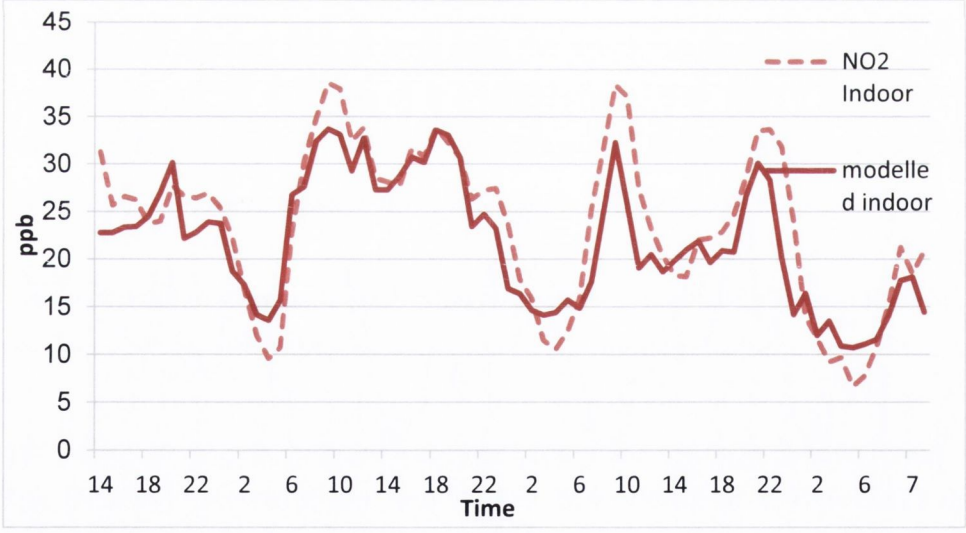


Figure 6.12 Site 4 indoor and modelled concentrations

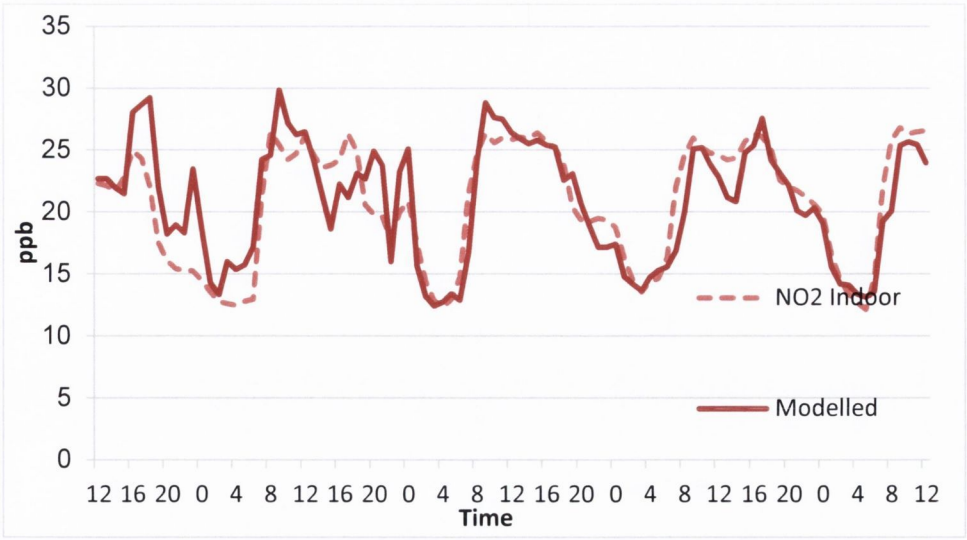


Figure 6.13 Site 10 indoor and modelled concentrations

Site 1 shows the largest estimate for the difference between modelled indoor and actual indoor concentrations. This difference is heavily influenced by the first day of monitoring which saw modelled concentrations over 10 ppb higher than outdoor concentrations. The first few hours of data are often when the largest differences are seen as they are calculated using only outdoor data which can be considerably higher than indoor data at that time. As the model moves forward in time steps the difference reduces as it will be using calculated indoor data and the outdoor data to calculate the next time step rather than just the outdoor concentrations.

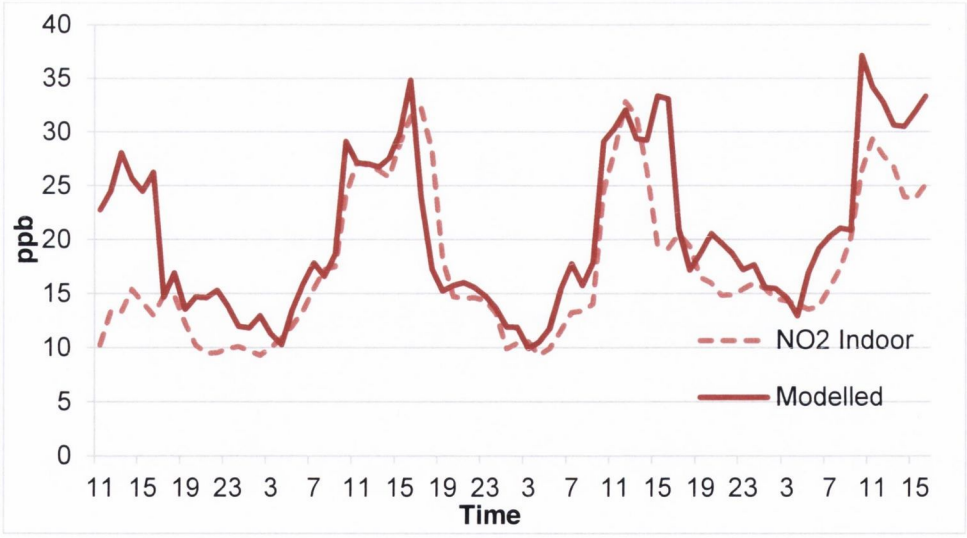


Figure 6.14 Site 1 indoor and modelled concentrations

6.7.2. Comparison with EPA data

This model is designed to use data collected at EPA monitoring stations and then downloaded by the user from online to calculate indoor concentrations. A number of tests, shown in Figure 6.15 to Figure 6.17 were carried out using EPA data and comparing them to the indoor concentrations.

A comparison was carried out of EPA data taken at Coleraine Street (roughly 2 km as the crow files from Site 3) on the same day as monitoring was also conducted at the mechanically ventilated office Site 3 for run 2. When inputted into the generalised model results were found to be as shown in Figure 6.15, with a R^2 = 43.4% between actual indoor and modelled indoor. This was reduced from the R^2 of 57.2% found outdoor data was taken at ground level from the site. However, the estimate of the difference (1.051 ppb) is still within the 95% CI for a 2 sample T-Test which had a range of -0.294 to 2.396 ppb, T-Value = 1.54, P-Value = 0.125 and DF = 145.

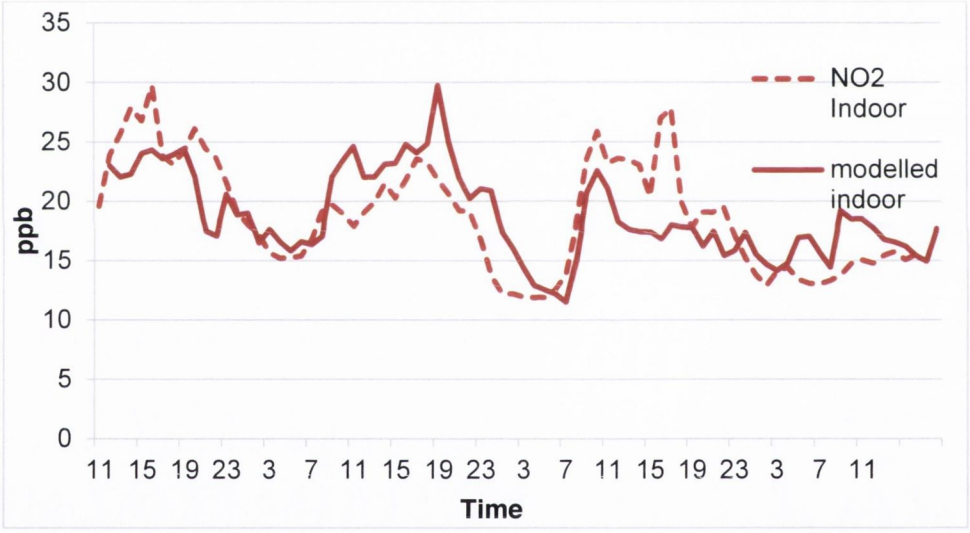


Figure 6.15 EPA modeled data for Site 3 12th - 31st March 2010

Indoor data for run 1 at Site 3 was compared to modeled data using outdoor EPA data from Coleraine Street, a R^2 = 41.1% was found but again a 2 sample T-Test found that differences between actual indoor and modeled indoor data were within 95% CI with a range of (-1.277, 0.862), an estimate of the difference of 0.208 ppb, T-Value = -0.39, P-Value = 0.701 and DF = 97.

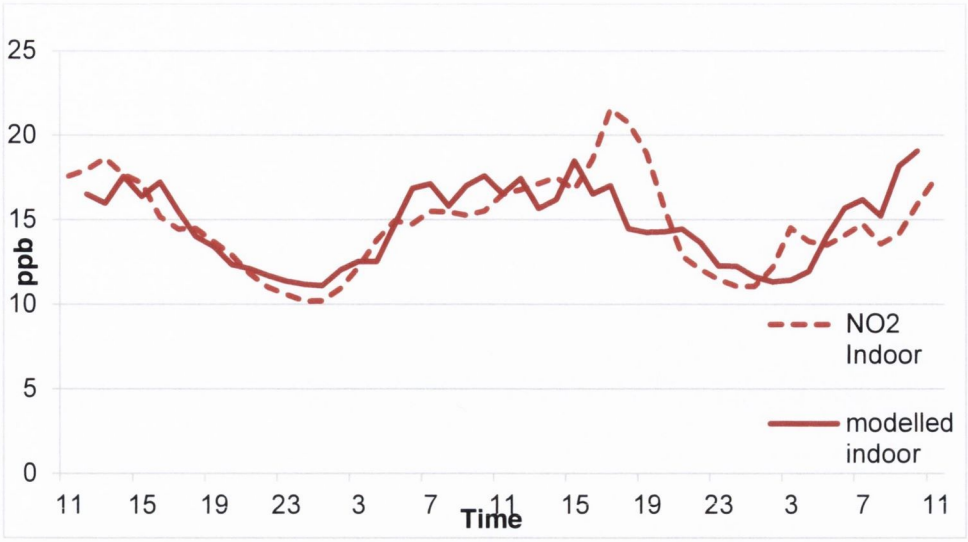


Figure 6.16 EPA modeled data for Site 3 6th – 9th July 2010

Indoor data for the naturally ventilated office at Site 6 is compared with the modelled indoor data using EPA data in Figure 6.17. This site found that the modelled data had a larger mean value with an estimated difference of 0.722 ppb, the 2 sample T-Test 95% CI for difference of -1.06 to -0.381. While this site did not find values within the 2 sample T-Test 95% CI, the estimate for the difference was low and reviewing the plot of data the major discrepancies between modelled indoor and actual indoor occurs in the final 12 hours of monitoring. This will occur due to localised fluctuations in the EPA data not seen at the monitoring site, even with such behaviour the estimates for the difference in mean exposures is low.

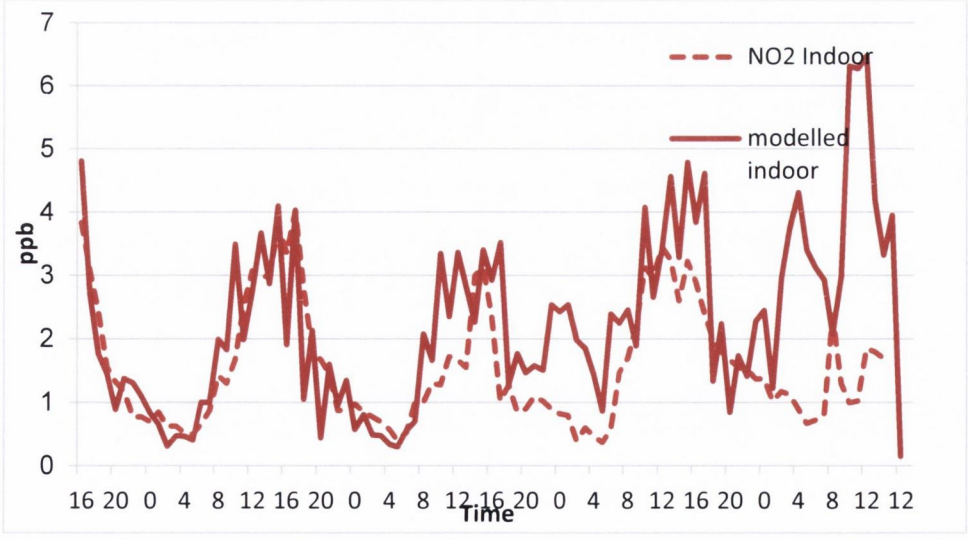


Figure 6.17 EPA modeled data for Site 6 27th June – 1st July 2011

6.8. Conclusions

The modelling procedure used in this chapter to predict indoor air quality using outdoor data is based upon the commonly used mass balance technique with some adjustments. The model combines the techniques of mass balance with the regression techniques in order to adapt these models due to the limited control and available data on inputs (such as the number of air changes per hour). Using the regression technique to calculate f_{inf} as well as source values, allowed values to be found that best represented the individual sites. f_{inf} can also be calculated as combination of some of the unknown parameters (a,k and p) as shown in Section Chapter 2 Section 10 and this meant that these inputs in the mass balance model could be replaced by the f_{inf} calculated in the mass balance part of the model, as the regression alone was not able to fully predict the indoor concentrations.

The best fit model uses information learnt on the f_{inf} and sources from the best fit model in order to calculate appropriate values of these for 3 different generic building types within both mechanically and naturally ventilated buildings. The best fit models for both NO_2 and $PM_{2.5}$ achieve mean exposure predictions that were within the 95 % CI for 2 sample T-tests at the majority of sites. The model was, however unable to account for short-term fluctuations in $PM_{2.5}$, with R^2 values ranging from 0.9-31.4 %, averaging at 8.52 %. This is due to the fact that the indoor fluctuations do not appear to correlate with those outdoors, and therefore the model will always struggle to predict such time series. NO_2 best fit models showed much higher R^2 values between actual indoor and modelled indoor with R^2 values on average of 63.56 % with all except three sites returning values above 60 %.

NO_2 was focused upon for the generalised model as the necessary input data (i.e. hourly concentrations) provided by the EPA is only available for this pollutant and not for $PM_{2.5}$. NO_2 showed high R^2 values which range from 20-72.2 % and average at R^2 = 52.2 % for the generalised model and all bar one site saw 2 sample T-tests returning estimates for the difference between actual indoor and modelled indoor which lay within the 95 % CI when using a null hypothesis.

For both NO_2 and $PM_{2.5}$ the best fit model found reasonably accurate exposure of the workers in the building studies, which is one of the main reasons for development of such a model. When the generalised NO_2 model used downloaded EPA data to calculate the indoor concentrations, strong comparisons resulted with estimates for the difference of in means of actual indoor and modeled indoor of less than 1 ppb.

7. Artificial neural networks model

7.1. Introduction

Artificial neural networks (ANN) is a robust non-linear computational method which can be applied to many fields of study including air pollution and was originally designed to emulate biological nervous systems (Kindangen, 1996, Sun and Hoff, 2009). ANNs have previously been used to predict future concentrations of air pollutants outdoors (Wang and Chen, 2002, Wang et al., 2003, Lu et al., 2003, Grinn-Gofroń et al., 2011). Forward prediction of air quality has previously been conducted in Dublin city by Pilla (2012) who found a strong ability of meteorological variables to predict outdoor fluctuations in PM_{10}. Other applications of ANNs include the prediction of health effects severe enough to cause hospital visits due to air pollution (Bibi et al., 2002, Wilson et al., 2004) and the ability to link indoor pollutant concentrations to illness (Sofuoglu, 2008). ANNs have also been used for the prediction of indoor air quality using outdoor data. The indoor air quality of swine deep pit buildings in the United State was carried out by Sun and Hoff (2009) using outdoor air quality and ANNs. The same work accurately forecasted long term (5 year) air quality of CO_2, NH_3 and H_2S outdoors. A study by Kindangen (1996) found the need for a greater level of work on the influence of architectural features in order to further the prediction of indoor air quality in naturally ventilated buildings. Such work was carried out by Stavrakakis et al. (2011) who used ANN's to predict the size of windows necessary in buildings in order to provide occupational comfort of those working within naturally ventilated buildings using a range of metrological variables and CFD. Another piece of work used ANNs to predict air flows inside naturally ventilated buildings due to different ventilation strategies (Kalogirou et al., 2001). The prediction of air flows could easily be adjusted to include pollutants in the ANN.

ANNs do not have assumptions such as prior hypotheses regarding variable relations pre-determined; they have a low sensitivity to error term assumptions and a high tolerance to noise. ANNs use previously collected times series data (e.g. indoor concentrations and meteorological data in the case of this research), that the model is being developed to predict. The algorithm is often used as it is simple yet robust. It originated from an algorithm developed by Levenberg (1944) in the 1940s which was combined with work by Marquardt (1963) in the 1960s, which resulted in the Levenberg–Marquardt algorithm, see Equation 7.1.

$$\left(J^T J + \lambda diag(J^T J)\right)\delta = J^T[y - f(\beta)] \qquad \text{Equation 7.1}$$

Where:

J – Local gradient of f with respect to β at X_i

β- Parameters

y – Independent and dependent variables

δ - Increment

The ANN has an inputs layer, at least one neuron layer (although usually a group of interconnecting neurons are present) and an outputs layer, as seen in Figure 7.1. Using input data the ANN is 'trained' by inputting a set 'target' values, in this case the target values are the indoor concentrations, which the ANN should achieve by processing the input data. Once trained and tested the ANN can be used to calculate future or past events where indoor concentrations are not available for each building.

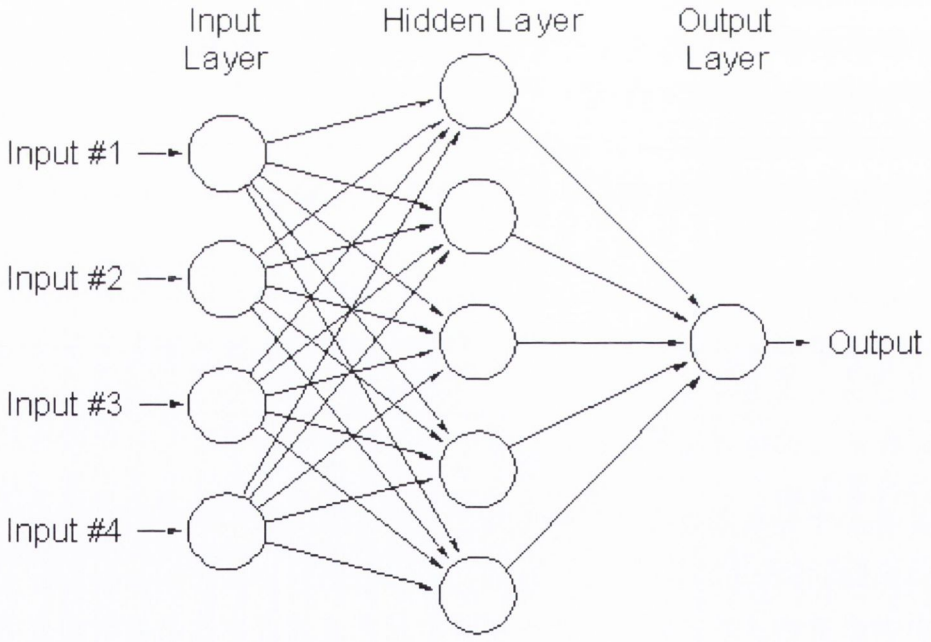


Figure 7.1 Artificial Neural Network

7.2. Scope and Application

The scope of the artificial neural networks is a modelling technique for the prediction of current indoor air quality in buildings using inputs that are available and a previously 'trained' neural network. The aim of this model is to provide realistic exposure estimations for the occupants of any commercial building, the model should also be able to account for short term fluctuations caused by meteorological parameters such as pressure changes.

The application of this is wide as it can be applied to any building where air quality data has been collected indoors. This can be matched with freely available outdoor air quality and meteorological data for that time period in order to train a network. Once trained the model can use up to date data in order to predict the current indoor air quality. However, the model require the software package MATLAB and therefore may not be as accessible to the general public as with the previous model in Chapter 6.

7.3. Input Parameters

A Matlab toolbox called 'Neural Network Time series Tool' using a non-linear auto-regression with external input networks (NARX) modelling technique was chosen to calculate interactions between indoor concentrations of $PM_{2.5}$ and NO_2, outdoor concentrations of $PM_{2.5}$ and NO_2 and weather data. The NARX network is a two-layer feed forward time delay neural network (TDNN) which uses a sigmoid transfer function in the hidden layer and a linear transfer function in the output layer. In order to train the system the usually closed feedback loop between the output and input are opened. The NARX tool is called up in Matlab using the command *'ntstool'*.

An example NARX network is shown in Figure 7.2 where x(t) is the number of input variables chosen and y(t) is the target values provided to enable the NARX network to be trained. 1:2 indicates the delay or lag time chosen: in this case it was required to test for a delay of two time steps forward and backwards for hidden interactions between input variables which may help with the prediction of the target variable. The number 10 in the middle of the figure represents the number of hidden layers chosen. W is a scalar weight and b is a scalar bias which the inputted data is multiplied by within the output layer. W and B are automatically calculated by the NARX network.

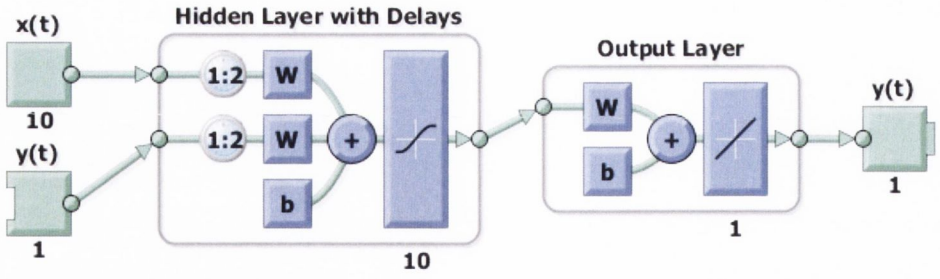


Figure 7.2 NARX network example

When choosing input variables it was decided to apply all available weather data to the ANN rather than carrying out best subset regressions to test for their contribution to the regression prediction, as hidden or unknown interactions may occur between these input parameters that a regression calculation would not reveal. These hidden layers or neurons are a vital part of the ANN and the number of these must be chosen before training the model. As well as choosing the number of hidden layers, the amount of lags to be tested must be inputted. For processes where there is xa large delay between input variables and target reactions this lag time should be increased while for interactions which see little lag the pre-set value of 2 can be retained.

The input variables chosen were; time of day, outdoor pollutant concentration, barometer level pressure (hPa), sea level pressure (hPa), temperature (ºC), relative humidity (%), wind speed (knots), wing direction (knots), stability class, global solar radiation (j/cm²) and outdoor concentrations. Building parameters are not required as these do not change, hence, the model will distinguish them within the hidden layers automatically.

The indoor concentration datasets, or targets, are divided into three sub-sets in order to train, validate and test the Matlab NARX model. The proportion of this division was chosen to be 75% for training, 10% for validation and 15% for testing of the model. Once the proportional breakdown is inputted into the Neural Networks toolbox the model will automatically choose and perform these procedures. Training involves automatically adjusting weighting on the inputs that are found to control the fluctuations in the target values, indoor concentrations in this case. This training teaches the network according to specified conditions until it performs the desired task correctly in the case of NO_2; one of these rules could be that when global radiation increases at dawn time that concentrations increase rapidly. As well as known connections such as this. training will discover on hidden neurons or interactions between the data, these may be a combination of several variations in metrological data that vary the relationship between indoor and outdoor concentrations. These neurons increase the

prediction ability of the ANN over a simple regression. While these hidden links are known to the trained network they are not provided by the user of the Matlab NARX model, so remain unknown. Once the data has been trained using a randomly assigned 75% of the input data, i.e. 75% of the total number of data points with the other 30% scattered throughout the input data, the next process that takes place is the validation of the training that has been carried out. This is used to further refine the neural network construction and to minimise over-fitting. Validation checks ensure that increases in the accuracy of the network training is due to increased accuracy over the data set that was not previously seen. Finally, once the Matlab has found the best solution to the training and validation of the network, testing of the remaining 15% of data is performed. Testing is carried out in order to confirm the actual predictive power of the network. If the R value for testing is low, e.g. below 40%, then the network is found to have a poor prediction value even if training and validation found reasonable R values.

7.4. Development of Neural Networks for individual sites

Each data set was inputted separately to the neural networks toolbox in MatLab. NO_2 data performed considerably better than $PM_{2.5}$ with respect to training for future prediction. This was expected as cross correlations of the $PM_{2.5}$ data sets showed the difficulties of predicting indoor concentrations using outdoor data at a real time basis.

7.4.1. NO_2 artificial neural network model performance

High Pearson's R values were achieved when regression analysis of trained data versus actual output was performed for each site for NO_2. Sites such as Site 9 run 2 which showed a lower dependence of indoor concentrations with respect to outdoor concentrations resulted in lower R values. In order to improve the prediction extra hidden neurons were applied and the data retrained which will be discussed for individual sites. Time series plots of the trained and tested data points, and the range of errors within the plotted time series is detailed below. Most errors fall between the range of -2 and +2 $\mu g\ m^{-3}$ for $PM_{2.5}$ or ppb for NO_2 although some range up to + 5 and -5 $\mu g\ m^{-3}$ for $PM_{2.5}$ or ppb for NO_2, these errors are provided by time series error plots generated by Matlab. Larger errors occurred when indoor concentrations were changing sharply, for instance at Site 6 Run 1 (shown in Appendix D) near hour 25 an error of almost -2 occurs, which is significant at Site 6 as the data range of indoors NO_2 is 3-9 ppb. At this time the indoor concentrations were rising sharply due to the morning peak and although the error is large it fits closely into the time series trend line. Errors

which do not occur at these sharp peak times may be due to interpolation of the input outdoor data, which was carried out as the NOx monitors carry out an automatic calibration at 12.15 am every-night lasting 30 minutes. This data is interpolated in order to prevent gaps in the data set. Previous work (Pilla, 2012) has found this to cause major discrepancies when comparing modelled and actual data sets for air quality. A regression analysis has also been plotted for each individual site. Table 7.1 contains a summary of number of predictors, hidden layers and delays inputted into the MatLab toolbox in order to develop the ANNs.

Table 7.1 Summary of network structures for NO_2

	NO_2		
	Predictor	**Hidden neurons**	**Delays**
Site 1 Run 2	11	10	2
Site 2 Run 2	11	12	2
Site 3 run 1	11	12	2
Site 3 run 2	11	10	2
Site 4 run 1	12	10	2
Site 4 run 2	11	10	2
Site 5 run 1	11	11	2
Site 6 run 1	11	10	2
Site 6 run 2	11	14	2
Site 7 run 1	11	14	2
Site 8 run 1	11	14	4
Site 9 Run 1	11	14	4
Site 9 Run 2	11	14	3
Site 10 Run 1	10	10	2
Site 10 Run 2	10	10	2

As no overnight data is available for Site 1 run 1 and Site 2 run 2, and the time series therefore contain gaps throughout the night, a neural network could not be computed. The individual results of the calculations are contained in Appendix D.

7.4.2. $PM_{2.5}$ artificial neural network model performance

The modelling of the $PM_{2.5}$ data shows a higher number of errors, a larger range of errors and lower Pearson's R values for regressions, than the previously described NO_2 models. Table 7.2 contains the number of inputs, hidden networks and delays contained within each individual Neural Network. The range of hidden neurons was from 10-14 and delays were up to 3 intervals. A time series and regression analysis of target data versus trained, test and validation data for each site was produced in order to discuss the Neural Network performance. Errors generally fall within the range of ±7 μg m^{-3} although most are much less than this. The significance of the error depends on when it occurs - those which drag or push the time series away from its target trend-

line are considerably more important than those which do not. The individual results of the calculations are contained in Appendix D.

Table 7.2 Summary of network structures for $PM_{2.5}$

	$PM_{2.5}$		
	Predictor	**Hidden neurons**	**Delays**
Site 1 run 2	11	14	2
Site 2 run 2	11	13	2
Site 3 run 1	11	12	2
Site 3 run 2	11	10	2
Site 4 run 1	11	14	2
Site 4 run 2	12	10	2
Site 5 run 1	11	10	2
Site 6 run 1	10	14	2
Site 6 run 2	11	13	2
Site 7 run 1	11	11	2
Site 8 run 1	11	14	2
Site 9 run 1	11	10	2
Site 9 run 2	11	12	3
Site 10 run 1	10	13	3
Site 10 run 2	10	12	2

7.5. Forward prediction using the trained Neural Networks

The training of open networks as shown in the previous section is a useful method to check if hidden connections between indoor, outdoor and other factors, in this case meteorological factors, can be found and therefore increasing the prediction power over that of a simple regression. However, the real power in the use of Neural Networks lies in forward prediction. Forward prediction is not built into the Neural Networks toolbox in *MatLab* and therefore a code was required to be written in order to direct *MatLab*. This code is contained in Appendix E.

The purpose of this code was to use a run at a specific site to train a network as was shown in Section 7.4. This network was then closed meaning that no more target data is to be provided. Once the network is closed, new inputs for the second run, i.e. the outdoor concentrations and meteorological conditions, are used in conjunction with the previously trained network to predict the new indoor concentrations.

In order for the code to run without error the data files must only contain numbers - the names of the inputs at the top of columns e.g. wind speed or rainfall are not necessary. The original inputs and targets must have an equal number of cells and be in CSV file

format. All files must be located in the one folder, the same folder in which the code file is saved within. Once the three input files (original inputs, original targets and inputs for forward prediction model) are specified the user must then decide if changes to the input delays or hidden networks are required, similar to when using the Neural Networks toolbox. The user may also decide to change the amount of data used for training, validation and testing of the open network. At this point the network is trained using the first run of data, as was done in Section 7.4. The option to show the results of this outputs are available within the code if the user wishes. Once the original network is trained the code automatically closes the network, this means no more target data i.e. indoor concentrations will be provided. The new input data for forward predictions is now fed into the trained network and the model will predict how the indoor concentrations will behave due to fluctuations in output and weather data.

7.6. Results of forward prediction of NO_2

Results for NO_2 showed a much stronger ability of the outdoor concentrations and meteorological variables to predict indoor concentrations compared to the predictions provided by $PM_{2.5}$. For this reason the forward predictions focused on NO_2 as $PM_{2.5}$ struggled to predict a small amount of test/validation points during the initial network set up.

The availability of monitoring data with two runs at the same monitoring locations left three opportunities to carry out a forward prediction for NO_2, at Site 4 and Site 6, one of which is a recently constructed mechanically ventilated site and the other is an older naturally ventilated site. Both sites showed different I/O ratios between the data for run 1 and 2 and a varying influence of metrological parameters, as calculated in Chapter 4 and 5.

Site 4 (Mechanically ventilated office)

Site 4 shows significantly lower indoor concentrations during run 1 compared to run 2 (see Figure 7.3), with outdoor concentrations showing a varied relationship, with some days showing very poor correlation while other days are more correlated, see Figure 7.4.

Figure 7.3 NO_2 Indoor concentrations at Site 4

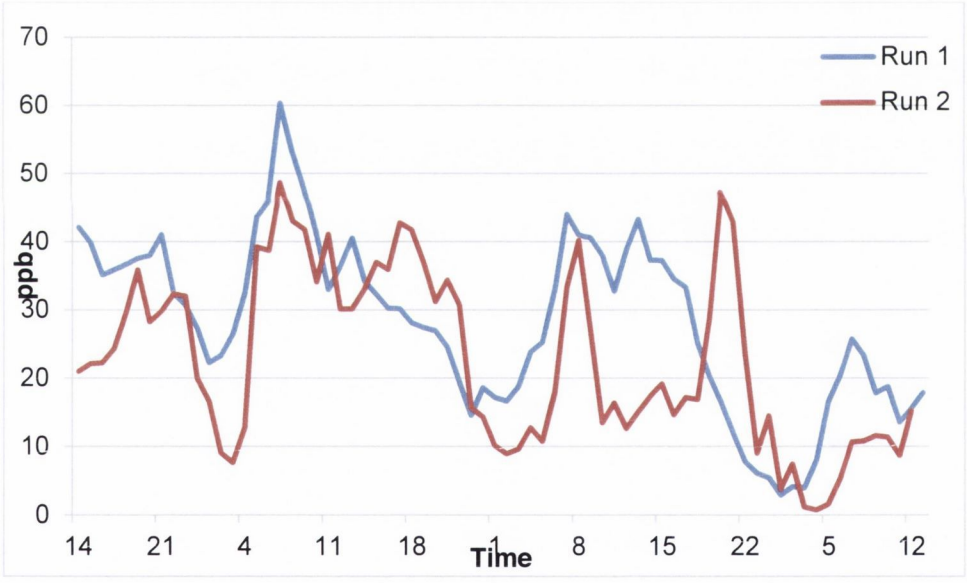


Figure 7.4 NO_2 Outdoor concentrations at Site 4

140 hours of data are inputted to the model using indoor and outdoor concentrations from run 1 plus outdoor concentrations from run 2; these were supplemented by meteorological conditions for the two runs. Figure 7.5 shows the modelled concentrations of NO_2 compared to the actually indoor concentrations. While the R^2 shown in Figure 7.6 is low, a 2 Sample T-Test of the indoor and predicted data gave reasonable result with a 95% Confidence interval for difference of (-4.68, 0.62) T-Value = -1.51, P-Value = 0.132 and DF = 129. The 95 % confidence interval for the

estimated for the difference in predicted and actual indoor concentrations suggests that statistically could be 0.

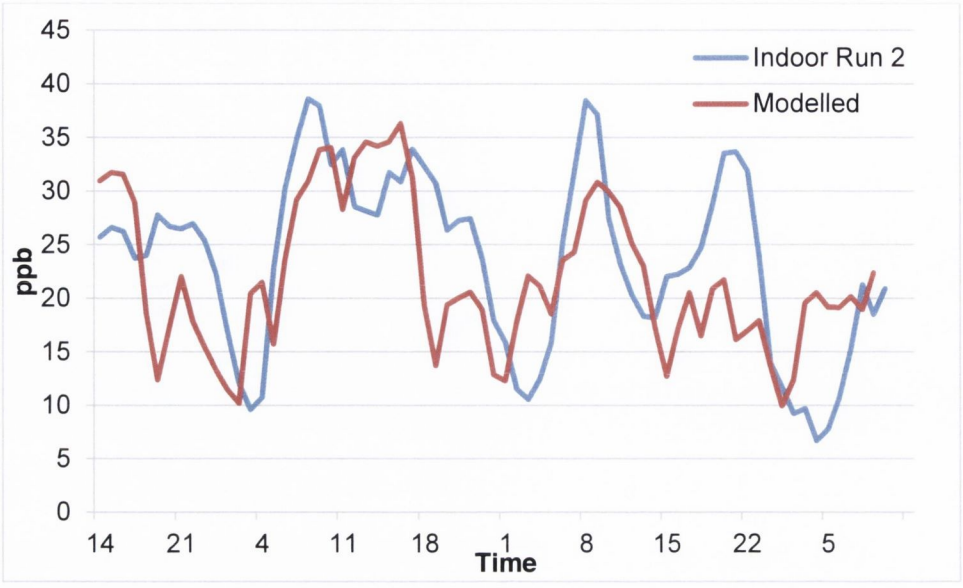


Figure 7.5 Modelled NO_2 concentrations

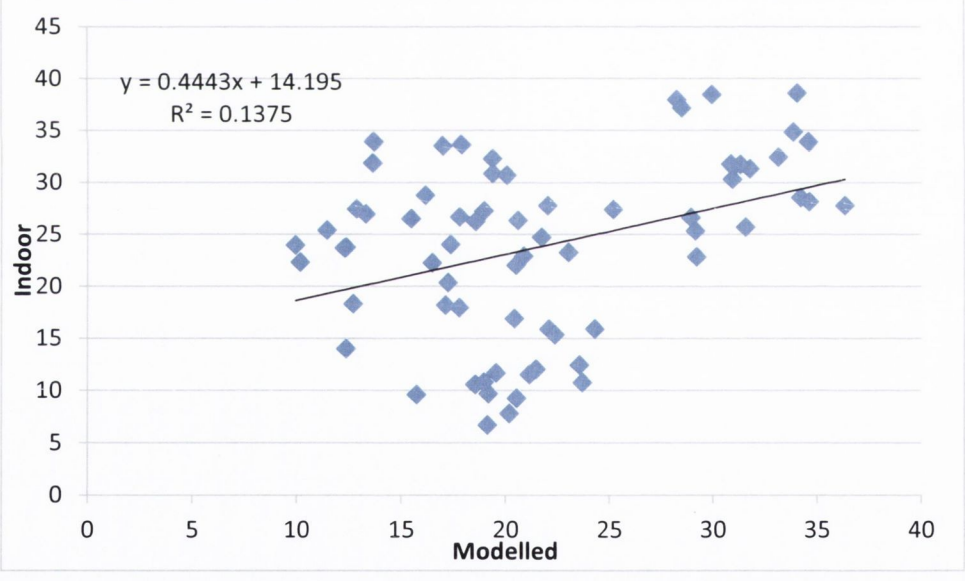


Figure 7.6 Scatter plot of indoor run 2 concentrations versus modelled concentrations

Site 6 (Naturally ventilated office)

Similar to Site 4, Site 6 also showed an outdoor data with similar mean values for run 1 and run 2 (29.13 ppb and 30.29 ppb respectively, see Figure 7.8) but indoor concentrations show a greater difference in mean values (5.36 ppb and 1.63 ppb respectively) with a varying beginning of the morning peaks giving the plot of the two

indoor concentrations in Figure 7.7 a lagged effect. The difference in average indoor concentrations affects the Neural Networks model but as the variable causing this decrease in concentrations e.g. a suspected increase in heterogeneous reaction rates indoors, is not included in the input variables the model has no way to account for this and so average concentrations are higher. This results in a relatively good prediction for Site 6 run 2 expect for the magnitude, see Figure 7.9. If it is assumed that the difference in mean indoor concentrations over the run (3.735 ppb) was caused by an unknown sink in NO_2 and remove 3.735 ppb from each time step of the modelled value and reduced the values found by the model by this, to account for the indoor reactions, an output as shown in Figure 7.10 can be found. Results from this adjusted model show a 2 Sample T-Test give a 95 % Confidence interval for difference: (-0.217, 0.494), T-Value = 0.77, P-Value = 0.443 and DF = 132. These results indicate that with 95 % confidence there is no statistical difference between the mean values of the adjusted modelled value and indoor concentrations for run 2, therefore, the estimate of removing 3.735 ppb was correct.

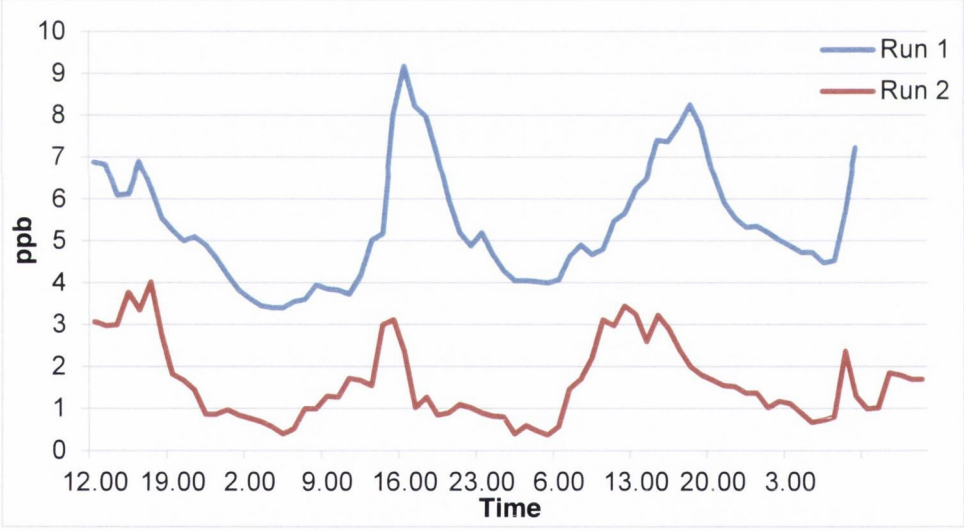


Figure 7.7 NO_2 Indoor concentrations at Site 6

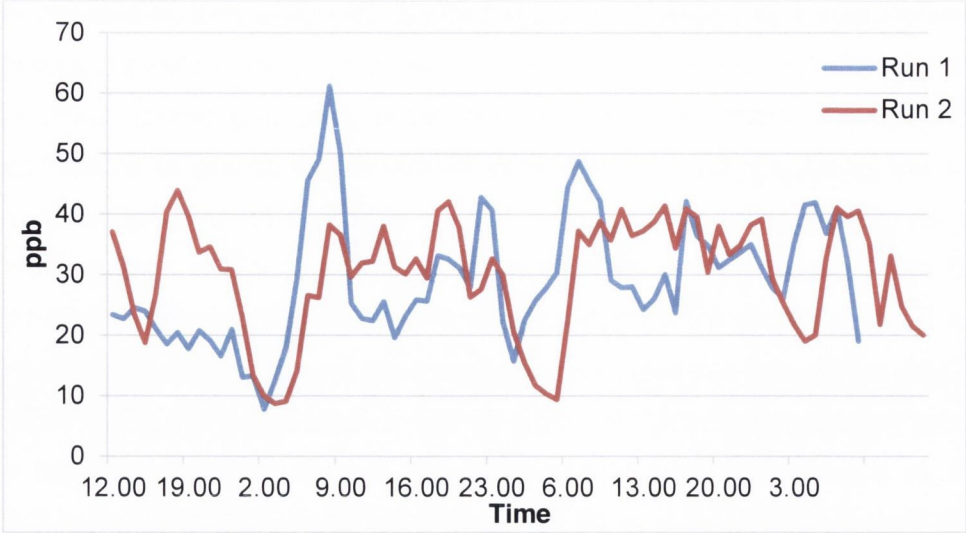


Figure 7.8 NO_2 Outdoor concentrations at Site 6

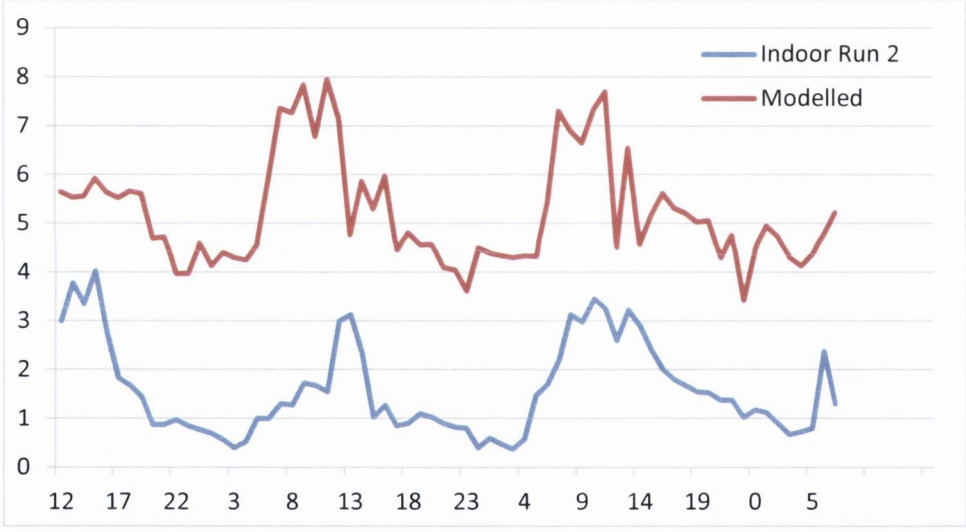


Figure 7.9 Indoor run 2 and modelled NO_2 concentrations

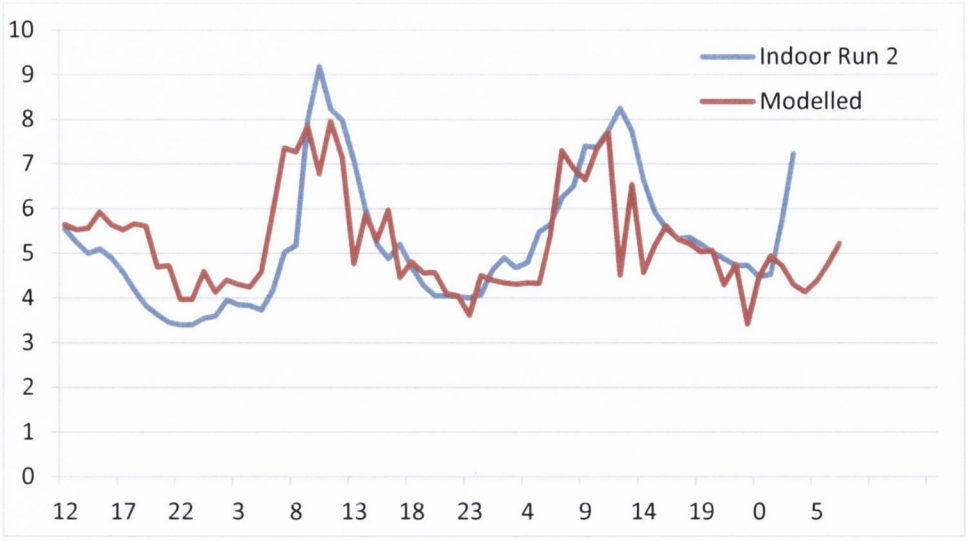


Figure 7.10 Indoor run 2 and modelled with reduction concentrations

7.7. Results of forward prediction of $PM_{2.5}$

As noted previously the relationship between pollutants for $PM_{2.5}$ showed a much greater amount of variability compared to that for NO_2. This leads to weaker network predictions for $PM_{2.5}$, and consequently a poor ability to forward predict using the trained network. However, forward prediction was carried out for Sites 4 and 6 and is detailed below.

Site 4 (Mechanically ventilated gallery space)

The relationship between indoor and outdoor for run 1 and run 2 differs significantly; this is due to considerable increases in concentrations indoors during run 2. These peaks, as seen in Figure 7.14 are not seen in ground level outdoor data, see Figure 7.11. While the relationship between outdoor data on the two runs is similar for the first two days on the plot they then show converse relationships for the remainder of the two runs. Due to the peaks indoors during run 2 which are not present outdoors at ground level, due to a change in meteorological conditions, or during the training period in run 1 it would be impossible for a trained network to anticipate their presence.

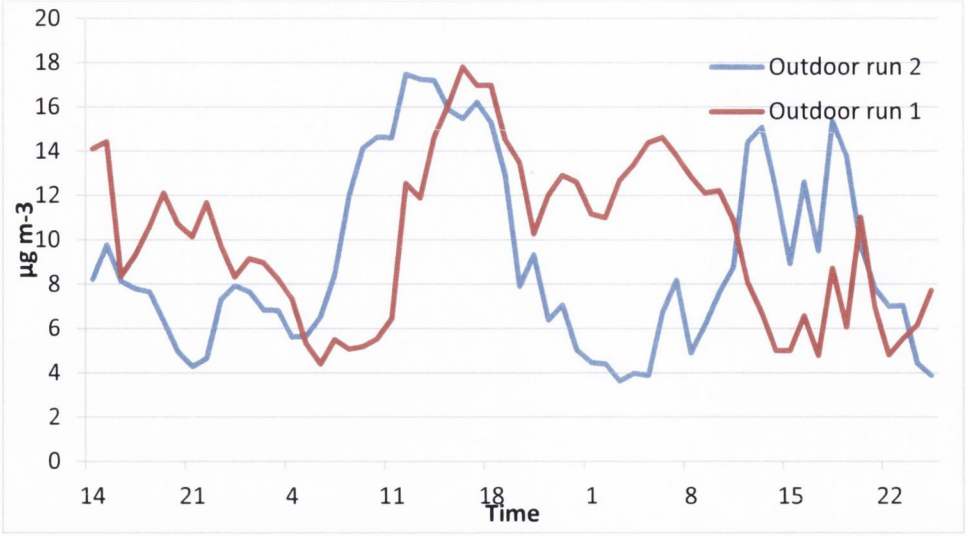


Figure 7.11 Outdoor PM2.5 concentrations run 1 and run 2

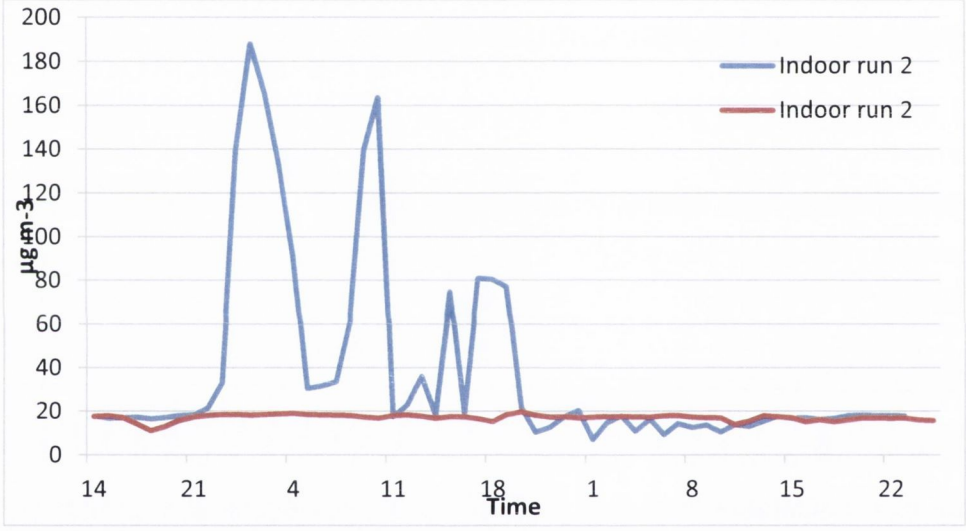


Figure 7.12 Indoor $PM_{2.5}$ concentrations run 1 and run 2

Figure 7.13 shows the Neural Networks forward prediction for run 2 and Site 4, while the model does achieve the indoor value range while the source is not present it shows no indication of the peaks indoors. As noted above the model is given no indication of such peaks. The use of outdoor roof level data which showed reduced versions of peaks (due to the use of the outdoor relative humidity correction) may have improved the predictions but as this data was not available for run 1 the network could not be trained using it.

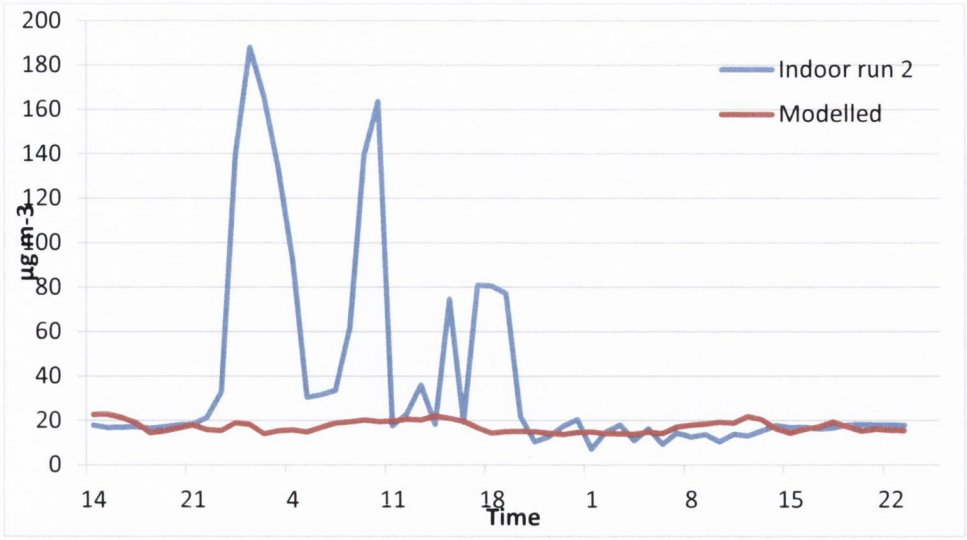


Figure 7.13 Modelled versus indoor $PM_{2.5}$ concentrations run 2

Site 6 (Naturally ventilated office)

Figure 7.14 and Figure 7.15 show the relationships between run 1 and 2 for indoor and outdoor concentrations for $PM_{2.5}$ at Site 6. Outdoor concentrations produce similar patterns with a clear diurnal pattern for both runs. Conversely, indoor concentrations do not show the same connection. Run 1 shows a considerably smoother pattern than run 2 with less variation and a higher mean. Similar to Site 6 for NO_2 which saw a sink in run 2 not present during run 1 this is a pattern that the trained network did not incorporate as it was due to indoor variations rather than meteorological changes or a difference in outdoor concentrations.

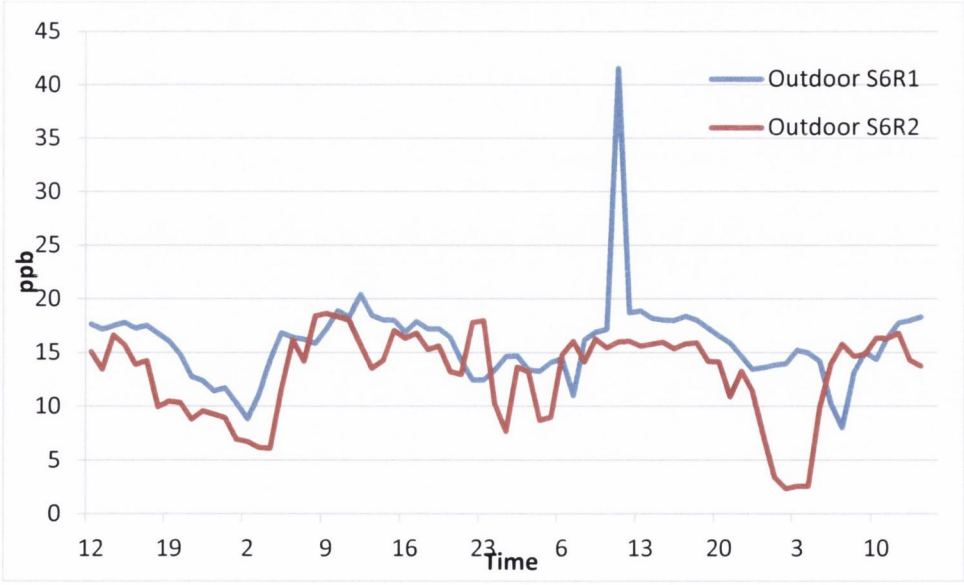


Figure 7.14 $PM_{2.5}$ outdoor concentrations Site 6 run 1 and run 2

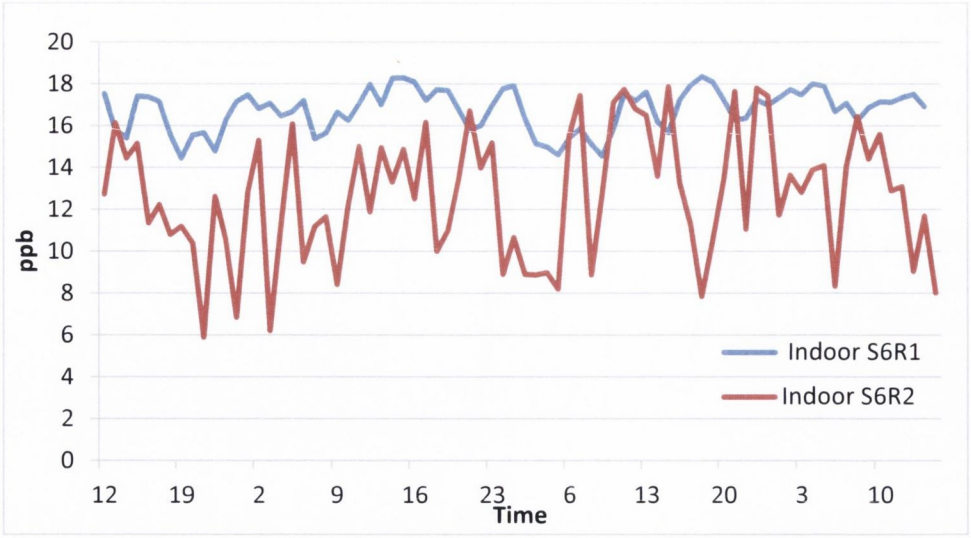


Figure 7.15 $PM_{2.5}$ indoor concentrations Site 6 run 1 and run 2

The forward prediction model was run using $PM_{2.5}$ data from Site 6 as inputs, with the resultant output concentrations shown in Figure 7.16. The model was run several times with results varying slightly, but showing the same generalised pattern which in a 2 Sample T-Test found with 95 % confidence that indoor run 1 and modelled indoor run 2 were not statistically significantly different (T-Value = -1.37 P-Value = 0.174 DF = 121). If this same 2 Sample T-Test found is run comparing the indoor modelled value and indoor run 2 concentrations, the results show that the two are significantly statistically different with 95 % confidence (T-Value = 8.98 P-Value = 0.000 DF = 92). Unlike with NO_2 where mean values differed indoor but the concentration trend remained the same the differencing patterns between runs indoors for $PM_{2.5}$ gives poor results which cannot be solved with the inclusion of a simple sink or source.

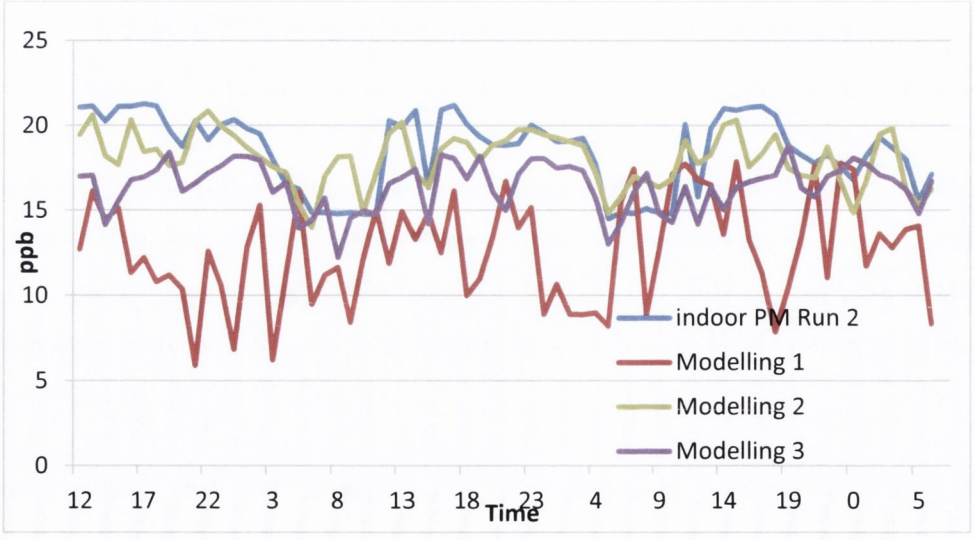


Figure 7.16 Indoor run 2 versus modelled concentrations

7.7.1. Forward prediction of a generic site

In order to test if a trained neural network from one site would be able to predict at another site of similar properties a number of tests were carried out, the results of which show a poor prediction ability. The initial network is trained using one site and then this trained network uses inputs (outdoor pollutant concentrations and meteorological data) from the second site in order to predict the concentrations indoors at the second site. This was due to the differing building characteristics between the sites which were not accounted for as the neural network was trained to the characteristics of another building. Three examples are shown below for; Site 4 predicting Site 3 for NO_2, Site 4 predicting Site 2 for NO_2 and Site 1 predicting Site 6 for $PM_{2.5}$. In the first two cases, a mechanically ventilated site was used to predict another mechanically ventilated site and in the third case, a naturally ventilated site was used to predict another naturally ventilated site. Figure 7.17 shows the result of a forward prediction of the indoor concentrations at Site 3 using a trained network from Site 4. These two buildings are similar; both built at the same time and located next to each other. The results show a poor prediction with an estimate of the difference between the mean exposures of 4.58 ppb and 11.1% of the in target indoor concentrations predicted by the trained network.

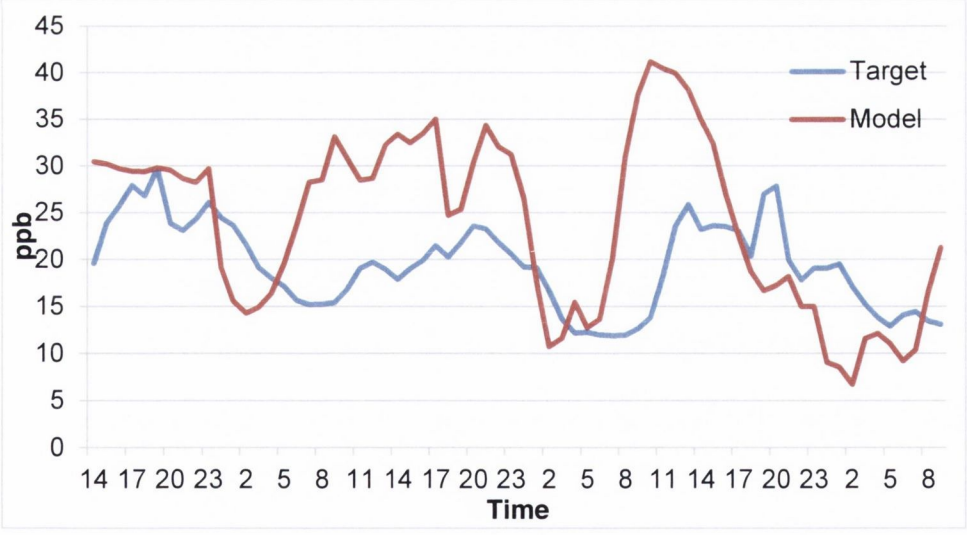


Figure 7.17 Modelled indoor Site 3 using Site 4 with reduction NO_2 concentrations

A second prediction attempt using the trained network from Site 4 was made in order to predict the concentrations indoors at Site 2. The output of this showed modelled indoor concentrations at Site 2 as seen in Figure 7.18. The result of this is a difference of mean exposures of 9.68 ppb and a low prediction value between the sites. The ANN

was not able to predict concentrations indoors at Site 2 using the trained network from Site 4 due to different indoor/outdoor relationships at both buildings.

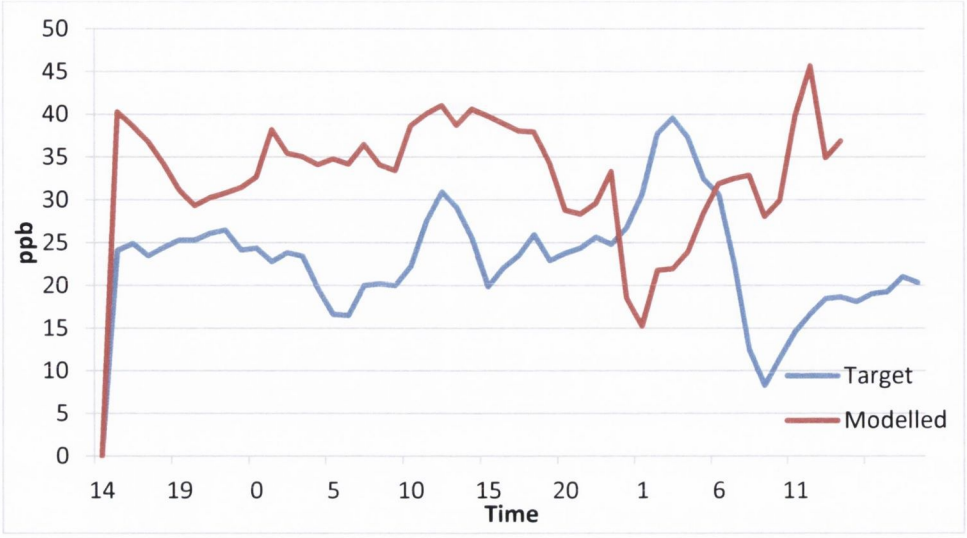


Figure 7.18 Modelled indoor Site 2 using Site 4 with reduction NO_2 concentrations

The final test was for a $PM_{2.5}$ at a naturally ventilated building, in this case the neural network which was trained using data from Site 1 was used to predict indoor data at Site 6, see Figure 7.19. As shown, the results are poor with the prediction by the neural network showing a much greater variance in the concentrations than the target values. A 2 sample T–Test found an estimate of the difference in the mean exposures of 2.40 $\mu g\ m^{-3}$. The mean exposure difference is not as large as expected due to the variance in the data both above and below the target values. Again, similar to the NO_2 case, it can be said that the trained ANN for one site is unreliable at predicting indoor concentrations at another site due to the nature of differing building characteristics.

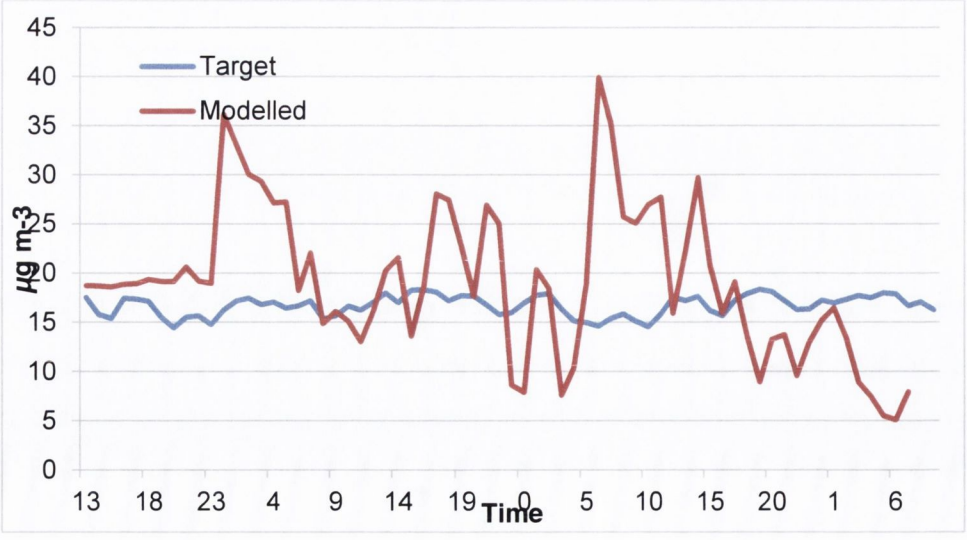


Figure 7.19 Modelled indoor Site 6 using Site 1 with reduction $PM_{2.5}$ concentrations

7.8. Summary and conclusions of Artificial Neural Networks modelling

Predictions using Artificial Neural Networks (ANNs) are much stronger for NO_2 than $PM_{2.5}$ due to the smoother NO_2 time series and more regular diurnal patterns which is affected by meteorological variables (e.g. global radiation etc) to a greater extent than $PM_{2.5}$. This is evident in Section 7.4 which trains ANNs for each site for both of the pollutants. R values for NO_2 data were usually above 0.90 for training, validation and testing with error points which usually did not affect the time series of the data. Therefore, if exposure were calculated over a day the values would not be affected. On the other hand $PM_{2.5}$ R values for training, testing and validation of the networks were considerably more varied with some below 0.53 ranging up to 0.97, with an average R value of 0.819. Error points for $PM_{2.5}$ have higher leverage causing the removal of peaks and troughs and therefore affecting the time series and ultimately the average exposure that would be calculated over a run. The R value decreases if training data is removed and only test and validation data calculated the value decreases to 0.604 for validation and 0.779 for testing. For NO_2 this value remains higher with R values of 0.893 for validation and 0.945 for testing.

No clear patterns with respect to the difference between ventilation strategies at buildings are evident. NO_2 and $PM_{2.5}$ at naturally ventilated sites found a marginally lower testing R value 0.94 rather than the 0.95 seen at mechanically ventilated sites, while $PM_{2.5}$ returned a testing R value of 0.788 for mechanically ventilated sites compared to 0.76 for naturally ventilated.

There are also no definitive differences between ground level and roof level intakes for mechanically ventilated sites. For instance Site 10 shows a higher R value for $PM_{2.5}$ during run 2 where outdoor concentrations were taken at the air intake while Site 3 found the opposite behaviour with ground level concentrations showing a larger R value. For NO_2 Site 10 found a greater correlation between indoor and ground level concentrations compared to the air intake at roof level. At Site 3 NO_2 found high correlations between both roof level and ground level intakes for predicting target data. During Site 4 run 2 for $PM_{2.5}$ the unique opportunity arose where indoor, ground level and roof level concentrations were monitored simultaneously. The results showed that both using roof level and ground level concentrations separately as inputs, combined with meteorological data, provided well trained networks. Training a network using a combination of the two provided marginally better results but as results were strong for individually trained networks, unless both sets of data were readily available, there is

no indication that great benefit would be found by simultaneous monitoring in the case of Site 4.

Use of the forward predictions for NO_2 show an ability of the neural networks to predict mean exposure values if no change in indoor chemistry or building characteristics occur between runs. This issue may be reduced if longer monitoring periods were used where an occurrence of varying indoor and outdoor conditions occurred. The ANN has an ability to adapt to such variations in the relationship between indoor and outdoor as shown at Site 5 where there are two notably different relationships between outdoor and indoor concentrations. At the end of run 1 at Site 4 a change in the pressure leads to a relationship between indoor and outdoor that was similar to the relationship seen in run 2. This may have resulted in the network's ability to predict indoor concentrations during run 2 using the forward prediction model. As this did not occur, or the heterogeneous reactions were not as strong a sink for NO_2 for the training run used when forward predicting at Site 6, the model was unable to correctly predict the level of indoor concentrations during run 2. The model however did predict patterns well and if the estimated sink for run 2 is removed the magnitude of the model also forecasts the indoor concentrations more satisfactorily.

Once trained these networks can be used to predict future indoor concentrations using updated outdoor concentrations provided by the EPA, and weather data by Met Eireann. The EPA does not monitor $PM_{2.5}$ data at hourly intervals therefore forward prediction would only be applicable for use in conjunction with NO_2 which is available in hourly resolution. However, the testing of $PM_{2.5}$ for forward prediction using data from Site 6 showed a poor result indicating that even if hourly data was available it is unlikely to predict indoor pollutant exposure to staff accurately.

The drawback of this model over the previously used recursive mass balance model, seen in Chapter 6, is that it requires training at individual sites. The trained networks inability to be used at sites of similar characteristics was shown in Section 7.7.1 where three attempts are briefly discussed. Training at individual sites is required as building characteristics cannot be changed within the trained network. This means that each model will require indoor data to be collected at the site in order to train the individual network.

8. Predictions for indoor air quality in Dublin buildings

8.1. Introduction

In Chapter 5 the concept of the I/O ratio was introduced to describe indoor concentrations as a function of outdoor concentrations in order to account for the fact that sites with higher outdoor concentrations would be expected to have higher indoor concentrations. Using the ratio was a way of reviewing the ability of the building to shield the occupants from these pollutants. This chapter looks at the indoor concentrations independently of outdoor concentrations, in order to assess concentrations inside different buildings and compare them with other buildings in Dublin. It also reviews the outdoor air quality concentrations collected in Dublin with other locations worldwide as well as discussing potential mitigation measures for reducing indoor concentrations of pollutants in order to improve the health of building occupants. They must be compared to each other but also to the legislative limit values for NO_2 and $PM_{2.5}$ designed for the protection of human health are shown in Table 8.1, against which the concentrations measured indoors at the 10 monitoring sites can be compared.

Table 8.1 Legislative limits for NO2 and PM2.5

Pollutant	Limit Value Objective	Averaging Period	Limit Value	Limit Value	Basis of Application of the Limit Value	Limit Value Attainment Date
			μgm^{-3}	ppb		
NO_2	Protection of human health	1 hour	200	105	Not to be exceeded more than 18 times in a calendar year	1-Jan-10
NO_2	Protection of human health	calendar year	40	21	Annual mean	1-Jan-10
$PM_{2.5}$ Stage 1	Protection of human health	calendar year	25		Annual mean	1-Jan-15
$PM_{2.5}$ Stage 2	Protection of human health	calendar year	20		Annual mean	1-Jan-20

The annual mean limit for $PM_{2.5}$ is 25 $\mu g\ m^{-3}$ in the EU, but is lower in the United States at 15 $\mu g\ m^{-3}$ while the WHO guidelines are lower again stating an annual mean limit of 10 $\mu g\ m^{-3}$ and a 24 hour mean limit of 25 $\mu g\ m^{-3}$ (World Health Organization, 2005). The rational for the low WHO limit is due to adverse health effects being recorded for $PM_{2.5}$ exposure as low as 3-5 $\mu g\ m^{-3}$ (Pope Iii et al., 2002). 10 $\mu g\ m^{-3}$ was chosen as the recommended limit value by the WHO as it was below the mean value for the most likely effect to health due to $PM_{2.5}$ as found in scientific literature including the six cities study in the United States (Pope Iii et al., 2002, World Health Organization, 2005, Dockery et al., 1993). The WHO recognises that these concentrations may not be achievable in urban areas but they should be strived towards as they would significantly reduce health issues.

8.2. Comparison of indoor concentrations between building types

This section compares some of the main differences between the buildings monitored (i.e. ventilation system and age) against their indoor air quality results independently to the outdoor air quality concentrations. The section

also discusses the effect of occupant movement and use of building on the concentrations seen across the 10 sites monitored in this study.

Overall it was found that indoor concentrations of $PM_{2.5}$ at naturally ventilated sites were on average higher during the working day than the concentrations within the mechanically ventilated buildings; (Figure 8.1 and Figure 8.2) with the exception of mechanically ventilated Site 4 run 2. The monitoring location for this site was located at ground level, and therefore infiltration of outdoor air may have played a larger influence on indoor concentrations compared to other mechanically ventilated sites which were located on upper floors further from the main entrance to the building. Also, it should be noted that the older ventilation system at Site 2 did not perform as well as the newer systems seen at other sites, although the elevated concentration may also have been associated with an indoor source from cooking.

Conversely, averaged working day concentrations showed very different behaviours for NO_2 than for $PM_{2.5}$ with naturally ventilated sites showing much greater reductions compared to the mechanically ventilated sites, as shown in Figure 8.3 and 8.4. Moreover, the oldest buildings of the naturally ventilated sites showed the lowest indoor concentrations.

The suspected reason for these greater reductions in NO_2 at the naturally ventilated sites is due to a combination of low number of air changes per hour, large interior surface area for heterogeneous reactions to occur and indications of damp conditions which are known to increase heterogeneous reaction rates. The low number of air changes provides a longer time period for reactions to occur than in the shop sites where customers opening and closing the door regularly, increases the number of air changes. A higher indoor concentration of NO_2 was noticed at Site 9 when windows were opened and the number of air changes increased. While a low number of air changes and large surface area should also increase the deposition of $PM_{2.5}$ this was not seen. This may be due to a local indoor source at Site 9 and resuspension from movement within the office at Site 6, this office was not regularly dusted and deposits of settled particulates were noticeable around the office. The movement of people within the office had a large potential to resuspend these particulates and keep concentrations high.

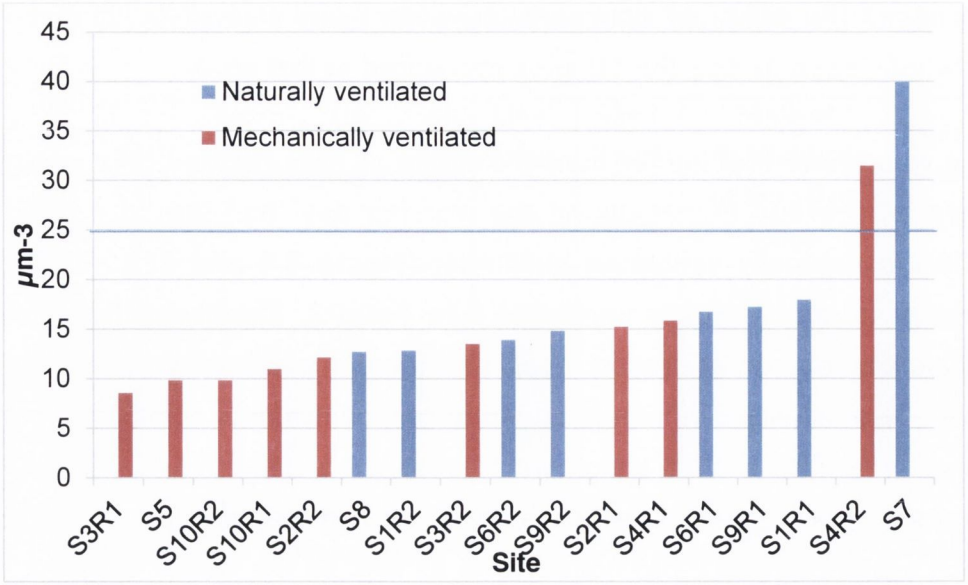


Figure 8.1 $PM_{2.5}$ indoor average working hour's concentrations

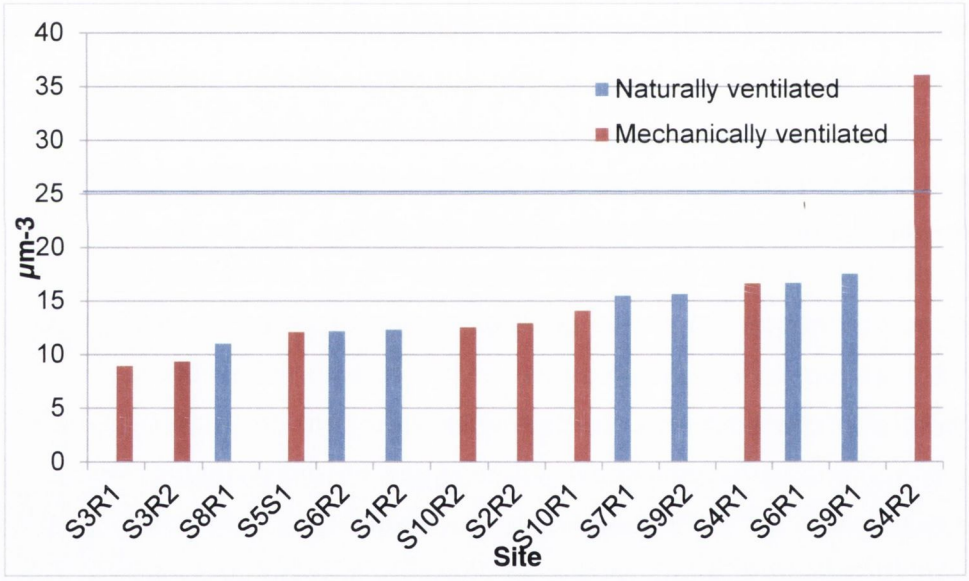


Figure 8.2 $PM_{2.5}$ indoor average non-working hours' concentrations

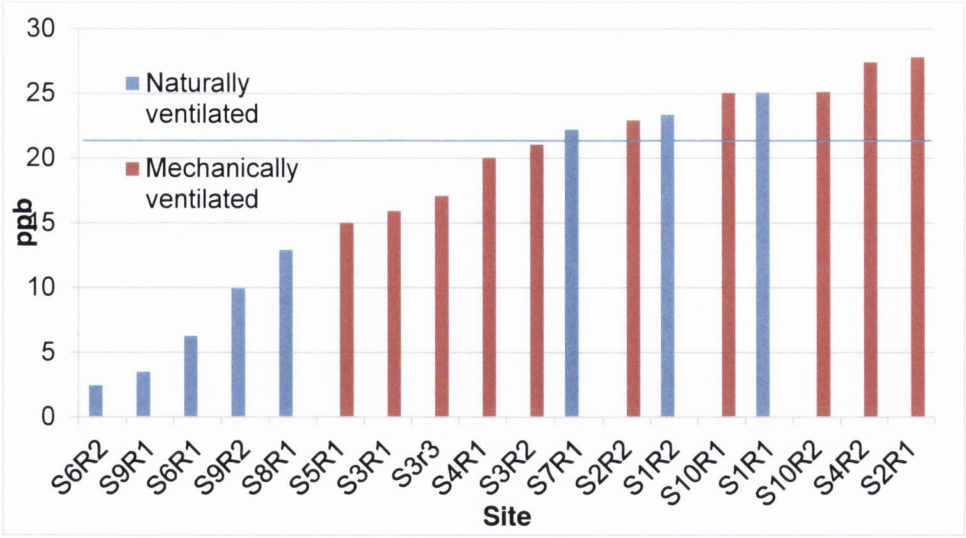


Figure 8.3 NO_2 working hours' concentrations indoors

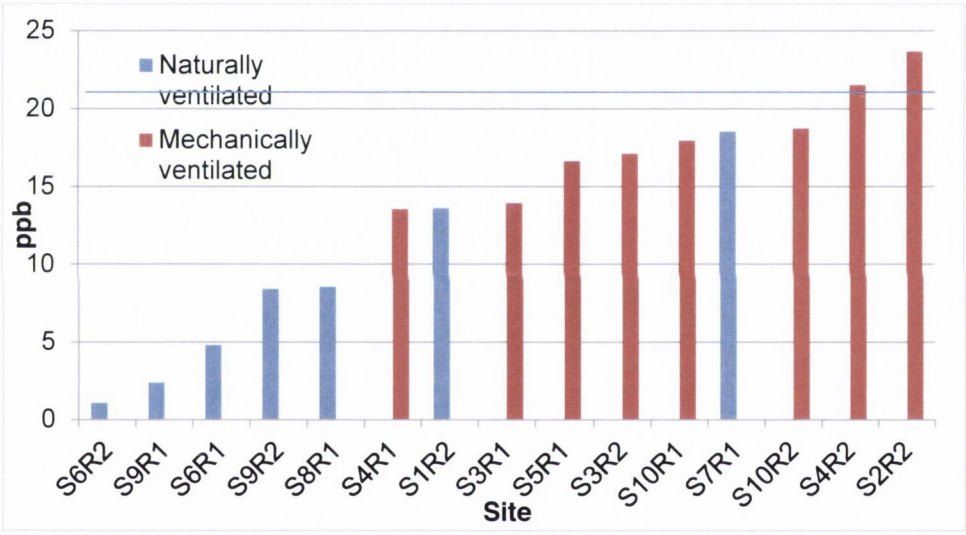


Figure 8.4 NO_2 non-working hours' concentrations indoors

8.2.1. Mechanically ventilated buildings

This section reviews the indoor environment of the mechanically ventilated building with respect to the occupant's health. Figure 8.5 and Figure 8.6 show the NO_2 and $PM_{2.5}$ concentrations for working and non-working hours. It can be seen that, on the whole, $PM_{2.5}$ concentrations are lower than NO_2 concentrations even though (on the same scale with units ppb for NO_2 and $\mu g\ m^{-3}$ for $PM_{2.5}$) the limit value for $PM_{2.5}$ is lower.

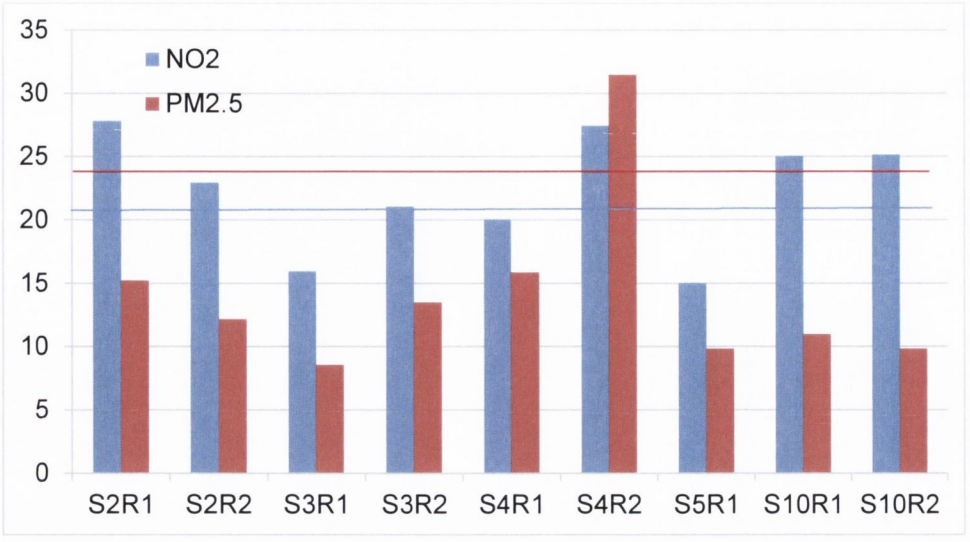


Figure 8.5 Indoor NO_2 and $PM_{2.5}$ concentrations for mechanically ventilated buildings during working hours

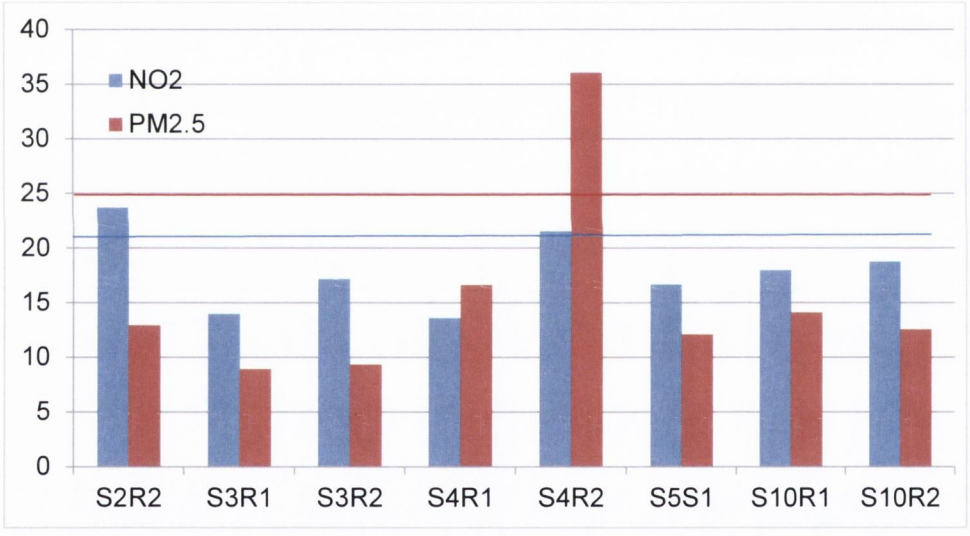


Figure 8.6 I Indoor NO_2 and $PM_{2.5}$ concentrations for mechanically ventilated buildings during non-working hours

Offices (Sites 3 and 5)

Out of all 10 sites the lowest working hours' concentrations of $PM_{2.5}$ were measured at Site 3 during run 1 (monitored in summer). Site 3 is a mechanically ventilated building constructed in the past 5 years. For run 2 which was taken in the week following run 1, the average working hours' concentrations increase by almost 5 $\mu g\ m^{-3}$. The system was well maintained with a specialised team on site for maintenance with filters changed at least

once every 3 months. Air changes at this site were automated by a BMS (building management system) and controlled in order to maintain a set point temperature. Three indoor runs were completed at Site 3: run 1 and run 2 have been discussed throughout Chapters 4 and 5 but a third run (which has only briefly been mentioned) occurred over 4 days in November 2010 when only indoor air quality was monitored. This run found indoor concentrations to lie between the two other runs (both of which were carried out in July 2010) at 17.1 ppb, indicating that time of year may not affect concentrations at this site. In order to confirm this, a longer term study should be carried out as the concentrations indoors during any of these weeks may have been unusual.

Site 5 had the next lowest average working hours concentrations of all sites for $PM_{2.5}$ which again was a well maintained mechanically ventilated building controlled by a BMS to a set point temperature. This building was located furthest from the centre of town and traffic volumes saw roughly 50 % less vehicles' per hour at peak times which would have contributed to lower outdoor concentrations (Dublin City Council, 2012). Concentrations were taken in January when outdoor $PM_{2.5}$ concentrations would be at their annual maxima and therefore it would be expected to see even lower concentrations during the summer months and possible greater indoor concentration reductions.

Run 1 at Site 3 and Site 5 showed very similar indoor concentrations for NO_2 and $PM_{2.5}$, with concentrations for both pollutants being slightly elevated for run 2 at Site 3. Concentrations during non-working hours reduced for Site 3 for both runs, but increased for Site 5. Both sites had ventilation units turned off during non-working hours and therefore changes in concentrations during these periods were due to infiltration/exfiltration.

These two office sites had the lowest indoor concentrations for $PM_{2.5}$ as well as having some of the lowest NO_2 concentrations monitored for mechanically ventilated sites. Neither site showed concentrations above the annual mean limit value set out by the EU indicating that working in such a building should be safe with respect to long term exposure.

Non office buildings (Sites 2, 4 and 10)

While Sites 2 and 10 are office buildings, they are considered as different from the previous office sites as monitoring was carried out in the canteen area for both buildings. In Site 2 a gas cooker was present and in Site 10 no cooking facilities were in place.

Site 2 is the oldest of the mechanically ventilated buildings with a forced ventilation system which was installed in the 1960s. This site saw average $PM_{2.5}$ concentrations of 12.16 $\mu g\ m^{-3}$ for run 2 but higher concentrations of 15.23 $\mu g\ m^{-3}$ during run 1 when a gas cooker was being used to a greater extent at the site. This cooker was used for preparation of staff meals in the canteen area. The second run was carried out during a week when some of the building occupants were on holidays, hence the decreased rate of cooking. The more typical indoor concentrations (outside of holiday periods) could be expected to be at the higher level of 15.23 $\mu g\ m^{-3}$ which is below Irish and EU legislation limits but above American limits.

Canteen Sites 2 and 10 both had indoor NO_2 concentrations for both runs above the limit value of 21 ppb. For Site 2 this can be attributed to the gas cooker in the room, which would also contribute to the increased $PM_{2.5}$ concentrations. Site 10 had no known NO_2 source indoors, and so the high concentrations are due to the seasonal patterns as monitoring took place during January, the time of year when NO_2 concentrations tend to peak. The indoor concentrations correlate strongly with the outdoor concentrations.

Site 10 showed $PM_{2.5}$ concentrations in the region of 10 $\mu g\ m^{-3}$ and unlike Site 2 this mechanically ventilated site was completely renovated in 2001 including a new ventilation system. This site is located at a very busy road junction and concentrations were taken during the winter months.

Both Sites 2 and 10 showed indoor concentrations below $PM_{2.5}$ limits in the EU and the lower United States limits for working hours and non-working hours. Unfortunately for staff, both sites also showed NO_2 concentrations exceeding safe exposure limits of 21 ppb during working hours, with Site 10 also exceeding limits during non-working hours. Both these sites were located on busy main roads and while they compared moderately to all other sites for $PM_{2.5}$ they had some of the highest NO_2 concentrations. This might have been

expected for Site 2 with the gas cooker in place, but was disappointing for Site 10 which showed little ability in its ventilation system or building structure to reduce roadside outdoor NO_2, particularly when monitored at the highest storey of the building.

Unlike the other two sites in this category, which are office buildings where monitoring happened to be carried out in a canteen, Site 4 is a gallery space/cafe/shop. This site shows the highest concentrations of $PM_{2.5}$ indoors during run 2 which saw sharp spikes in the data, which interestingly were picked up at the ventilation intake on the roof of the building but not at ground level near the door. While run 1 has none of such peaks, it did show consistently higher levels (15.85 $\mu g\ m^{-3}$) than outdoor concentrations during monitoring indicating a high indoor source for $PM_{2.5}$. If the peaks are removed from run 2 the average concentration reduces to just above 14 $\mu g\ m^{-3}$ below both Irish and EU limits, but above American limits. It should be noted however, that these are still on the high side for average indoor concentrations monitored during this study. The reason for the high indoor concentrations for $PM_{2.5}$ at this site may be due to the location of monitoring. Unlike the other mechanically ventilated sites this building has a large open space used as a gallery area on the ground floor (other mechanically ventilated sites were all offices on upper floors) and therefore the surface area was lower for deposition. This space also contained a cafe area which, although it carries out relatively limited cooking involving the heating of soups or making toast etc, these activities could be acting as fairly significant indoor sources. Customers visiting the gallery and cafe walked in and out of the building regularly which leads to the door of the building opening allowing an influx of outdoor air. In addition, this monitoring was carried out in December when annual background averages are generally at their peak. As well as revealing concentrations above the outdoor limit value for $PM_{2.5}$ Site 4 run 2 also shows high average NO_2 concentrations during working hours concentrations of 27.41 ppb. During run 1 this average concentration was just under the limit at 20.02 ppb. As previously mentioned, while this site was recently built it was the only mechanically ventilated building in which monitoring took place on the ground floor. As the door to the building is often left open the influence of traffic from the nearby road is likely to increase indoor concentrations. These local traffic sources would contribute a different source than the high concentrations picked up from the roof level. Comparing with all other sites, both mechanically

and naturally ventilated, Site 4 produced mediocre results for run 1 for NO_2 but poor results for run 1 $PM_{2.5}$ and run 2 for both NO_2 and $PM_{2.5}$ indicating that this location, while having a new ventilation system and being recently constructed, did not keep infiltration of NO_2 and $PM_{2.5}$ to the same standards as the other sites.

Effect of mechanical ventilation location

All of the 5 mechanically ventilated sites used air intakes located on the roofs of the buildings. All buildings were of a similar height and between four and five storeys tall (Site 5 and 10 are five and Sites 2, 3 and 4 are four storeys tall) and all located on heavily trafficked roads. Site 5 was located slightly further from the city centre, on a road which was marginally less trafficked and importantly (from a pollutant dispersion point of view) was in an area where buildings were less densely packed, thereby allowing pollutants emitted to dissipate quicker with less of a canyon effect.

The prevailing wind in Dublin is from the south-west which should be taken into account when choosing the placement of ventilation systems on the roofs of buildings. At Site 5 the ventilation system faced to the south and south-east (2 different intakes), facing the road below. The ventilation system facing south may be exposed to windblown particles being transported from the road and should have considered using a system facing away from the road. Utilizing the building facade to disperse pollutants being drawn across the city by prevailing winds, and from the road below, may have reduced concentrations at the point of intake. This may have been considered and rejected during design of the system as other nearby pollutant sources could have been deemed to pose a greater threat. These included a nearby bus depot 100 m to the north-west and Dublin Port to the north-east.

At Site 2 the average reduction in concentrations between street and air intake at roof level was just under 50 % for both NO_2 and $PM_{2.5}$ during working hours. It should be noted that concentrations were monitored on separate runs and therefore may not be directly comparable, but the reductions were consistent throughout. Indoor concentrations were lower than street level but above roof level, this may be due to the influence from the street level concentrations and indoor sources such as cooking. While infiltration of air through windows and

doors cannot be avoided, especially in an older, poorly sealed building such as Site 2, the placement of the ventilation system did produce good reductions, and therefore provided air through the ventilation system which was of considerably better quality than street level. This building located its intake to the north-west, with the building facade acting as a barrier between the intake and the road facing the back of other commercial units and pedestrianised zones. Although Site 2 performed poorly with respect to NO_2 indoors the concentrations may have been considerably worse if this system was not located away from the main road.

Site 10 was located at the junction of two busy roads, both of which saw large volumes of traffic. Similar to Site 2 this system faced the North East and efforts were made to place it on the far side of the roof from the traffic of the streets below. On average a 25% reduction for $PM_{2.5}$ concentrations and a 29% reduction for NO_2 concentrations were seen between ground level and air intake level, but again like the other sites they were monitored over two different runs rather than simultaneously, so these reductions may vary slightly from the true value. These reductions increase to 36% for NO_2 and 35% for $PM_{2.5}$ during working hours for comparison with Site 2, (as only working hours concentrations were available for run 1 at Site 2). Even with the increased reductions, if only working hours concentrations are reviewed, these are still considerably less than those at Site 2 and may be due to no building facade acting as a barrier to reduce pollutant concentrations. While the vertical distance from the street should reduce concentrations of both pollutants, the lack of a physical barrier to force pollutants to disperse (as was seen at Site 2 and in many previous studies (Green et al., 2001, Mfula et al., 2005) means that concentrations are not as low as they would have been predicted.

Sites 3 and 4 had ventilation systems with air intakes within 30 m of each other; these two sites were designed and constructed by the same company. The air intake at Site 3 was located about 25 m from a train station and even closer to the train line. This can be seen in Figure 8.7, with the air intake circled and the train station also marked in the bottom left hand side. The ventilation intake faces towards the train track which is elevated above ground level, roughly 3 storeys below the air intake. As noted in Chapter 4, 91 commuter trains, which are diesel powered, on a weekday plus other trains which are run on electricity pass through the station. Out of these 91 trains

passing, 83 of the journeys have Pearse station as their initial or final station, therefore idling in the station for a longer period. These passing trains can be considered a significant source of both $PM_{2.5}$ with reductions between street and ground level showing only a 13 % decrease for the entire runs and even less at only 3 % during working hours when trains were passing. The reductions between roof and ground level were considerably more for NO_2 with reductions of 54 % when day and night are considered which increased to 59 % when only working hours are considered. This points towards the trains acting as a strong source of $PM_{2.5}$ preventing the normal reductions seen between roof and ground level. Barriers around the ventilation intake were put in place to dissipate pollutants shortly after construction but these results indicate they do not produce adequate results. After discussions with building staff it was learnt that another new building on the other side of the train station has been experiencing similar high concentrations of particulates and ventilation filters required changing at every 6 weeks rather than the usual 16 weeks.

Figure 8.7 Air intake location at Site 3

Site 4 is located next to Site 3 and its ventilation system was located on the opposite side of the building from the train track, directly above a heavily trafficked road. Only $PM_{2.5}$ concentrations were available for comparison as the NO_2 monitor showed technical issues during the run. This building was the only site where simultaneous roof and ground level monitoring took place for $PM_{2.5}$.

The comparison showed that the air at roof level had significantly higher concentrations of $PM_{2.5}$ than at ground level, with levels at roof level on average twice that at ground level for the entire run and 1.5 times the street level during working hours. These increased concentrations from roof level were also seen indoors but were not picked up at ground level. During the previous run at this site, outdoor concentrations of $PM_{2.5}$ were significantly less than indoor concentrations; this may be due to an indoor source or may be due to air at the intake level having higher concentrations in general than at ground level. Either way, the ventilation system does not provide satisfactory $PM_{2.5}$ results and therefore mitigation measures should be considered for the health of staff.

Interestingly Site 2 which was designed in the late 1960s, unlike the other 4 systems, all of which were designed within the past 10 years, provided a greater decrease between ground level concentrations and the air that is taken into the ventilation system. It should be noted however, that as no ground level concentrations were available at Site 5 the ability of this site to reduce concentrations between ground level at the main door to the building and air intake level at the roof cannot be assessed.

Difference in mechanically ventilated buildings between working and non-working hours

In order to assess the variance among sites between working and non-working hours the differences have been compiled and shown in Figure 8.8.

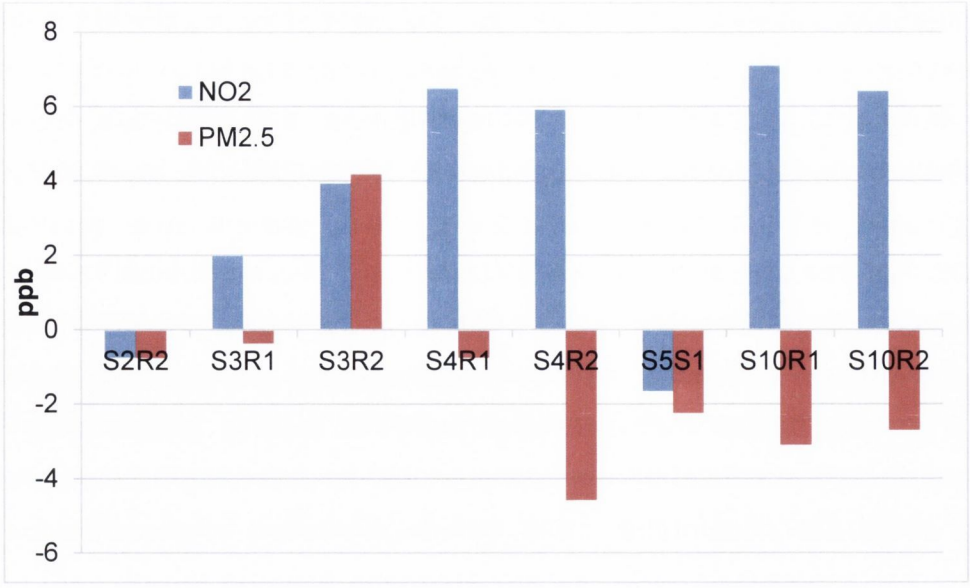


Figure 8.8 Difference between working and non-working hours mean air quality cocentrations at mechanically ventilated sites

The results show indoor reductions of NO_2 during non-working hours for most mechanically ventilated sites. The only two sites with increases during non-working hours were Sites 5 and 2. At Site 5 sharp reductions were seen overnight with the exception of the final night where indoor and outdoor concentrations saw little reduction and some unusually noisy behaviour. The increased NO_2 concentrations during non-working hours were due to indoor concentrations reaching morning and evening peaks outside of the 8.30 am to 5 pm period during which the ventilation system was turned on. The effect was that when non-working and working hours were averaged, the non-working hours were slightly above working hours. The same pattern occurred at Site 2. If staff worked longer hours at these sites e.g. starting at 8 am rather than 9 am, then these morning and evening peaks would have been included with the working hour's exposure. Instead, they were classified as non-working hours peaks pulling up the overall concentrations indoors during non-working hours from the lows seen in the middle of the night. All other sites saw expected reductions in NO_2 concentrations with Sites 4 and 10 seeing the largest reductions of between 6 and 7 ppb.

$PM_{2.5}$ displayed the opposite behaviour to NO_2 with concentrations at most sites recording increases in concentrations overnight at all sites except Site 3 run 2. Indoor $PM_{2.5}$ concentrations do not show as strong, if any, a diurnal

cycle with the concentrations generally varying around a mean value. Many sites saw large unexpected peaks overnight i.e. no corresponding outdoor fluctuation, which pulled up the mean concentrations. As the buildings were empty these were not due to occupants' movement at the times of these peaks. Site 4 run 2 saw the largest negative difference between working and non-working hours. After consulting time series plots of the data it was found that a large increase in concentrations reaching over 200 $\mu g\ m^{-3}$ occurred from 9 pm until 5 am during the first night of monitoring. Another sharp peak occurred soon after again pulling up non-working hours concentrations; this peak also was present for 1 hour during working hours but then rapidly declined, returning to normal indoor values for the site.

While the air quality measured during non-working hours is not directly relevant to the health of staff; it is still important in understanding the behaviour of the pollutants within the buildings when air changes are at a minimum. NO_2 for mechanically ventilated sites show greater diurnal cycles and while indoor concentrations show a baseline level of 10-12 ppb below which concentrations rarely drop indoors, they do reduce over-night compared to day time values. If working hours are short e.g. 9 am to 5 pm, the morning and evening peaks give an average value which mute the low concentrations seen during the middle of the night. $PM_{2.5}$ results show less of a diurnal cycle than NO_2 and the increases in non-working hours concentrations are often down to one or two very high peaks overnight.

Another possible contribution to the higher overnight concentrations for indoor $PM_{2.5}$ may be as a result of humidity in the air. Outdoor concentrations were corrected for relative humidity(RH), see Chapter 3, but the indoor concentrations did not require such a correction as RH did not reach above 60%, the point (according to literature) at which a correction is required. The high $PM_{2.5}$ peaks at Site 4 run 2 for instance had corresponding peaks outdoors at roof level but when the RH correction was applied these outdoor peaks were significantly reduced as they occurred at a time when RH was high. As no correction was applied indoors the concentrations remain elevated. Unfortunately, no continuous RH data is available for indoors but recorded values at 8.30 am showed RH at 48%, well below the point where the RH correction must be applied. Hence, it is recommended for future work that RH levels indoors are continuously monitored as well as the validity of the outdoor

corrections for environments like Ireland where RH increases to above 85 % most nights.

8.2.2. Naturally ventilated buildings

Two types of naturally ventilated buildings were looked at for this research, 3 of them were naturally ventilated shops while the other two were offices. Unlike the larger offices that were mechanically ventilated, the naturally ventilated offices were much smaller with fewer occupants. The naturally ventilated shops had less control over the number of air changes per hour with customers often leaving doors open and therefore allowing large volumes of air to enter the building unfiltered from the road. Figure 8.9 and Figure 8.10 show the indoor concentrations of both pollutants for working and non-working hours which will be discussed throughout this section.

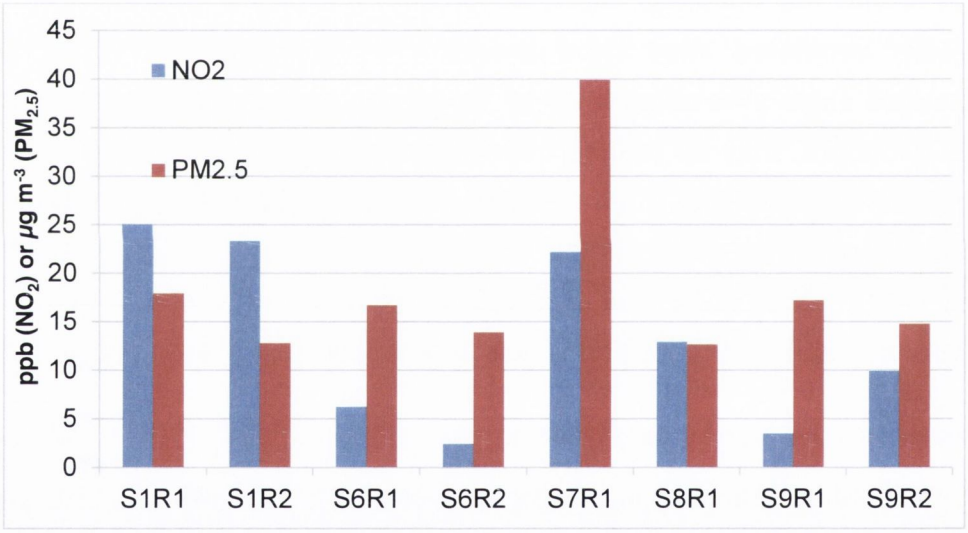


Figure 8.9 Indoor NO_2 and $PM_{2.5}$ concentrations for working hours in naturally ventilated sites

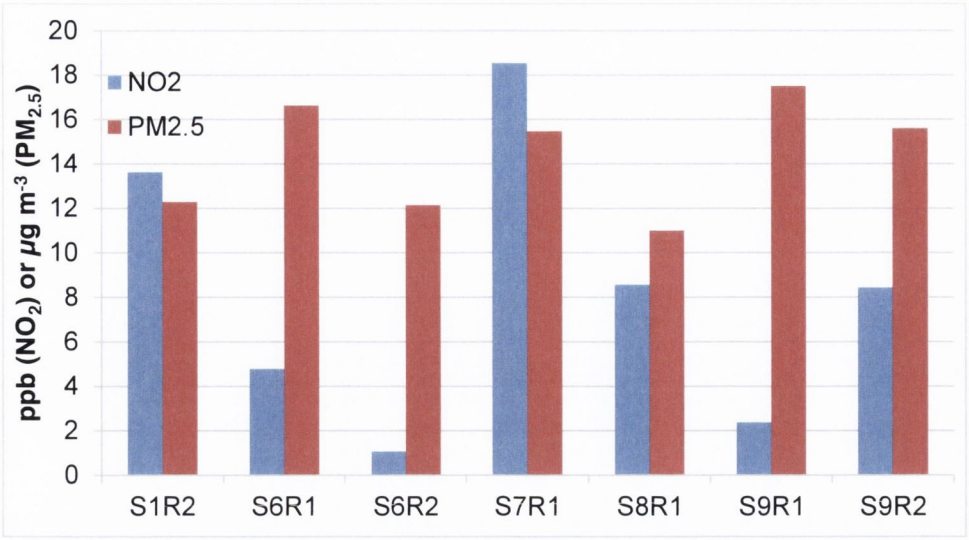


Figure 8.10 Indoor NO_2 and $PM_{2.5}$ concentrations for non-working hours in naturally ventilated sites

Office (Sites 6 and 9)

The naturally ventilated office at Site 9 showed a difference in $PM_{2.5}$ concentrations between run 1 and 2. This difference was due to increased air changes in the second run (which was taken directly after the first and weather conditions remained similar) as a result of a window of the small office where monitoring took place being opened for this run. This increased the number of air changes, and resulted in a reduction in concentrations from 17.2 μg m^{-3} to 14.8 μg m^{-3} between runs 1 and 2. After investigations an indoor source in an adjoining room was traced to being a significant source for $PM_{2.5,}$ as concentrations indoors were higher than even outdoor concentration at road level (5 storeys down). Even with the reduced concentrations due to the higher number of air changes, indoor concentrations remained considerably higher than outdoors for $PM_{2.5.}$ Conversely, NO_2 concentrations increased by 6.5 ppb when the air exchange rate was increased. NO_2 diurnal cycles are often similar indoors and outdoors but at Site 9 little to no connection (R^2=0.01) could be made to street level concentrations with respect to the fluctuations. On the other hand, roof level concentrations taken during run 1 had a higher correlation with indoor concentrations at R^2= 50 %, indicating that this naturally ventilated office, located on the 5^{th} floor of the building, had a greater connection with roof level fluctuations for NO_2 than those which occurred at the ground. The higher number of air changes which acted to increase the concentrations may be due to less time for NO_2 to degrade through

heterogeneous reactions on the walls and carpet of this room. Site 9, which showed some of the highest $PM_{2.5}$ concentrations, also showed low indoor NO_2 concentrations of 3.51 ppb and 9.94 ppb for run 1 and run 2 respectively.

As discussed in previous chapters, Site 6 in particular had very low indoor NO_2 concentrations with working day averages of 6.25 ppb and 2.46 ppb for run 1 and run 2 respectively. The occupants of this site complained of some damp in the room which, coupled with the carpeted floor and large surface area within the room, may have caused a high heterogeneous reaction rate reducing the concentrations to these low levels. This site had no operable windows and with heterogeneous reaction rates as high as suspected, it is hypothesised that air changes at such a site were very low, as occupants of the office rarely left the room apart from lunch time. Low air changes left time for reactions to occur on the surfaces within the room; this office had a large interior surface area for the reactions to occur and due to the reported damp in the walls may have increased reaction rates as discussed previously. Site 6 was significantly below the limit values for both EU and United States for run 2 and marginally above United States standards for run 1 but still below EU standards. The indoor concentrations for run 1 were in the higher range with results similar to Site 9 run 1 while run 2 compared more favourably to other sites, again results were very similar to Site 9. The difference in concentrations between runs may have been due to annual diurnal cycles of $PM_{2.5}$; run 1 saw higher concentrations (16.74 $\mu g\ m^{-3}$) in April compared to run 2 (13.91 $\mu g\ m^{-3}$) conducted in July.

The increase of air changes at Site 9 resulted in reductions in $PM_{2.5}$ but increases in NO_2, as previously discussed, due to heterogeneous reactions. The products of these reactions may be also detrimental to human health. For this reason keeping the window open and allowing a higher number of air changes may be beneficial for the occupants of the office. Both naturally ventilated office sites saw $PM_{2.5}$ concentrations on the higher side compared to the naturally ventilated shops. This may be due to the dust gathering and then being regularly resuspended at Site 6, while at Site 9 the elevator shaft in the room next to the office may have been causing an indoor source. In shops stock would be regularly sold and updated with shelves cleaned reducing the available particulates for resuspension.

Shop (Sites 1, 7 and 8)

The lowest average run concentration for $PM_{2.5}$ at 12.68 μg m^{-3} in naturally ventilated sites was at Site 8. This site was monitored during the summer months, the time when average annual outdoor $PM_{2.5}$ concentrations are lowest. The site was located on a busy road, close to Sites 3 and 4, and saw lower indoor concentrations for both $PM_{2.5}$ and NO_2 for all runs except $PM_{2.5}$ Site 3 run 1. Unlike the naturally ventilated offices this shop had customers entering and leaving the building throughout the day increasing the number of air changes.

Site 1 run 2 saw marginally higher $PM_{2.5}$ concentrations (12.81 μg m^{-3}) than Site 8; this was also monitored during the summer months. The shop door was left open more during run 1; this may have resulted in the higher working hours' concentrations measured at 17.93 μg m^{-3} as air exchange rates increased allowing pollutants to enter the building from the road outside. The NO_2 concentrations in Site 1 showed concentrations of 25.07 ppb for run 1 and 23.34 ppb for run 2, both above the annual mean limit of 21 ppb, in fact this site saw the highest recorded NO_2 concentrations for indoors for a naturally ventilated site during working hours for both run 1 and run 2.

Apart from Site 1, Site 7 is the only other naturally ventilated building which saw average working hours' concentrations above the limit value for NO_2. This site was located on a busy road and while the front door to the shop was generally closed (except when customers entered or left the shop), the back door to the site was often left open promoting a large number of air changes per hour. This back door faced onto a small walled yard where a member of staff smoked next to the open door. $PM_{2.5}$ concentrations were like many of the other naturally ventilated shops above the WHO and United States guide lines for the protection of human health but also above EU limits with an average working hours concentration of 39.93 μg m^{-3}. This high concentration was due to sharp spikes of indoor concentrations, with no associated outdoor peaks, Site 7 was found to have the highest indoor $PM_{2.5}$ concentrations of any site during working hours. Overall, Site 7 did not compare well within its group or when compared to other sites. This was an older building and a shop with some stock that may not have had a high turnover rate therefore an ability of particulates to build it is possible.

Sites 7 and 8 are both naturally ventilated shops located within a few hundred meters of each other, with similar number of customers entering and leaving the shops and are of comparable ages, but produced two very different results with respect to air quality. There are two standout differences between the sites to explain the differences in air quality. Firstly, Site 7 is located directly on a very busy road while Site 8 is located on a street about 15 m off the same main road. Moving the door of the shop, and therefore the main method of air entering the shop, just a few meters resulted in considerably lower outdoor concentrations of NO_2. Both runs were carried out during summer months and Site 7 measured similar concentrations to EPA data whilst Site 8 measured outdoor concentrations significantly higher. The second possible reason for higher concentrations at Site 8 is due to the staff smoking directly outside the backdoor of the shop; smoking is a strong source of both $PM_{2.5}$ and NO_2.

While Site 7 saw the highest $PM_{2.5}$ concentrations Sites 1 saw the highest NO_2 concentrations for any of the naturally ventilated sites. Unlike the naturally ventilated offices these shops showed considerably higher concentrations resulting in greater exposures and therefore worse possible health effects to the staff working in these buildings. Where the shop was moved even a few meters away from the main road, this resulted in significant reductions in concentrations, and while this is obviously not possible to do for existing buildings it can be taken into consideration when an individual is considering different leases on a potential property for a business in the city centre.

Difference in naturally ventilated buildings between working and non-working hours

A larger difference between working and non-working hours for mechanically ventilated buildings compared to naturally ventilated buildings was found during this study. The range of difference for the mechanically ventilated buildings for NO_2 was (-1.64,7) and for $PM_{2.5}$ was (-4.58,4.17). Apart from $PM_{2.5}$ at Site 7 and NO_2 at Site 1 the difference for working hours and non-working hours is minimal, particularly at Sites 6 and 9, see Figure 8.11. These were the two naturally ventilated offices which saw few people enter the monitoring locations and less movement than other naturally ventilated sites. The naturally ventilated shops saw the greatest differences, although at Site 7 the large difference was due to a number of large peaks indoors during one day of

monitoring. These peaks impacted on the average working hour's concentrations and if removed the difference between workings hours.

At Site 1 a source during working hours may have been present due to use of electrostatic equipment used when carrying out work within the computer repairs shop, as concentrations on average were 9.7 ppb higher during working hours than during non-working hours. The indoor concentrations at Site 1 also saw little of the morning peaks outdoors until the shop opened at 10 am indicating a very low number of air changes when the shop was shut.

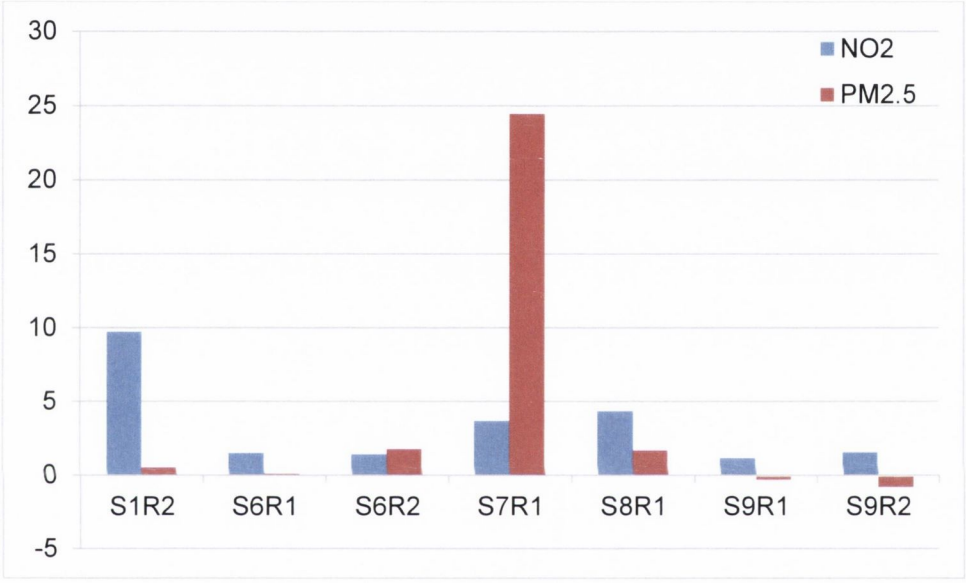


Figure 8.11 Difference between working and non-working hours for naturally ventilated sites

8.3. Comparison of Dublin with other cities with respect to outdoor urban air quality

This section reviews the outdoor air quality in Dublin with concentrations in other cities. While there are many indoor air quality studies, a large proportion of them are residential studies and may not be directly comparable. Chapters 4 and 5 showed the strong influence of outdoor concentrations, particularly for NO_2, on indoor concentrations. Therefore, favourable outdoor concentrations should lead to lower indoor concentrations, and so as there is not as much research of indoor air quality in commercial buildings, using outdoor concentrations as a guide should indicate how Dublin fairs compared to other cities.

8.3.1. $PM_{2.5}$ comparison

A detailed collection of 1083 cities worldwide complied by the Guardian data blog using WHO statistics found that outdoor PM_{10} concentrations in Dublin ranked 208 out of 1083 with average concentrations of 15 μg m^{-3}; the lowest concentrations of 3 μg m^{-3} seen in Whitehorse, Canada, a small city in a mountainous region, and the highest concentrations of 372 μg m^{-3} seen in Ahwaz, Iran (Guardian Data Blog, 2011). Ahwaz suffers from dust and sand storms which would have a significant effect on the concentrations of PM_{10} in the city. The United Kingdom has a similar climate and geography to Ireland and therefore is more appropriate for comparison: Birmingham was found to have concentrations of 16 μg m^{-3}, Aberdeen, Blackpool, Newcastle Upon Tyne and Leicestershire 17 μg m^{-3}, Coventry and Belfast 18 μg m^{-3}, Manchester and 20 μg m^{-3} with the highest average concentrations in the United Kingdom being found for London at 29 μg m^{-3}. For $PM_{2.5}$ there was no available data for Dublin apart from this study, in which the average $PM_{2.5}$ concentration from all the street level outdoor monitoring was 13.15 μg m^{-3}. This is similar to reported average concentrations in London at 13.5 μg m^{-3} (urban background). However, it should be noted that the Dublin data were collected at urban roadside locations and therefore probably significantly higher than the urban *background* concentrations. In Berlin where an urban background and an urban traffic site were utilised, average concentrations were 20.8 μg m^{-3}. Athens found concentrations of 27.4 μg m^{-3} when a mixture of urban background and traffic sites were monitored. Lisbon had lower concentrations than Dublin of 11.9 μg m^{-3} again using one urban background and one urban traffic monitoring station, and Madrid found the same $PM_{2.5}$ concentrations as Dublin using a mixture of monitoring stations including; urban background, urban traffic and suburban background. Gothenburg, Sweden was found to have urban traffic concentrations of 14.1 μg m^{-3} similar to Dublin although the city only has a population roughly half the size.

8.3.2. NO_2 comparison

EEA reports show that Ireland has relatively low NO_2 concentrations in general with Dublin concentrations in the range of 16 – 21 ppb on average, whilst the rest of the county experiencing concentrations below this range, see Figure 8.12.

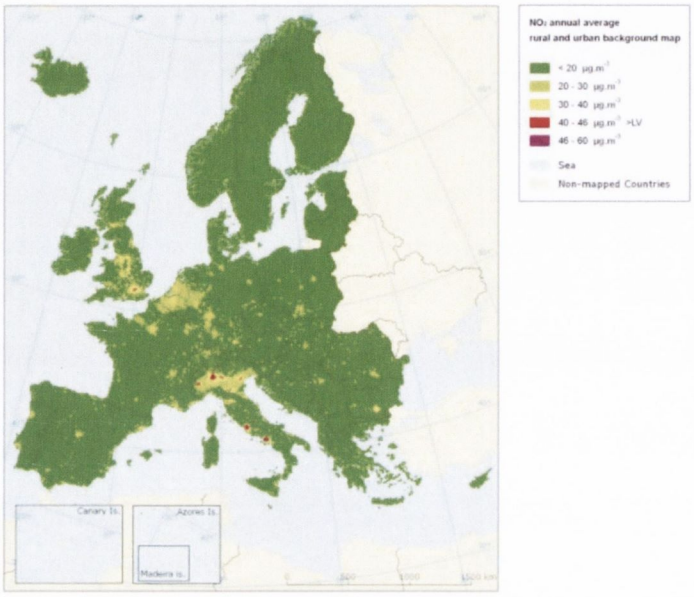


Figure 8.12 NO_2 concentrations across Europe (Guerreiro, 2010)

Roadside ground level concentrations at the 10 sites had an average concentration at 22.36 ppb and a max 1 hour concentration of 79.55 ppb in heavily trafficked areas of Dublin City centre. In comparison, roadside concentrations at Marylebone Road, London were found to have an average of 32 ppb but ranged up to 110 ppb (Carslaw, 2005). Another English study found background concentrations averaging at 15 – 20 ppb in Rothamsted, an area roughly 30 miles north of London (Hargreaves et al., 2000). Gothenburg, Sweden which was found to have similar $PM_{2.5}$ concentrations showed urban NO_2 co ncentrations ranging from 5 to 45 ppb (Ekberg, 1995). Urban NO_2 values in Hong Kong ranged from 20 – 80 ppb in non-smoking areas surrounding commercial buildings (Lee et al., 1999). Osaka city, Japan found average winter concentrations of NO_2 of 53 ppb and summer time concentrations of 49 ppb for urban monitoring, both significantly higher than the concentrations for Dublin. In 2008 43.2 ppb was found to be the European

average for trafficked sites. This is almost double the average roadside concentration found during this study of Dublin (Guerreiro, 2010).

1 hour maximum concentrations at urban trafficked site in Madrid found 327 ppb, with a kerbside monitoring station in Camden, London showing 1 hour max concentrations of 121 ppb over a 3 year period, and an average concentration of 39 ppb (Guerreiro, 2010). These are significantly higher than the max 1 hour concentrations of 79.55 ppb recorded by this study in Dublin.

Dublin compared well to other cities of comparable size, with lower average concentrations although the average concentration was just above the legal limit of 21 ppb. It should be noted that monitoring for such legislative limits is often not carried out directly at the roadside for the safety of monitors. For instance in Dublin monitoring at one of the main urban EPA sites in Dublin is carried out 20 m back from the road. For monitoring the air quality entering the buildings in this study, it was necessary to carry out monitoring at the roadside but for maybe other studies (especially, long term studies), monitors would have to be further away from the roadside.

The greatest influence on the quality of indoor air for the vast majority of buildings is the quality of outdoor air. Once outdoor air is at a standard which protects human health, the implication is that indoor air is more than likely close to this level. For most sites any indoor concentrations that were above outdoor concentrations were only slightly higher (e.g. a few ppb or $\mu g\ m^{-3}$) and high indoor concentrations were usually a result of high outdoor concentrations. Indoor air quality in cities with higher outdoor air pollution (for example, London and Hong Kong) reported much greater concentrations than those recorded for this work (Field et al., 1992, Kukadia and Palmer, 1998).

8.4. Suggestion of mitigation measures

The purpose of mitigation is to remove the ill effects of air pollution on the occupants of commercial buildings. Carrying out such measures can be also financially beneficial to the employer; for example it has been estimated that between $12 billion to $125 billion could be saved per year in the United States due to improved productivity. Other work has shown that even small decreases in pollutant concentrations can improve the mental state of the workforce and reduce environmental dissatisfaction (Fisk and Rosenfeld, 1997, Mendell et al.,

2002). In the UK it is estimated that £24 billion can be saved by 2050 by committing to a low carbon economy and optimising climate change policy to account for air quality (DEFRA, 2010).

This section details several methods which can be utilised in order to reduce concentrations of NO_2 and $PM_{2.5}$ within the workplace.One of the main sources of NO_2 and $PM_{2.5}$ in residential buildings is cooking on a gas stove (Namieśnik et al., 1992). Fortunately, commercial buildings such as shops and offices rarely have such appliances and therefore this major source of air quality issue is significantly reduced. For buildings which contain a canteen for staff, it is recommended that electric cookers are used in preference to gas and to ensure that the kitchen contains commercial extract fans in order to remove steam and particulates generated during cooking. If changing to an electric cooker is not an option other mitigation methods to reduce pollutant concentrations could be considered.

Filters in HVACs are used to remove pollutants but as windows, doors and cracks in the buildings also allow air into the building without filtration of incoming air, the efficiency of the filtration system can be diminished. One method to clean air in naturally ventilated or mechanically ventilated buildings where the infiltration air exchange rate is high, or an indoor source such as a gas cooker is present (e.g. Site 2), is the use of portable air cleaners. While many portable air cleaners may not be capable of removing contaminants from a building, some of which are fitted with a HEPA filter can significantly reduce contaminants (Hacker and Sparrow, 2005, Shaughnessy et al., 1994, Skulberg et al., 2005, Ward et al., 2005). For example, work carried out in a Californian school found that portable air cleaners using a MERV 16 filter reduced $PM_{2.5}$ by 75 % independent of the HVAC system (SCAQMD, 2009). Such apparatus would be ideal in naturally ventilated sites which in this study saw higher concentrations of $PM_{2.5}$ as well as at Site 4 which saw high indoor $PM_{2.5}$ concentrations above even those monitored at kerbside of a busy road.

Normal filtration units have been found to remove minimal NO_2 but chemical filtration, or sorption, can be used in order to reduce such gaseous pollutants concentrations at sites such as Site 2 which have gas cookers, or Site 10 which simply had high concentrations infiltrating in from outdoors. An activated carbon bed alone in conjunction with a HEPA portable air cleaner was found to

be able to remove 50 % NO_2 (Shaughnessy et al., 1994). 50- 70 % of NO_2 can be removed using a combination of charcoal, aluminium oxide and potassium permanganate (Partti-Pellinen K, 2000), which, for example would reduce indoor concentrations at Site 10 from 25 ppb down to concentrations in the range of 7-10 ppb. The sorption filtration method can also reduce other gaseous pollutants, for example activated alumina impregnated with potassium permanganate showed good VOC removal efficiencies. Charcoal sorbent which is used for NO_2 was also found to remove 52 % of benzene and 15 % of other VOCs (SCAQMD, 2009). VOCs are common with sites which have recently been painted or new furniture installed. Some companies such as Google are now implementing a policy where all new furniture and paints must not emit VOC and formaldehyde via a healthy materials program as part of their sustainable pursuit policy. Activated carbon which showed good NO_2 removal efficiencies however, has been shown not to remove VOSs such as aldehydes and dichloromethane. Therefore, a full round of monitoring for all pollutants should be carried out in order to assess the best sorbent material for a specific site, or if the use of activated carbon is chosen a policy such as Google's should be implemented when purchasing new products (Shaughnessy and Sextro, 2006). Changing of these sorption filters should be carried out frequently as pollutants can be re-emit or emit reaction products from the matter collected on the filter (Daisey and Hodgson, 1989, Fisk, 2008).

Research has also looked at titanium dioxide (TiO_2) based photocatalysts in order to reduce NO_2 both indoors and outdoors. In the presence of UV light (wavelength <387.5 nm), TiO_2 generates hydroxyl radicals ($OH^{\cdot}$) which are strong oxidizing agents. These can degrade or oxidize the pollutants into more environmentally friendly products (Yu, 2002). TiO_2 can be used to chemically reduce concentrations of NO_2; for example Japan paving blocks containing TiO_2 reduced NO_x by 45 mg per m^2 (for 12 hours at a wind speed of 0.036 m s^{-1} and UV intensity of 0.6 mW cm^{-2}). As well as paving, indoor components of buildings such as paints and ceiling panels containing a TiO_2 are now being marketed due to their self-cleaning ability. Mechanically ventilated buildings often use ceiling panels to hide ducting within rooms, and as these buildings also showed the highest NO_2 concentrations in this study. Hence, the use of TiO_2 panels instead of the regular ones could be considered. For instance Site 2 was a building which used false panels and also had high concentrations of

NO_2 due to its location next to a busy road with buses pulling up outside the door, as well as the gas stove located in the canteen.

A major factor with respect to pollutant concentrations entering a building is proximity to a road. This was seen with the difference between Sites 7 and 8 where Site 8 experienced greatly reduced concentrations as it was located just off the same main road that Site 8 was on. As moving buildings away from the roads is not a realistic measure for many shops and offices (unless at a planning stage of town development or prior to choosing a premises) as they require being located in busy central commercial locations, other methodologies must be put in place in order to reduce pollutant concentrations indoors.

One of the main ways used in the buildings monitored to reduce pollutant concentration is via a mechanical ventilation system. Use of filtration within these units can significantly reduce particle concentrations provided the air intakes are placed in the correct location - unlike at Sites 3 and 4 where concentrations at air intake levels were similar or higher than street level. The most common rating system for filters is known as the MERV or Minimum Efficiency Reporting Value although a European efficiency guide is also available (ASHRAE, 2007, Environmental Protection Agency, 2009). The rating system is as follows:

- MERV 1 to 4 or G1/G2 (European efficiency guide); remove only a portion of the largest particles in the airstream that passes through the filter.
- MERV 5 to 8 or G3/G4; filters are medium efficiency filters that remove some additional types of particles such as mould spores and cat and dog dander, but do not remove the finer particles produced on roadways.
- MERV 9 to 12 or F5/F6; filters begin to remove particles smaller than $PM_{2.5}$
- MERV 13 to 16 or F7/F8; filters are rated to remove a portion of the ultrafine and submicron particles emitted from vehicles. F7 filters have a average efficiency of 80-90% removal. This type of filter is now the minimum required by EN779:2012 update however a F9 filter which provides 95% removal is advised.

It should be noted that the filter efficiency provided by manufactures is often the maximum efficiency that a filter can achieve. For instance while F7 filters claim 90% removal, they must only achieve a minimum efficiency of 35% over the filters lifecycle, while F8 filters must achieve a minimum efficiency of 55%.

For commercial buildings aiming to ensure the health of staff, which in turn can lead to better productivity, HEPA (high efficiency particle air) filters are equivalent to MERV 17 – 20 removing 99.75 % to 99.99 % of particles less than 0.3 microns. Fisk et al. (2000) found that the use of higher efficiency filters can reduce submicron particles by 90 % more than normal filters.

Noh and Hwang (2010) found that MERV 11 was necessary in order to remove contaminants from buildings during a modelling study. MERV 16 or F8 panel filters were found to reduce particles by 90 % in buildings using HVACS. F8 filters were in use at Sites 3 and 4, and even with these filters, concentrations indoors at both sites exceeded ventilation intake concentrations at certain points of the day. For working hours at Site 3 only an 11 % reduction between street level and roof level concentrations was found, while at Site 4 roof level and street level concentrations were lower than indoor concentrations. This indicated a strong indoor source as well as poor filtration ability of these F8 filters not matching up to what the filter standards suggest.

While the removal rate of a filter is important to consider, the user most also look at the filter material. The standard synthetic filters which are purchased by the 2/3 to ¾ of companies in the UK, due to the lower cost and lack of understand the differences in product abilities. The synthetic filter uses electrostatic charge to aid in the removal particles, this charge however loses its electrostatic charge rapidly after only 1 month. This loss radically reduces the filter to only 10% of its removal capacity. Use of the marginally more expensive glass microfibre filters which use a barrier removal method rather than the electrostatic charge method ensures that the removal ability of the filter is maintained throughout the lifetime of the filter.

TiO_2 which was discussed above regarding paints, paving etc can also be included in the filtration process with 500,000 filters being sold in Japan annually in order to reduce the concentration of NO_2 indoors (Yu, 2002). This

can help reduce NO_2 and other gaseous concentrations which the filtration process cannot.

Moving operable windows and doors away from the side of the building where the greatest source is present is also a technique that can be used to reduce the infiltration of pollutants indoors. While reducing the number of windows and openings may marginally reduce indoor concentrations it is important not to create a stagnant environment with little or no air changes. This can lead to issues such as mould growth within the building causing other issues in the building. Irish building regulations state a minimum of 0.35 air changes per hour are needed if a building is naturally ventilated , this reduces to 0.15 air changes per hour for infiltration in mechanically ventilated buildings(Energy Research Group(UCD), 2008).

Use of parked cars, low boundary walls, vegetation as well as other barriers can reduce pollutants infiltration into buildings at a street level (Gallagher et al., 2011, McNabola et al., 2008). For instance, the use of sound walls have been shown to reduce pollutants by up to 50 % when placed between building entrances and busy roadways (Ning et al., 2010, Baldauf et al., 2008, Bowker et al., 2007). These could be implemented at many of sites, including Site 1 which has a wider footpath. Implementing a barrier such is seen at many restaurants to create an outdoor seating area around shop or office entrances could act as a barrier to particulate pollutants. Positioning of these must be carefully considered as the potential of a pollutant trap with higher levels of pollutants occurring behind these walls may also occur, or for them to become smoking areas for staff. Use of these in businesses with a small garden or yard at the front, like at Site 9, as an alternative to railings could potentially reduce the amount of pollutants on the building façade. Vegetation such as trees have been shown to be an effective filtration method for particles and may absorb gaseous pollutants although it may obviously be difficult to plant these in cities unless potted plants are used (Baldauf et al., 2008, Nowak et al., 2006, Pardyjak et al., 2008). Vegetation barriers may not be applicable in urban areas as studies show that the density of the vegetation is important to its effectiveness (Hagler et al., 2012). However, some vegetation can also trigger asthma and allergies, and some emit reactive VOCs that contribute to the formation of ozone and therefore the conversion of NO to NO_2.

Offices and shops should be aware of any local sources of air pollutants (as well as traffic), before deciding on the placement of air intakes. The location of the air intake for the ventilation unit is important for the quality of the indoor air; placement near air exhausts, sewers or rubbish bins deteriorates the quality of indoor air. This many not have been fully considered at Sites 3 and 4 but the greater reductions between street and ground level at Site 2 shows better design (Turiel et al., 1983, Morawska et al., 2009). Relocation of poorly placed ventilation intakes such as was seen at Site 3 and 4 can give up to 55% improvements on the quality of the air brought into the system (Morawska et al., 2009). The issue at these two sites is that a train line runs along one side of the building while a busy road run along the other. This would have left ventilation system designers at the sites with difficult decisions. From reviewing concentrations at these sites, while not ideal, locating the ventilation intake away from the road and closer to the train line produces greater reductions in concentrations with respect to NO_2 and leaves $PM_{2.5}$ concentrations at levels similar to at ground level. Smoking areas must also be considered with respect to ventilation intakes. These should not be placed close to or upwind of mechanical ventilation or natural air intakes for buildings. When windows are being opened, choosing ones at the back of a building away from the roadside may reduce pollutant concentrations. Ideally, monitoring of the site prior to ventilation design would be beneficial, as this may indicate the most efficient placement of the air intake.

Another method for the mitigation of pollutants within buildings is use of a BMS (building management system) to control air intake and ensure that air changes are kept to a minimum at times of high outdoor concentrations. Use of high ventilation rates overnight when air pollutant concentrations are at a minimum outdoors, and then significantly reducing the air exchange rate when concentrations rise with morning rush hour, can keep indoor pollutant rates to a minimum (Green et al., 2001). If ventilation systems were turned on at Site 4 and 5 at 11 am rather than 8 am and 8.30 am respectively, this would keep concentrations indoors lower for at least the initial part of the day when concentrations outdoors are high due to morning rush hour. An early morning purge of stale air in the building by turning the ventilation system on prior to dawn and morning rush hour combined with natural ventilation ensure that enough fresh air was available for staff during this morning non ventilated

period. The same could be done for evening rush hour, although these peaks were usually not as large as those in the morning.

8.5. Conclusions

The only exceedances of $PM_{2.5}$ concentrations above EU legal limits indoors was due to high peaks during Site 4 run 2 and at Site 7. Provided these peaks were a once-off or irregular occurrence, it is unlikely that the annual average for $PM_{2.5}$ would be above the 25 $\mu g\ m^{-3}$ limit. Three sites monitored for this study showed runs under the recommended WHO limit value; Site 3, run 1, Site 5 and Site 10 run 2. These were all mechanically ventilated office buildings and either constructed or reconditioned in the past 10 years. Achieving this limit value recommended by the WHO will result in a better working environment for staff and not cause as significant impact on their health. Sites 3 and 10 both showed high NO_2 concentrations indoors for at least one run but Site 5 also showed low NO_2 indoor concentrations 6 ppb below the limit value. Due to its favourable results for both pollutants Site 5 can therefore be considered the healthiest overall building to work in. Other sites which showed lower concentrations for one of the pollutants often reported high values of the other, e.g. Site 9.

A far greater number of sites exceeded the annual mean limit value of 21 ppb for NO_2 when working hours are averaged. These limits values are averaged using 24 hour values over the full year, so while the working hours value was what building occupants were exposed to the mean values did not account for the lower values seen overnight. Once overnight values are taken into consideration only two sites exceed the annual mean limit, Site 2 run 2 and Site 4 run 2. The WHO state that there is a lack of information regarding the basis for choosing an annual mean limit guideline for NO_2 through any direct toxic effect but recommended concentrations are the same as EU limit values. Recent indoor studies have provided evidence of effects on respiratory symptoms among infants at NO_2 concentrations below 21 ppb (World Health Organization, 2005). Site 2 run 2, one of the two sites which experienced average concentrations above the recommended level, contains a gas stove which are known as strong NO_2 indoor sources. These values were collected in July when NO_2 concentrations are generally lower, although it should be noted that at this time both EPA and monitored data showed outdoor concentrations

above the annual mean value for the year(although the indoor concentrations still remained 4 ppb higher than the outdoor concentration at that time).

Naturally ventilated sites showed two different behaviours for $PM_{2.5}$ and NO_2. The lowest indoor concentrations occurred in the two naturally ventilated offices, while naturally ventilated sites on the whole were found to have higher $PM_{2.5}$ concentrations than mechanically ventilated sites. The older ventilation system seen at Site 2 showed high indoor $PM_{2.5}$ concentrations compared to the sites with the newer systems installed.

Dublin compared well to other European cities when comparing the kerbside concentrations collected during the monitoring of the 10 sites. Roadside concentrations in Goteborg, Sweden showed similar concentrations to Dublin while urban background concentrations also showed similar concentrations. The annual mean of all ground level concentrations for Dublin was found to be 13.15 $\mu g\ m^{-3}$ which is below both the EU and United States annual mean limits, but above the recommended limit by the WHO. NO_2 also compared favourably with other cities although the mean roadside value was slightly above the EU limit. It should be noted the monitoring locations were kerbside rather than set back from the road as with EPA monitoring. If the monitors had been moved back to be more in line with the standard inner city air monitoring locations, lower concentrations would be expected. However, the European average for trafficked sites is 43.2 ppb and the average kerbside concentration monitors during this study was 22.36 ppb, again similar to background concentrations in suburbs of London.

Finally, mitigation measures such as use of portable filtration units containing a sorbent material have been discussed and are one of the many positive strategies building occupants can implement in order to reduce indoor concentrations. Changes to both the natural and mechanical ventilation strategies can also be used in order to help reduce indoor pollutant concentrations. Site 4, for instance, saw higher concentrations of pollutants at the ventilation intake than at kerbside. Hence, the position of the ventilation intake needs to be carefully considered in building design. Equally, the position of windows and whether they can be opened should be considered with respect to indoor air quality, particularly in naturally ventilated buildings. Use of mitigation measures such as the ones listed above will bring long term benefits

to both health and productivity to staff which in turn will have financial benefits for the company employing them.

9. Conclusions

9.1. Introduction

This chapter will discuss and make final conclusions of the work carried out during this research, combining the concluding points from previous chapters in order to summarise the comprehensive behaviour patterns of the studied pollutants under various sub headings.

9.2. $PM_{2.5}$ and NO_2 air quality

The pollutants studied in this research were documented as the two of most concern to Dublin City Council in the 2008-2012 Dublin Regional Air Quality Management Plan report. This was reiterated in the most recent EPA 'Air Quality in Ireland Report' where it was stated that they remain a concern. Air quality data gathered by DCC in 2011 indicate an increase on 2010 concentrations for certain urban road-site monitoring stations for $PM_{2.5,}$ but reductions in NO_2 concentrations. This study found an average of all $PM_{2.5}$ roadside concentrations of 13.15 $\mu g\ m^{-3}$ and all NO_2 concentrations of 22.36 ppb, with max 1 hour concentrations of 79.55 ppb for NO_2. The average roadside working hour's values were higher for both $PM_{2.5}$ and NO_2 at 19.13 $\mu g\ m^{-3}$ and 24.59 ppb.

$PM_{2.5}$ concentrations tended to have a large amount of noise around a mean value, showing a slight diurnal pattern between day and night outdoors, but with little of this diurnal pattern indoors. Regressions of outdoor data to predict indoor concentrations showed R^2 values that ranged from 0 to 11.4 %, with an average of 3.25 %, indicating that the fluctuations indoors and outdoors had little connection to each other. Equally, this shows time lags between respective indoor to outdoor $PM_{2.5}$ profiles had a much greater amount of noise than NO_2, with only one building (Site 1 run 2) showing a strong daytime lag of 0 to 15 minutes consistently over the 4 days of monitoring. While other sites indicated lags on certain days the length and cross correlation value of these lags varied greatly.

NO_2 on the other hand showed clear diurnal patterns in time series plots for both indoors and outdoors, with considerably higher correlations between the two than $PM_{2.5}$ (R^2 in the range of 0.1 to 79.5 % and averaging at 43.72 %). NO_2 also had clear lag

times of up to an hour between outdoor and the linked indoor fluctuations within the data.

Indoor/outdoor ratios of both pollutants, but particularly NO_2, increased significantly overnight as outdoor concentrations reduced to a much greater extent than indoors. These increased ratios were muted slightly for non-working hours due to sharp peaks seen for NO_2 in the early morning outdoors. A baseline concentration was seen in the mechanically ventilated buildings below which concentrations indoors did not drop; this was in the range of 10-12 ppb for all mechanically ventilated sites (with the exception of Site 2 which showed a very strong relationship between indoors and outdoors throughout the night). Such a base-line was not picked up for the naturally ventilated buildings with average overnight concentrations of NO_2 ranging from 0.5 to 12 ppb.

The greatest influence on the quality of indoor air for the majority of buildings was the quality of outdoor air. Hence, once outdoor air is at a standard which protects human health the implication is that indoor air will more than likely be close to this level. EU and Irish air quality legislation only applies to outdoor pollutant concentrations, but is set at levels which are considered acceptable for the protection of human health. Therefore, when evaluating the concentrations indoors it would seem to be logical to use the same limits for comparative purposes. The only exceedances of $PM_{2.5}$ concentrations above EU legal limits indoors were due to high peaks at Site 4 (run 2) and at Site 7, one a mechanically ventilated office, the other a naturally ventilated shop. Provided these peaks were a once off or irregular occurrence, it is unlikely that the annual average for $PM_{2.5}$ would be above the 25 $\mu g\ m^{-3}$ annual mean EU limit. However, the WHO sets a 24 hour limit of 25 $\mu g\ m^{-3}$ for the protection of human health (World Health Organization, 2005) which would have been considered to be broken at both sites.

The WHO state that there is a lack of information regarding the basis for choosing an annual mean limit guideline for NO_2, but recommended concentrations are the same as EU limit values (World Health Organization, 2005). While only 2 sites (Site 2 run 2 and Site 4 run 2) exceeded the limit value of 21 ppb for NO_2 if the entire data set is averaged, a far greater number of sites exceeded it when only working hours were considered. These limit values are averaged using 24 hour values over the full year, so while the working hours value was what building occupants were exposed to, the mean values did not account for the lower values seen overnight.

9.3. Mechanically ventilated versus naturally ventilated

Naturally ventilated buildings showed higher $PM_{2.5}$ concentrations during working hours compared to mechanically ventilated buildings, with the exception of the mechanically ventilated Site 4. At Site 4 $PM_{2.5}$ concentrations at the mechanical ventilation systems air intake were on average twice that of ground level for the entire run, and 1.5 times the street level during working hours. The consequence of this was high indoor concentrations of $PM_{2.5}$ as more polluted air was being drawn into the ventilation system. Site 3 also measured concentrations at the ventilation system air intake, at levels which were not as expected. These concentrations showed only a 3 % reduction of $PM_{2.5}$ concentrations during working hours between street and roof level. This is significantly less than the reported 73-80 % reductions at 20 m height difference, only a few meters higher than the location of the air intakes at this site (Wu et al., 2002, Väkevä et al., 1999). The near-by train line is a major suspected source of $PM_{2.5}$ due to resuspension and combustion from the 91 trains which pass daily using diesel engines. Conversely, Site 2 displayed 50 % reductions for $PM_{2.5}$ for working hours between ground and air intake level. This greater reduction may be attributed to the improved location of the air intake which used an upper part of the building facade as a barrier between it and the busy road below.

While naturally ventilated buildings showed higher $PM_{2.5}$ concentrations, NO_2 concentrations at naturally ventilated offices were found to be significantly reduced compared to outdoor levels. Results showed that the naturally ventilated office buildings studied for this research provided a greater reduction in NO_2 compared to mechanically ventilated, with Site 6 being a prime example of this. The two naturally ventilated offices monitored had a particularly low I/O ratio for NO_2 due to suspected heterogeneous reactions on surfaces acting as sinks to indoor NO_2. At Site 9, the indoor concentrations increased in line with higher air changes per hour which were increased by opening a window within the room. This gave less time for surface reactions to occur and so concentrations increased. The number of air changes is usually low in these sites as these two offices have a low occupancy rate and the door remains shut for most of the day, unlike in the shops where customers are frequently opening and closing the door allowing a fresh influx of air. The information gathered from NO/NO_2 ratios further signifies a sink indoors at these two naturally ventilated offices, due to the ratios being notably reduced compared to outdoors. It is suspected that damp conditions at Site 6, as reported by occupants in this office, enhanced heterogeneous reaction rates.

Certain mechanically ventilated sites showed a greater influence with respect to ground level air pollutant concentrations than roof level values, For example, for NO_2 at Site 10, there was a greater correlation between indoor and ground level concentrations compared to the air intake at roof level. Equally, at Site 3, NO_2 found high correlations between both roof level and ground level intakes for predicting target data, although the I/O ratio was closer to 1 for ground level outdoor monitoring. Sites 4 and 10 also saw I/O ratios close to 1 for street level concentrations of NO_2 while 2 further mechanically ventilated sites. However, at Site 10 a higher R^2 value for $PM_{2.5}$ was found when outdoor concentrations were taken at the air intake rather than street level.

9.4. Outcomes of two modelling techniques

Two modelling techniques were utilised during this research; firstly, a coupled regression and mass balance technique and secondly artificial neural networks. Both modelling techniques used outdoor pollutant concentrations combined with a variety of other parameters in order to predict indoor air quality. The use of artificial neural networks showed potential if an extended data set of previous monitoring had been carried out at the building however if this was not the case the model failed to produce realistic exposure of its occupants to $PM_{2.5}$ and NO_2. The use of regression and mass balance as discussed in Chapter 6 proved useful for predicting NO_2 concentrations indoors using building characteristics.

The Artificial Neural Networks (ANNs) model predictions showed stronger predictive abilities for indoor NO_2 concentration fluctuations when compared to $PM_{2.5}$ using outdoor concentrations, with meteorological variables. This is due to the typical NO_2 diurnal pattern which is affected by meteorological variables such as global radiation to a much greater extent than $PM_{2.5}$.

Use of the forward predictions for NO_2 showed an ability of the neural networks model to accurately predict mean exposure values as long as similar meteorological conditions occurred to the data set that the model was trained upon. If longer monitoring periods, which covered a variety of meteorological conditions and indoor/outdoor relationships, were used in order to initially train the network errors may be reduced. This was proven at Site 4 where the pressure changed altering the indoor/outdoor relationship of NO_2 at the end of the training run. When a similar pressure was seen during run 2, the network adjusted the indoor/outdoor relationship suitably. The ANN also showed an ability to adapt to such variations in the relationship between indoor and outdoor as shown at Site 5 where there are two notably different

relationships between outdoor and indoor concentrations. Unfortunately, it was found that the ANN could not use a network trained using data from one site to predict indoor concentrations at another site. This was due to the differences in various buildings relationships between indoor and outdoor concentrations. Hence, its use as a predictive model is very limited and only applicable to sites which have gathered detailed indoor and outdoor air quality data previously.

The combined regression and mass balance model strength is that it only uses information that is available to the average occupant of such buildings rather than expensive modelling packages not accessible by the general public. Initial interviews with building occupants showed an enthusiasm to learn about their air pollution exposure but a lack of willingness to have any disruption to the work. Hence, using a technique such as the one developed here would allow estimates of indoor air quality to be made using the outdoor air quality monitoring results, and general information about the building which the staff should be able to identify relatively easily. The model works in two stages, initially regression of known outdoor concentrations and indoor concentrations facilitated the calculation of a variety of source and infiltration factors for the various buildings types monitored in this study. This information could then be imputed into a recursive mass balance equation which took account building features such as opening hours, ventilation strategy and deposition rates. The output was an hourly change in indoor air quality, which proved to be accurate for NO_2 within the 95 % CI for 2 sample T-tests at the majority of sites and also an average of 52.2 % (range 20-72.2 %) of fluctuations in the data. The model showed even better predictive abilities of up to 78.1 % for NO_2 when indoor monitoring data was available for a number of days which provided the model with more accurate f_{inf} and source values. However, the model was unable to account for short-term fluctuations in $PM_{2.5}$, with R^2 values which range from 0.9-31.4 %, averaging at 8.52 %. This is because the fluctuations do not correlate with outdoors and therefore the model cannot account for them. The short-coming of this technique is it does not account for the influence of meteorological variations on buildings although this could be built into the model in future to improve estimates.

The generalised model has only been fully developed for NO_2 due to a lack of available data for $PM_{2.5}$. However, the WHO has previously stated that NO_2 is strongly correlated with other toxic traffic related pollutants, such as $PM_{2.5}$, benzene and toluene. Therefore, NO_2 could be used as a surrogate to indicate concentrations of various other pollutants. In addition achieving guideline concentrations for NO_2 may result in

public health benefits that exceed those anticipated in estimates of NO_2 toxicity (World Health Organization, 2005).

9.5. Overview

The four main objectives of this research were discussed in Chapter 1, all have been met. The first two aims involved choosing the 10 commercial buildings which represented buildings in Dublin City centre and then developing a methodology monitor. This was achieved by monitoring 5 different mechanically ventilated and 5 naturally ventilated buildings, a selection of shops, offices and other types of commercial buildings. The methodology included how to choose, monitor and correct monitored data collected at these buildings, as discussed in Chapter 3. The third objective was the synthesis of the monitoring data and detailed analysis; this was contained within Chapters 4, 5 and 8. Collected data was reviewed through several methods such as; I/O ratios cross correlations and NO/NO_2 ratios, the results of which were discussed throughout the thesis with conclusions made above. The final aim was to develop a predictive model for the indoor exposure of occupant's commercial buildings in urban centres using freely available EPA air quality data. This model needed to be simple to use, as it was anticipated that the potential user would have no prior knowledge of air quality. This objective was met by the development of the generalised recursive mass balance model as discussed in Chapter 6 which combined user inputs of building characteristics combined with EPA monitoring data to estimate the indoor exposure.

9.6. Recommendations for further research

- The robustness of the relative humidity correction for the Irish climate needs further investigation. This correction showed high reductions outdoors overnight when relative humidity increased above the 90% limit each night. These reductions increased the I/O ratios significantly as no correction was applied indoors as stipulated in previous research (Ramachandran et al., 2003). Such reductions were also seen during working hours, i.e. Site 4 run 2, when considerable reductions outdoors were found due to high relative humidity, but again indoor relative humidity was not adjusted. Further investigation into the type (i.e. condensing or non-condensing) of relative humidity and its effect on the nephelometer monitoring device and hence correction factor as well as its effect on indoor environments would be beneficial.

- Some long term monitoring (i.e. over a year) of indoor and outdoor air quality should be carried at commercial sites in order to investigate and then account for seasonal variability. Urban and rural seasonal variations can show different patterns, this combined with seasonal pressure variations effecting the I/O ratio should be explored in greater detail.

- Further investigations on the effect of air intake location and possible alternatives for sites where outdoor sources have high influence at roof level. This could include testing at various locations of building in order to find the ideal location if a retrofit of a ventilation system was to take place, and use of barriers in order to disperse the highest concentrations of pollutants and reduce the amount entering the ventilation system.

- Finally, there should be more research with the aim to extend the combined mass balance and regression model to include the influence of meteorological influences on the indoor/outdoor relationship. The effects of pressure changes or temperature differentials can influence the number of air changes, and therefore may have a bearing on the I/O ratio. Including the influence of meteorological changes into the mass balance model would improve the model ability to predict fluctuations in the data further.

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Appendix A. Lag Time Plots for Non-Working Hours

Appendix A is a continuation of the work conducted in Chapter 5.3. Detailed analysis of the lag times during non-working hours in discussed.

Non-working hours' time lag for NO2

Calculations of XCORR were carried out for non-working hours to see if, and how, they differ from during the working day while the buildings are open to staff and customers. A variation compared to the working hour lags would be expected as the buildings are shut with no opening or closing of doors or windows for several hours. The calculations are conducted in two different time sections, the first is from close of business to midnight and the second is from 12.01 am to the opening of the business. This was done to see if behaviours differ at the start of the night when concentrations are high outdoors and indoors, as closing time coincides with evening rush hour and the second section was to review the behaviours when the sharp morning peak occurs in NO_2 and the effect of this on indoor concentrations. Table A. 1 contains the first half of the night while Table A. 2 shows results from the second half. As with the working hours data these data sets have been prepared for individual nights.

Table A. 1 Close of shop to 12 am average lags and XCORR

	Day 1			Day 2		
	XCORR 0 lag	**Optimum lag (hours)**	**XCORR optimum lag**	**XCORR 0 lag**	**Optimum lag (hours)**	**XCORR optimum lag**
S1R2	0.34	-0.75	-0.44	-0.09	-2.25	0.48
S2R2	0.16	1.75	-0.7	0.97	0.0	0.97
S3R1	0.46	0.0	0.46	0.75	0.0	0.75
S3R2	0.76	0.0	0.76	0.48	0.0	0.48
S4R1	0.4	-0.75	0.7	0.9	0.0	0.9
S4R2	-0.04	-0.75	-0.27	-0.03	1.5	0.72
S5	-0.66	0.25	-0.71	0.88	0.0	0.88
S6R1	-0.04	2.5	0.25	-0.43	0.0	-0.43
S6R2	-0.5	0.0	-0.5	0.38	0.5	0.72
S7	0.61	0.0	0.61	0.83	0.0	0.83
S8	0.28	1.5	0.57	-0.4	1.0	-0.43
S9R1	-0.46	0.5	-0.5	-0.72	0.5	-0.77
S9R2	-0.65	0.0	-0.65	-0.5	1.0	-0.68
S10R1	0.62	-0.25	0.68	0.44	-0.5	0.63
S10R2	0.67	0.25	0.69	0.54	0.0	0.54
	Day 3			**Average of 3 days**		
	XCORR 0 lag	**Optimum lag (hours)**	**XCORR optimum lag**	**XCORR 0 lag**	**Optimum lag (hours)**	**XCORR optimum lag**
S1R2	0.82	0.0	0.82	0.35	0.0 to -2.25	0.28
S2R2				0.57	0.0 to 1.75	0.14
S3R1				0.61	0.0	0.61
S3R2	0.61	0.0	0.61	0.62	0.0	0.62
S4R1	0.9	0.0	0.9	0.73	0.0 to -0.75	0.83
S4R2	-0.54	0.75	-0.68	-0.21	1.5 to -1.5	0.12
S5	0.12	0.0	0.12	0.11	0.0 to 0.25	0.09
S6R1	0.26	-1.25	0.56	-0.07	0.0 to – 1.25	0.13
S6R2	-0.18	0.25	-0.41	-0.1	0.0 to 0.5	-0.06
S7	-0.04	0.0	-0.04	0.47	0.0	0.47
S8	0.47	0.0	0.47	0.12	0.0 to 1.5	0.21
S9R1	0.62	0.0	0.62	-0.19	0.0 to 0.5	-0.22
S9R2	0.13	-1.5	-0.47	-0.34	0.0 to -1.5	-0.6
S10R1	-0.12	-1.5	-0.43	0.31	-0.25 to - 1.5	0.29
S10R2	-0.04	-2.5	-0.48	0.39	0.0 to -2.5	0.25

Table A. 212 am to open of shop average lags and XCORR

	Day 1			Day 2		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.84	0.0	0.84	0.69	0.0	0.69
S2R2	0.84	-0.25	0.85	0.98	0.0	0.98
S3R1	0.72	0.0	0.72	0.63	-0.5	0.83
S3R2	0.32	-0.75	0.46	0.64	0.0	0.64
S4R1	0.84	-0.25	0.89	0.82	0.0	0.82
S4R2	0.33	-2.0	0.65	0.51	0.0	0.51
S5	0.88	0.0	0.88	-0.06	1.75	-0.83
S6R1	-0.03	0.0	0.35	0.41	-1.25	0.65
S6R2	0.59	-0.5	0.72	0.57	-1.0	0.66
S7	0.6	0.0	0.6	0.97	0.0	0.97
S8				-0.09	1.75	-0.3
S9R1	-0.28	-2.25	0.35	0.34	-1.5	0.54
S9R2	-0.59	-1.5	0.65	0.51	0.25	0.57
S10R1	0.68	0.0	0.68	0.78	0.0	0.78
S10R2	0.54	-0.25	0.55	0.86	0.0	0.86
	Day 3			Average of 3 days		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.52	-0.25	0.6	0.68	0.0 to – 0.25	0.71
S2R2				0.91	0.0 to -0.25	0.92
S3R1				0.67	0.0 to -0.5	0.77
S3R2	0.06	2.0	-0.34	0.34	0.0 to 2.0	0.25
S4R1	0.76	-0.75	0.77	0.81	0.0 to -0.75	
S4R2	0.59	0.0	0.59	0.48	-0.25 to - 2.25	
S5	0.32	-1.25	0.49	0.38	-1.75 to 1.75	0.18
S6R1	-0.6	0.0	-0.6	-0.07	0.0 to – 1.25	0.13
S6R2	0.76	-0.75	0.77	0.64	-1.0 to -0.5	0.72
S7	0.55	-0.5	0.62	0.71	0.0 to -0.5	0.73
S8	-0.12	2.0	0.24	-0.11	1.75 to 2.0	-0.03
S9R1	0.8	0.0	0.8	0.29	0.0 to -2.25	0.56
S9R2	0.26	-1.25	0.44	0.06	0.25 to -1.5	0.55
S10R1	0.78	0.0	0.78	0.75	0.0	0.75
S10R2	0.69	-0.75	0.88	0.69	0 to -0.75	0.76

The results show that many individual sites return XCORR values which are similar between the first and second sections of the night. For example, Site 8, a naturally ventilated shop, shows very poor correlations (for both sections of the night) while a

mechanically ventilated office building, Site 10 run 2, shows high XCORR values. The pattern of XCORR values for Site 10 run 1 night one are shown in Figure A. 1 with both the first and second half sections of the night shown. A similar pattern can be seen for both parts of the nights although the second half shows a slightly longer influence from longer lags. The highest correlations were seen for lag of 0 to 15 minutes for night 1. Similar peak XCORR values and lags were also seen for the other days apart from the 1st half of the 3rd night with a lower correlation of -0.43 and a lag of -1 2/4. Run 2 for Site 10 also indicates a short time lag with a strong pattern similar to that shown in Figure A. 1

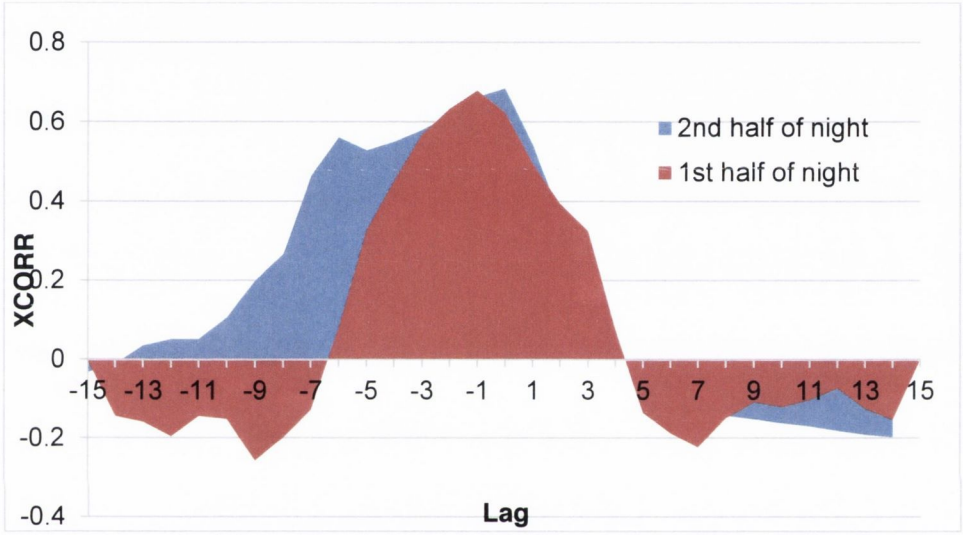

Figure A. 1 XCORR values 1st and 2nd sections of night Site 10 run 1 night 1

The pattern displayed for Site 8 is very different from that of Site 10, with sharp peaks on both the positive and negative y axis. The sharp fluctuations in the data combined with the low XCORR values indicate little interaction between indoors and outdoors throughout the night. Again though, there is a consistency in the pattern between the first and second section of the night. Site 8 also shows low correlations between indoor and outdoor data for working hours.

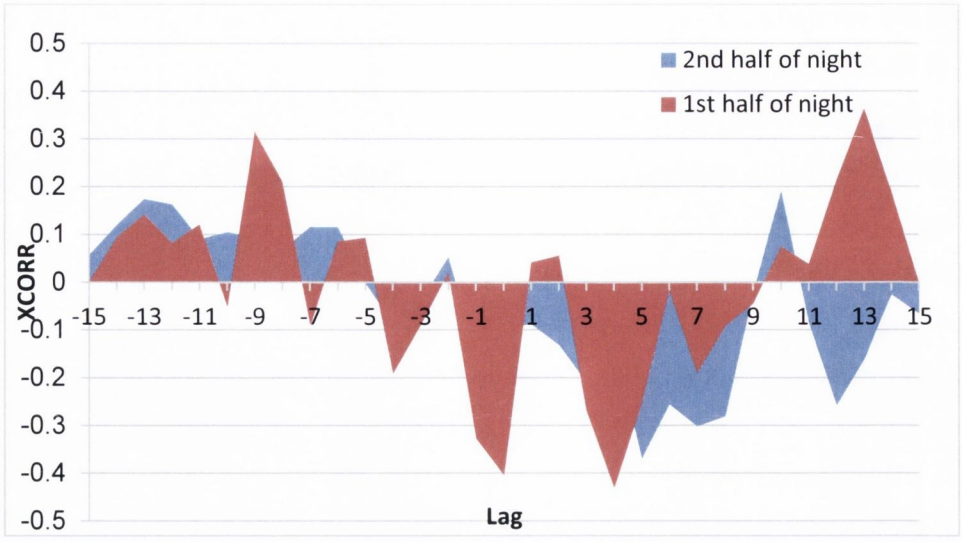

Figure A. 2 XCORR values 1st and 2nd sections of night Site 8 run 1 night 2

As noted above, many sites show stronger clearer patterns for the second half of the night compared to the first for certain nights over the monitoring period. For example, Site 2 run 2 on night 1(Figure A. 3) showed a weak correlation near 0 lags (although a peak at +7 lags was seen) for the first half of the night but a high correlation of 0.85 at a lag of 15 minutes for the second section of the night. This indicates that the first half of the night showed less stable noisier interactions between indoor and outdoor for the first half of the night. A very different comparison is revealed for the 2nd night of monitoring (Figure A. 4) at this site where both the first (XCORR = 0.97) and second section showed a high XCORR value (XCORR = 0.98) and clear stable relationship between the indoor and outdoor at a no time lag. This site shows overall lower XCORR values for working hours than non-working hours. This was a mechanically ventilated site with an indoor NO_2 source in the form of a gas cooker, which showed a high overall run XCORR of 0.881 and a lag of 15 minutes. The lower XCORR during the day might be due to staff opening windows, the cooker as an indoor source and other interactions of NO_2 in the ducting system creating an unstable relationship between indoor and outdoor during the day. At night, there would be fewer fluctuations occurring both indoors and outdoors and the correlations increase correspondingly. Very high R^2 values were found when a regression of indoor versus outdoor concentrations was conducted with values reaching 79.1 %. During the first half of night 1 both pressure and relative humidity notably changed compared to the 2nd half and this also occurred on night 2. This may be behind the noisier XCORR

values during the 1st half of night 1 compared to the others, with the fluctuating meteorological conditions affecting the relationship between indoor and outdoor.

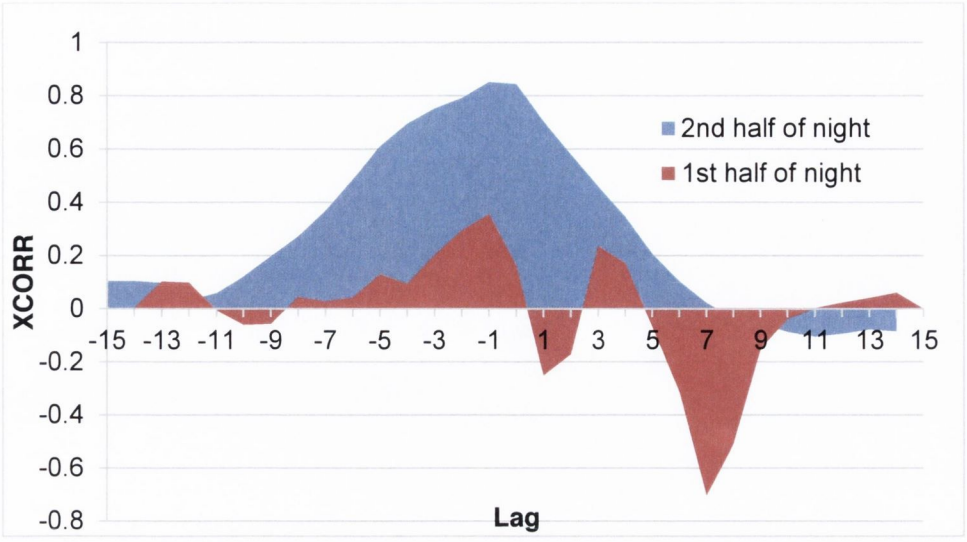

Figure A. 3 Site 2 run 2 night 1

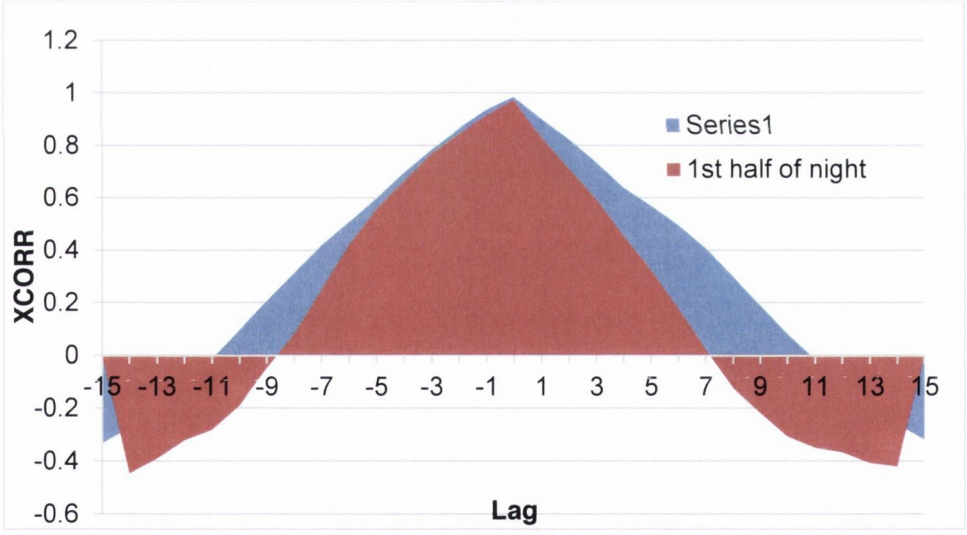

Figure A. 4 Site 2 run 2 night 2

A similar interaction between indoor and outdoor can be seen for Site 1 run 2 as was seen in Site 2. There are good correlations for the second half of the night (XCORR = 0.84, 0.69 and 0.60 for nights 1, 2 and 3 respectively) and a lag of 0 to 15 minutes, while for the first section of non-working hours data these correlations are lower (XCORR = -0.44, 0.48 and 0.82 for nights 1, 2 and 3 respectively) and the lag varies from 0 up to -2 ¼ hours. The overall run max XCORR value was

0.621 with a lag of 1 hour. Figure A. 5 shows an example from night 1 of these low correlations for the first half of the night with noisy peaks and a much higher correlation of 0.842 and 0 lag for the second half of the night.

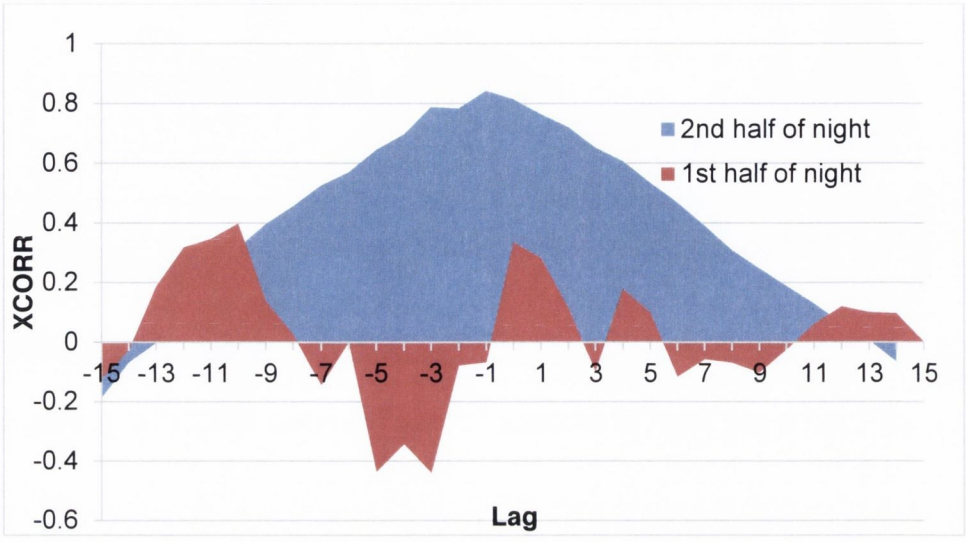

Figure A. 5 Site 1 run 2 night 1

Site 4, a mechanically ventilated office, showed different lags over the two runs, even though outdoor monitoring equipment for NO_2 was placed at the same point for each of the runs. Run 1 showed high XCORR values, similar to those returned at other mechanically ventilated sites such as Sites 2 and 10 but the second run did not show such strong XCORR patterns during the night. Both runs showed similar lags when the entire run was used in the calculation with an overall lag of 1 ¼ hours for run 1 and 1 1/2 hours for run 2. The XCORR pattern and values are similar for all nights during run 1, with night 2 shown in Figure A. 6 as an example. A longer lag time at night would be expected as ventilation units are turned off at 8 pm until 8 am, but this was not found to be the case for run 1 which saw very short lags of up to 15 minutes for 2 of the 3 nights, with the 3rd night having a longer lag of 45 minutes which was similar to the lag found for that day.

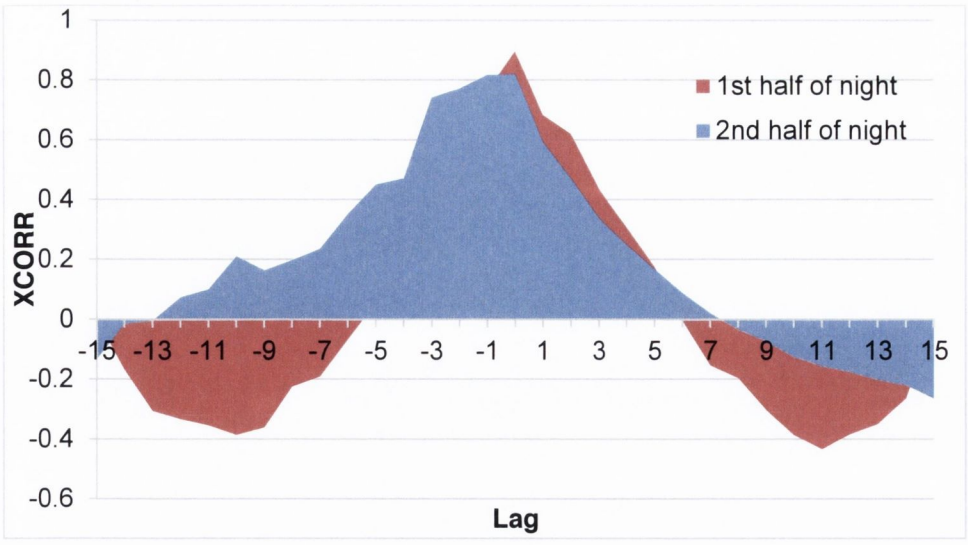

Figure A. 6 Site 4 run 1 night 2

Run 2 saw much longer lags overnight of between an hour and 2 ¼ hours, as well as more variance in the lag times; the XCORR value was decreased for this run in general. Figure A. 7 shows an example of the XCORR pattern for run 2 showing very different behaviours for the first and second half of the night, consistent again with previous sites, the second half of the night showing a pattern with a short lag. The positive lag shown for the first half of the night is very unlikely to occur. To investigate this section, the data was plotted in Figure A. 8. Here the indoor data stays relatively stable decreasing slowly over the 4 hours from 32.1 ppb to 26.9 ppb while the outdoor concentrations fluctuate. This behaviour produces the illusion that indoor is leading outdoor data for sections of the plot. Taking the same section from run 1, where higher correlations were found, gives a much more stable outdoors plot with considerably fewer fluctuations. This produces the XCORR plot shown in Figure A. 9 with the high peak and slow reduction influence of the outdoor on the indoor with increasing lags both positively and negatively in time.

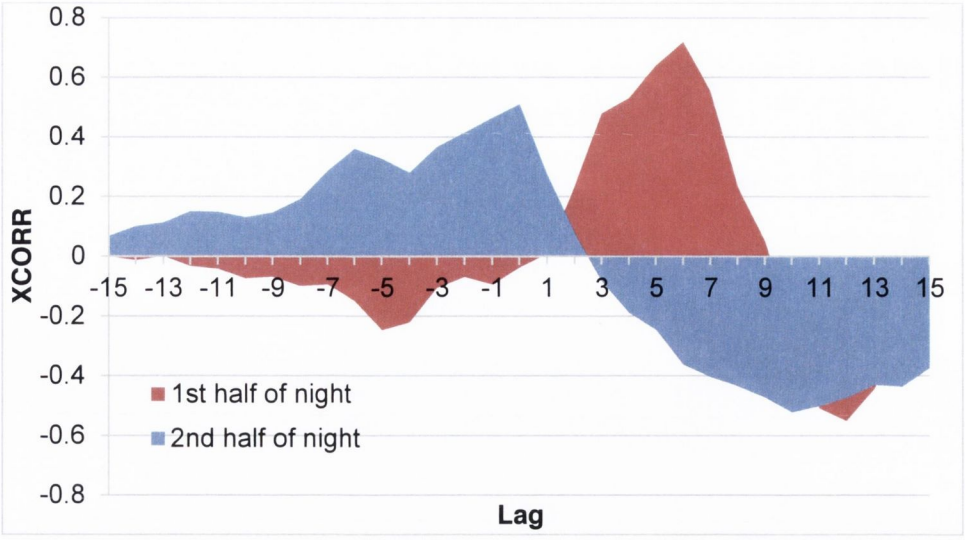

Figure A. 7 Site 4 run 2 night 2

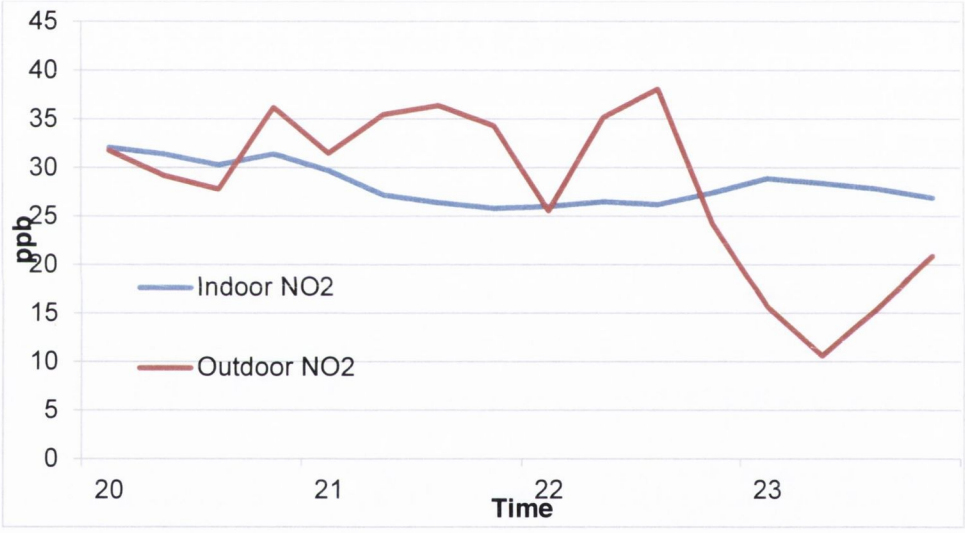

Figure A. 8 Site 4 run 2 night 2 (section: 8 pm to midnight)

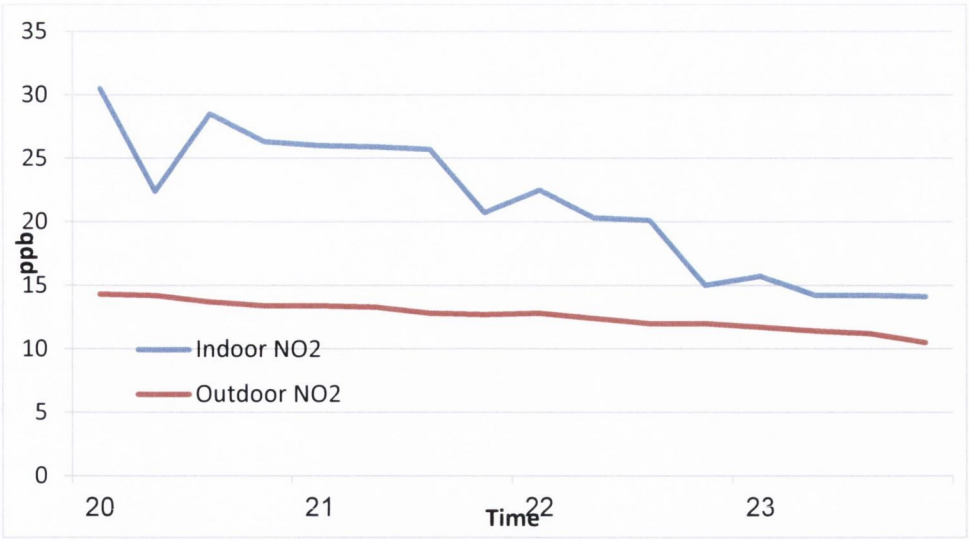

Figure A. 9 Site 4 run 1 night 2 (section: 8 pm to midnight)

In general the mechanically ventilated sites showed a greater stability in the lag time across the day and night than naturally ventilated sites. This is intuitive as they have a steady air flow into the building. These buildings are also more likely to be offices which see most of the movement into and out of the building at set times. Shops, on the other hand, with natural ventilation would have had customers entering through the front door, allowing blasts of outdoor air in at irregular time intervals.

NO_2 comparison of working hours and non-working hours

The lags for each site on individual days and how they vary from day to night are shown in Tables 5.9-5.11. These contain the estimated time lag using the XCORR method for individual days of monitoring at each site that was calculated previously. For site 1, a naturally ventilated shop, little difference between the working hours (day) time lag and 1st section of non-working hours data is present, with a reduced lag of up to zero lag found for the second half of the night. Similar can be said about Site 7 another naturally ventilated shop which saw very short to no lags. Another naturally ventilated building Site 6 found reduced lags overnight. This office building saw greater variance and longer length in the lags than the naturally ventilated shops of Site 1 and 7. Site 9, a naturally ventilated office building was the first of the naturally ventilated sites to record an increase in some overnight lags compared to the working hours lag. This building was different from the other naturally ventilated buildings as it was much larger with the monitor located further from the outdoor monitor because of the scale of building. Site 8, a naturally

ventilated shop, also showed this behaviour with 2 out of the 3 days showing an increase in lag times overnight compared to working hours.

Reviewing the mechanically ventilated sites, Site 2 behaves like many of the naturally ventilated sites and shows a decrease in lags overnight. This is an older rather leaky (with respect to air changes) building. Site 3 and 4 were built at the same time, and while one is a sports complex (monitoring took place in the offices within the building) the other is an open gallery space. Both sites showed reductions in the lag times during non-working hours, with a great variance between a zero lag up to a lag of 2 hours 30 minutes over the 3 days. The same can be said for Site 10. The only mechanically ventilated building which showed increases in the lag time during non-working hours is Site 5, a recently built well sealed office building. This building was designed to a high specification and was intended to be very energy efficient, with ventilation systems turned off during non-working hours and therefore increases in the lag time would be expected during non-working hours.

Table A. 3 Optimum lag (hours) for day 1 NO_2

	Day 1	Night 1st half 1	Night 2nd half 1
S1R2	0.75	-0.75	0.0
S2R2	2.75	1.75	-0.25
S3R1	-0.25	0.0	0.0
S3R2	-2.5	0.0	-0.75
S4R1	-1.0	-0.75	-0.25
S4R2	1.0	- 0.75	-2.0
S5R1	0.0	0.25	0.0
S6R1	0.0	2.5	0.0
S6R2	1.25	0.0	-0.5
S7R2	-0.25	0.0	0.0
S8R2	1.75	1.5	0.0
S9R1	0.0	0.5	-2.25
S9R2	0.75	0.0	-1.5
S10R1	-0.25	- 0.25	0.0
S10R2	0.0	0.25	-0.25

Table A. 4 Optimum lag (hours) for day 2 NO_2

	Day 2	Night 1st half 2	Night 2nd half 2
S1R2	0.75	-2.25	0.0
S2R2	-0.25	0.0	0.0
S3R1	0.0	0.0	- 0.5
S3R2	0.0	0.0	0.0
S4R1	0.0	0.0	0.0
S4R2	-1.5	1.5	0.0
S5R1	0.0	0.0	1.75
S6R1	-2.0	0.0	-1.25
S6R2	-2.0	0.5	-1.0
S7R2	-0.5	0.0	0.0
S8R2	-0.25	1.0	1.75
S9R1	0.25	0.5	-1.5
S9R2	-1.5	1.0	0.0
S10R1	-0.25	- 0.5	0.0
S10R2	-0.25	0.0	0.0

Table A. 5 Optimum lag (hours) for day 3 NO_2

	Day 3	Night 1st half 3	Night 2nd half 3
S1R2	0.0	0.0	-0.25
S2R2	-0.5	0.0	0.0
S3R1	0.0	0.0	0.0
S3R2	1.25	0.0	2.0
S4R1	-0.25	0.0	-0.75
S4R2	-1.5	0.75	0.0
S5R1	-0.25	0.0	-1.25
S6R1	-0.25	- 1.25	0.0
S6R2	-2.0	0.25	- 0.75
S7R2	0.5	0.0	-0.5
S8R2	0.5	0.0	2.0
S9R1	-0.75	0.0	0.0
S9R2	2.0	-1.5	-1.25
S10R1	1.25	-1.5	0.0
S10R2	0.0	-2.5	-0.75

Non-Working hours' time lag for $PM_{2.5}$

The XCORR values for non-working hours are contained within Table A. 6 and Table A. 7with the first and second section of the night calculated separately as was carried out previously with the NO_2 data. In general the night time data for $PM_{2.5}$ showed lower correlations and longer lags than for NO_2. The data was also noisier than NO_2 data with plots which show many peaks rather than one clear peak.

Table A. 6 XCORR 1st section of night

	Day 1			Day 2		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.75	0.0	0.75	0.62	0.0	0.62
S2R2	-0.02	1.5	-0.6	0.14	3.0	0.33
S3R1	0.33	-1.0	0.72	-0.08	-0.5	-0.6
S3R2	0.04	-1.25	0.34	-0.65	0.0	-0.65
S4R1	-0.15	1.25	-0.31	0.29	0.0	0.29
S4R2 Gr	0.78	0.0	0.78	-0.12	-2.0	0.52
S4R2 RF	0.58	0.5	0.73	0.15	-3.25	0.45
S5	-0.66	0.25	-0.71	0.22	1.25	0.63
S6R1	0.42	0.25	0.48	0.76	-0.25	0.77
S6R2	0.18	0.25	0.61	0.13	-3.0	-0.61
S7	0.05	0.75	0.53	-0.45	-3 3/4	0.38
S8	-0.43	-0.5	-0.68	-0.18	-1.25	0.62
S9R1	-0.14	1.25	-0.49	0.18	1.75	0.63
S9R2	0.08	1.25	0.34	-0.02	0.75	0.47
S10R1	0.34	-0.5	0.65	0.05	2.0	0.31
S10R2	0.28	-0.75	0.59	0.24	-1.0	0.43
	Day 3			Average of 3 days		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.91	0.0	0.91	0.76	0.0	0.76
S2R2				0.06		-0.14
S3R1				0.13		0.06
S3R2	-0.22	-2.25	0.48	-0.28	1.5 to 3.0	0.06
S4R1	0.06	0.5	0.57	0.07	-1.0 to 0.5	0.18
S4R2GR	0.33	-0.75	0.48	0.33	-1.25 to 0.0	0.59
S4R2 RF	0.9	0.0	0.9	0.54	0.0 to -2.0	0.69
S5	0.38	1.25	0.55	-0.02	0.25 to 1.25	0.16
S6R1	-0.03	-1.25	-0.65	0.38	-1.25 to 0.25	0.20
S6R2	-0.13	2.25	0.58	0.06	-3.0 to 2.25	0.19
S7	0.04	2.0	-0.56	-0.12	-3.75 to 2.0	0.12
S8	0	-2.0	-0.48	-0.2	-2.0 to -0.5	-0.18
S9R1	-0.47	1.0	-0.57	-0.14	1.0 to 1.75	-0.15
S9R2	-0.09	-0.25	-0.36	-0.01	2.0 to -0.25	0.15
S10R1	-0.29	2.5	0.32	0.03	2.5 to – 0.5	0.43
S10R2	-0.4	0.25	-0.4	0.04	0.25 to -1.0	0.21

Table A. 7 XCORR 2nd section of night

	Day 1			Day 2		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.59	0.0	0.59	0.83	0.0	0.83
S2R2	0.12	3.75	0.37	0.89	0.0	0.89
S3R1	0.42	0.75	0.58	0.25	-0.25	0.38
S3R2	0.05	0.75	0.41	0.08	1.25	0.58
S4R1	0.19	-1.5	0.41	0.43	0.0	0.43
S4R2GR	0.51	-0.75	0.53	0.12	2.0	-0.26
S4R2 RF	0.65	1.25	0.68	0.02	-2.0	0.43
S5	-0.16	-0.75	-0.29	0.19	1.75	0.41
S6R1	-0.31	0.5	-0.36	-0.1	3.75	-0.47
S6R2	-0.07	-0.75	0.34	0.01	2.0	-0.19
S7	0.09	-1.0	0.51	0.34	-1.75	-0.53
S8	0.09	1.5	-0.77	0.16	-1.75	0.24
S9R1	-0.45	-0.25	-0.47	0.13	0.5	0.31
S9R2	0.46	-2.0	0.54	0.14	0.75	0.52
S10R1	0.22	-0.25	0.28	0.32	0.0	0.32
S10R2	0.54	-0.25	0.58	-0.19	-2.5	0.31
	Day 3			Average of 3 days		
	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag	XCORR 0 lag	Optimum lag (hours)	XCORR optimum lag
S1R2	0.89	0.0	0.89	0.77	0.0	0.77
S2R2				0.51	0.0 to 3.75	0.63
S3R1				0.34	-0.25 to 0.75	0.48
S3R2	-0.1	-1.25	0.36	0.01	3.75 to -1.25	0.45
S4R1	0.4	-0.75	0.38	0.34	-0.75 to 0.75	0.41
S4R2GR	0.45	0.0	0.45	0.36	-0.75to 2.0	0.24
S4R2 RF	0.37	-3.25	-0.63	0.35	-3.25 to 0.25	0.16
S5	-0.12	3.0	0.33	-0.03	-0.75 to 0.75	0.15
S6R1	0.89	0.0	0.89	0.16	3.75 to 0.0	0.02
S6R2	0.09	-3.0	0.24	0.01	-3.0 to 2.0	0.13
S7	0.42	-1.00	0.49	0.29	-1.0 to -1.75	0.16
S8	-0.11	-1.25	-0.42	0.05	1.5 to -1.75	-0.32
S9R1	-0.34	1.0	-0.67	-0.22	1.0 to -0.25	-0.28
S9R2	-0.42	-0.25	-0.51	0.06	-3.0 to 0.75	0.19
S10R1	0.48	-0.5	0.73	0.34	-0.5 to 0.0	0.44
S10R2	0.36	0.25	0.45	0.23	0.25 to -2.5	0.45

Site 1, a naturally ventilated shop located on a busy shopping street, shows a very strong XCORR with 0 time lags which, as mentioned before, means less than a 15 minute lag. This is in contrast to the very low XCORR value when calculated across the entire run. The data shows one sharp clear peak for both night time sections of night 3. Many other sites including Site 9 run 2, another naturally ventilated site, showed some correlation but contained many sharp spikes in the data indicating that no set lag is present in the data as shown in Figure A. 11. The first half of the night shows a large number of spikes at very low correlations of less than 0.2 while the second half shows fewer spikes at larger correlations. The behaviour occurred on each of the nights for Site 9 run 2 with the lag varying widely depending on the night.

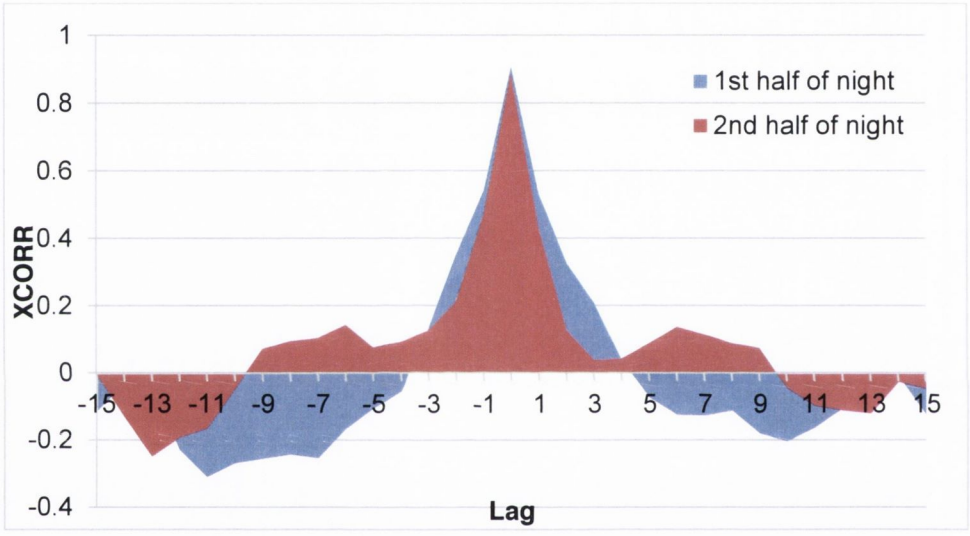

Figure A. 10 $PM_{2.5}$ XCORR Site 1 Run 2 night 3

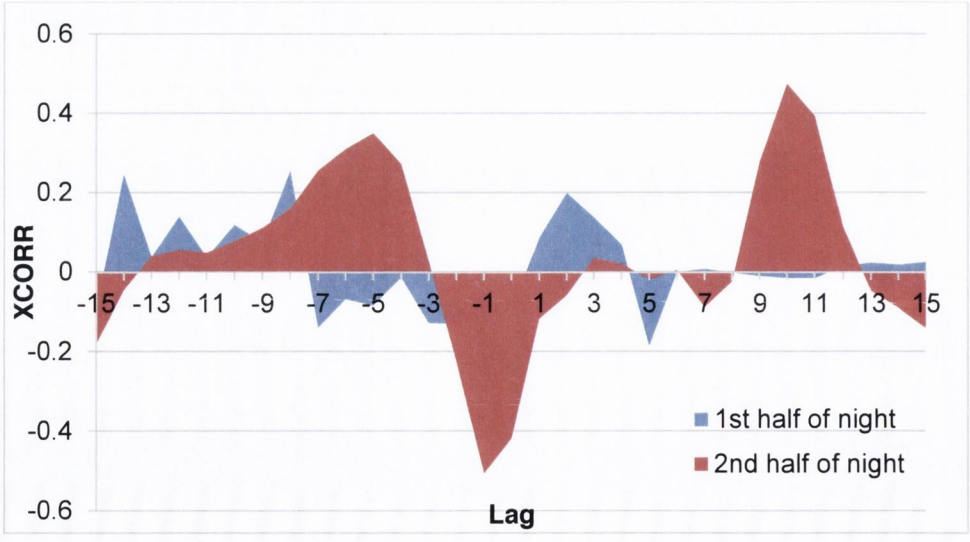

Figure A. 11 $PM_{2.5}$ XCORR Site 9 run 2 night 3

Site 6 during run 2 also produced plots with ambiguous outcomes for non-working hours. When compared to working hours, and the entire run, marginally higher correlations were seen during the night time periods but nothing which would indicate a steady lag time between indoors and outdoors for Site 6. Run 1 on the other hand showed some improvement with more prominent correlations and smoother patterns. Figure A. 12 shows the plot for night 3 with the second half of the night showing a 0 lag and a XCORR value of 0.8895, the first half of the night shows a longer lag of 1 ¼ hours but reviewing the other nights' peak XCORR values, a lag of 0 to 30 minutes is most likely. This naturally ventilated office is located next to the main door to the building, which overlooks a busy main road.

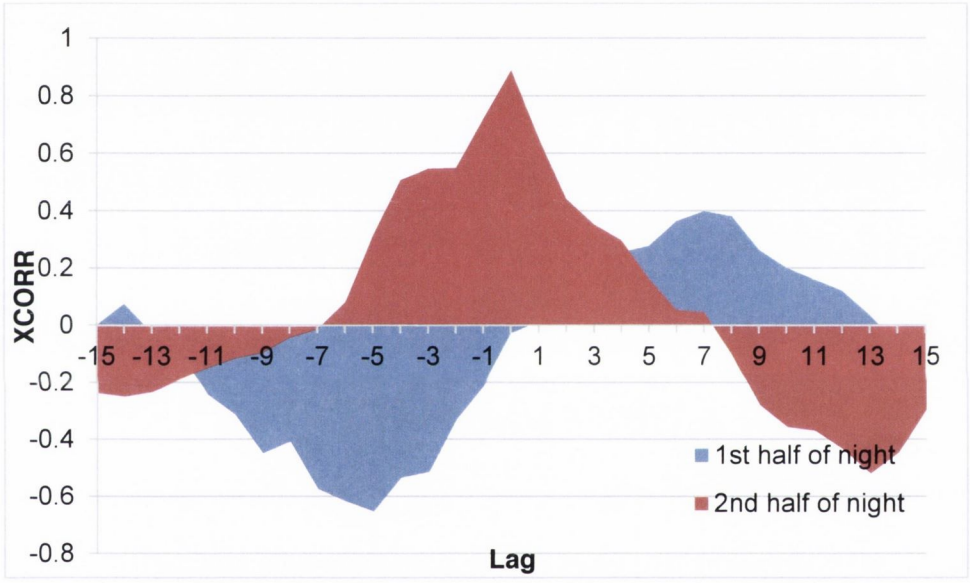

Figure A. 12 $PM_{2.5}$ XCORR Site 6 Run 1 night 3

Alongside Site 1, Site 7 was another naturally ventilated site which showed a stable XCORR pattern with slowly decreasing influence of increasing lags away from the peak. Lags varied throughout the run but best results at lags of up to an hour were consistent with the results found during the day.

Site 4 data collected from both roof and ground level for $PM_{2.5}$ during the entire run 2 suggested higher correlations between roof level and indoor data than ground level and indoor data. The lags increased from 15 minutes (roof to indoor) to 30 minutes (ground to indoor) and the XCORR value from 0.673 to 0.752. Similar values were found for NO_2 data during the same run. When looking at non-working hours data, no clear lags were present. Some nights saw very long lags over 2

hours for roof level data and 0 lags for ground level i.e. night 3 during the second half. Other nights, such as night 1 during the first section, saw high correlations with lags within half an hour of each other (Figure A. 13). This also occurred on the second half of this night and on night 3, although on night 3 correlations were lower for outdoors.

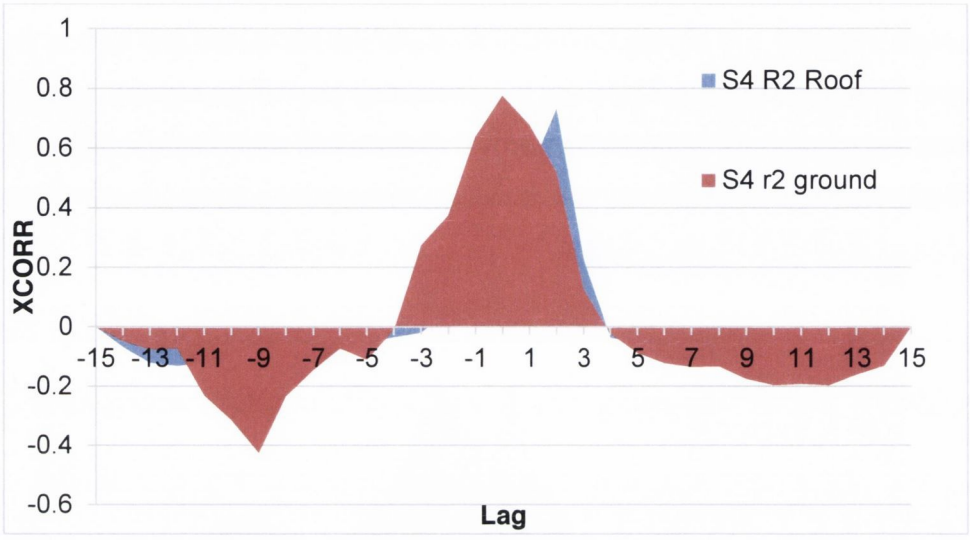

Figure A. 13 Site 4 run 2 first half of night 1

Sites 10, 5, 2 and 3 are the four other mechanically ventilated sites. Both sections of non-working hours monitoring at these sites show the XCORR between ground level and indoor concentrations provided irregular plots with many peaks and low correlations. Although Site 10 run 1 did show 2 out of 6 night time sections with a high correlation (-0.652 and 0.73) and a lag of 30 minutes, the other 4 sections (i.e. first and second section from each of the 3 nights) showed low correlations and no clear lag with the noisy data as observed at other sites. No data for ground level night time concentrations are available for Sites 2 and 5 due to monitoring restrictions, implemented by building occupants. This indicates that little interaction occurs between the street level concentrations and indoors in the mechanically ventilated office buildings, which tended to be larger buildings than the naturally ventilated buildings and better sealed (with the exception of Site 2). Site 2 was the oldest of the mechanically ventilated buildings and as mentioned previously it had a large number of poorly sealed windows in the monitored room. From the two nights of collected data, the first section of night 1 and second section of night 2 showed very high correlations (-0.602 and 0.892) while the other two sections showed low correlations of (0.369 and -0.33). The results from the second night of monitoring can be seen in Figure A. 14. While the first night showed a high XCORR peak value, this occurred at a lag of 1 ¾ hours in the opposite (positive) direction

indicating that indoor leads outdoor concentrations (Figure A. 15). For most of this section the XCORR values were below 0.2 so this peak may be a false indication of a lag where in fact there is little to no interaction between indoor and outdoor throughout the night.

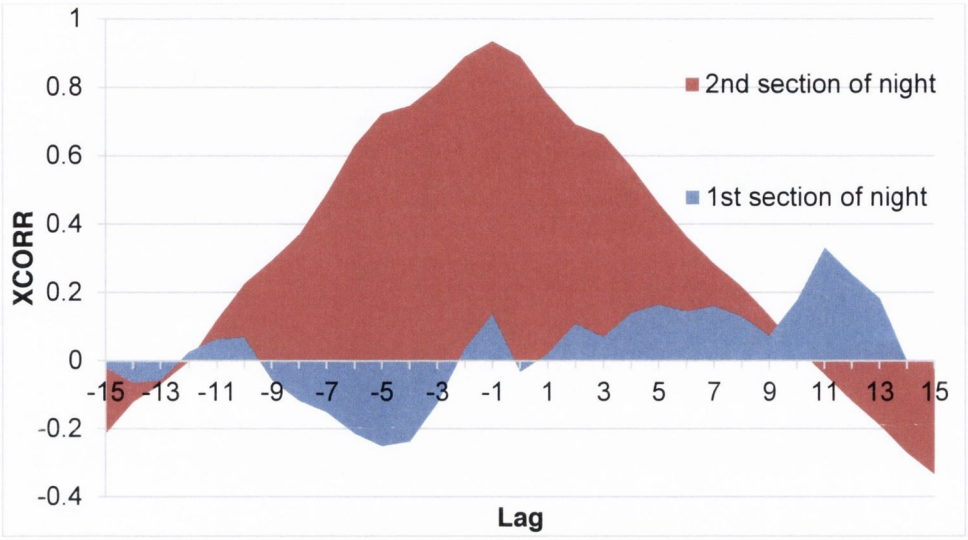

Figure A. 14 XCORR Site 2 run 2 night 2

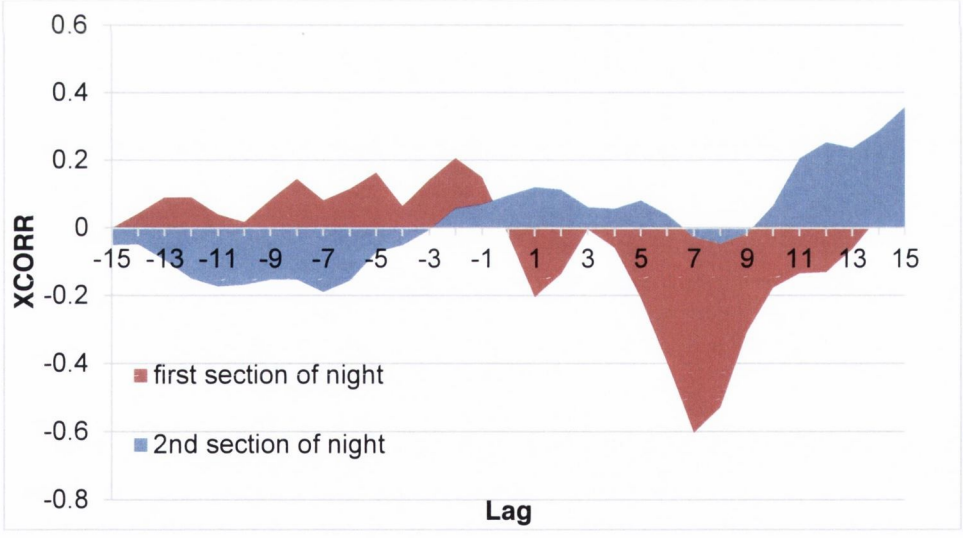

Figure A. 15 XCORR Site 2 run 2 night 1

Site 5 shows good XCORR values for the first section of each of the nights but poor values for the second sections, with long lags of up to 3 hours. Figure A. 16 shows the first and second sections of night 1 for Site 5. The ventilation in the offices where the indoor monitoring was carried out was turned off at 5 pm, but a separate air handling unit in the toilets ran until 7 pm. These extended ventilation hours, as

well as staff leaving past the official close of business, may have provided part of the increased XCORR values for the first section of night time monitoring. In the second half of monitoring there is very little interaction between roof level concentration fluxes and indoor concentrations.

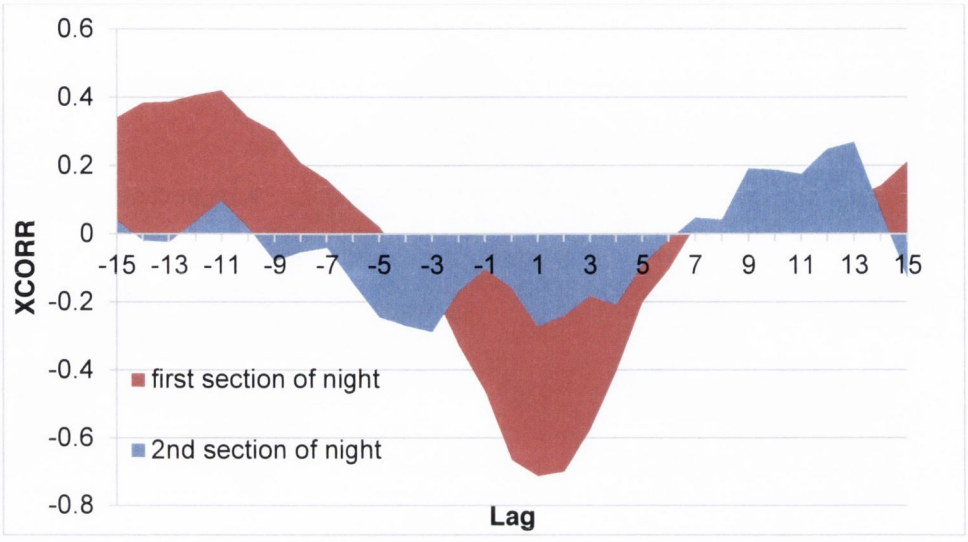

Figure A. 16 XCORR Site 5 Night 1

Site 3 run 1 shows a much stronger correlation for night 1 with a XCORR value of 0.715 and a lag of 1 hour. A similar lag of 1 hour 15 minutes was seen during the day but the XCORR value was lower at 0.225. For days 2 and 3 the lag was 0 and 45 minutes but with lower correlations. Night 2 saw a high correlation with a lag of 30 minutes and XCORR 0.600 but in the opposite direction indicating that indoor variations lead (or had an influence on) the outdoor concentrations. Reviewing the data suggested this was due to outdoor concentrations being particularly low that night, and the higher indoor concentrations resulted in the XCORR appearing to be led by the indoor data rather than the outdoor concentrations. For run 2 at Site 3 the night-time XCORR was reduced from run 1. During these night-time hours the offices are unoccupied and the ventilation system is shut off. While some air changes still occur through the ventilation ducting (run 1 was carried out at roof level) the roadside $PM_{2.5}$ concentration fluxes would be expected to have less influence than during the day. concentration fluxes would be expected to have less influence than during the day. Finally, the XCORR analysis of the data showed that there was little influence of outdoor $PM_{2.5}$ at ground level over indoors.

$PM_{2.5}$ comparison of working hours and non-working hours

In general XCORR values were not as strong for NO_2 and these have been discussed previously. The highest correlation for working hours and the 2 non-working hour sections are laid out in Table A. 8, Table A. 9 and Table A. 10 for each individual run. Naturally ventilated Sites 6, 7, 8 and 9 all showed long time lags which showed a large amount of variation between days and time of day, with little pattern to indicate a difference between working and non-working hour lags. Site 6 showed the greatest XCORR values for lags of 0 to 30 minutes but with no indication that the XCORR values were more stable at night. The final naturally ventilated building, Site 1, showed no lag for working or non-working hours indicating that the building is poorly sealed and outdoor concentration fluctuations quickly influence the indoor environment both day and night.

For NO_2 Site 5 indicated the strongest lag increase for overnight data, and for $PM_{2.5}$ the lags increased on 2 out of 3 of the days for this mechanically ventilated office space. On the other hand Site 3 shows some reductions in the lags overnight as does Site 4. These lags vary greatly between each day with low to medium XCORR values. The same can be said for Site 2 and Site 10, with low XCORR values and lags varying from 3 hours to a 0 lag. Again for Site 10 the lowest lags show the strongest XCORR value.

Table A. 8 Optimum lag (hours) for day 1 $PM_{2.5}$

	Day 1	Night 1st half 1	Night 2nd half 1
S1R2	0.0	0.0	0.0
S2R2	0.0	0.25	2.0
S3R1	-1.25	0.0	-0.75
S3R2	1.75	-1.75	-1.75
S4R1	1.5	0.5	-0.25
S4R2	-8.25	-2.0	-0.25
S5R1	1.25	0.0	0.0
S6R1	-0.25	-2.0	0.0
S6R2	1.0	-0.25	-1.5
S7R2	-3.0	0.0	0.0
S8R2	-3.75	-0.25	-2.25
S9R1	1.5	-2.0	-3.0
S9R2	-3.5	-0.5	0.0
S10R1	-0.25	-0.25	2.5
S10R2	0.5	1.75	1.0

Table A. 9 Optimum lag (hours) for day 2 $PM_{2.5}$

	Day 2	Night 1st half 2	Night 2nd half 2
S1R2	0.0	0.0	0.0
S2R2	0.25	3.0	0.0
S3R1	0.0	-0.5	0.0
S3R2	-1.75	0.0	-2.25
S4R1	0.5	0.0	0.5
S4R2	-2.0	-2.0	- 0.75
S5R1	0.0	-3.25	0.0
S6R1	-2.0	1.25	1.25
S6R2	- 0.25	-0.25	-1.25
S7R2	0.0	-3.0	2.25
S8R2	-0.25	-3.75	2.0
S9R1	-2.0	-1.25	-2.0
S9R2	- 0.5	1.75	1.0
S10R1	- 0.25	0.5	- 0.25
S10R2	1.75	2.0	2.5

Table A. 10 Optimum lag (hours) for day 3 $PM_{2.5}$

	Day 3	Night 1st half 3	Night 2nd half 3
S1R2	0.0	0.0	0.0
S2R2	2.0	0.0	0.0
S3R1	-0.75	-0.25	0.0
S3R2	-1.75	1.25	-1.25
S4R1	-0.25	0.0	-0.75
S4R2	-0.5	2.0	0.0
S5R1	0.0	-2.0	-3.25
S6R1	0.0	1.75	3.0
S6R2	-1.5	3.75	0.0
S7R2	0.0	2.0	-3.0
S8R2	-2.25	-1.75	-1.0
S9R1	-3.0	-1.75	-1.25
S9R2	0.0	0.5	1.0
S10R1	1.5	0.75	- 0.25
S10R2	1.0	0.0	- 0.5

Appendix B. Individual Regressions and Best Fit Models

Best fit NO_2 regressions

i) Best fit NO_2 model - Site 1

Site 1 is a naturally ventilated shop located on a busy road. According to results shown in Figure B. 1 and Figure B. 2 an indoor source is present during working hours. This source increases marginally as the working day goes on and then reduces sharply once the shop is closed. It is known that electrostatic equipment (e.g. photocopying machines and laser printers) emits O_3 and NO, as well as VOCs (Wolkoff et al., 1997). As this shop repairs computers this source may be from use of equipment within this shop, as the source times line up with opening and closing times of the business. Infiltration was high during the day at this site as the door was frequently left open allowing outdoor air to enter the building. This rate dropped during the night and morning periods as the shop was not open and shutters were pulled down; the rate was particularly low in the early morning between dawn and the shop opening as concentrations indoors do not rise with the same intensity that outdoor concentrations did.

2 sample T tests found an estimate for the difference between the modelled indoor concentrations and measured indoor concentrations of (-3.94, 0.58) with a T-Value =-1.47, P-Value = 0.145 and DF = 152. The regression of modelled indoor concentrations versus actual indoor concentrations returns a value of R^2 = 71.9 % and regression equation of: indoor = 2.84 + (0.765 x modelled). Inputs for this best fit model are shown in Appendix C.

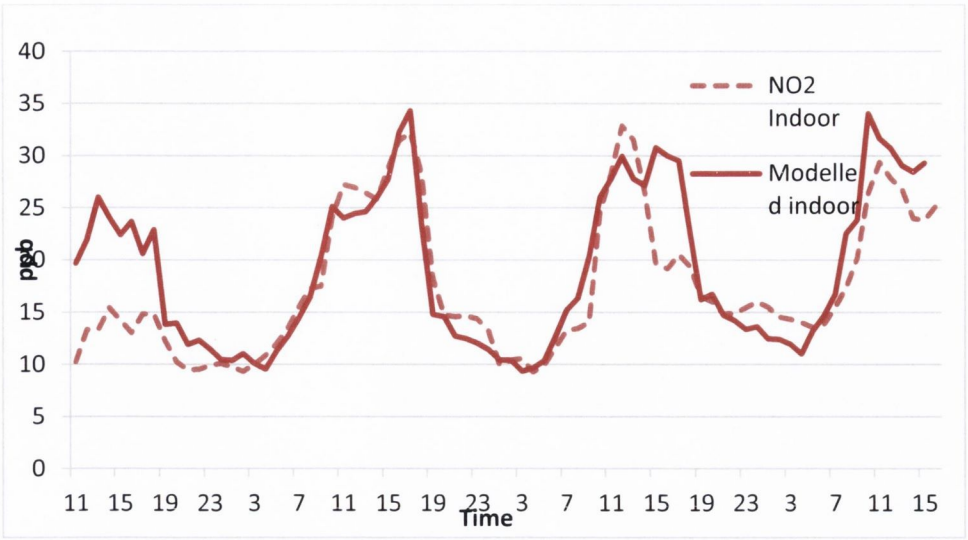

Figure B. 1 Indoor and modelled concentrations for Site 1 run 2

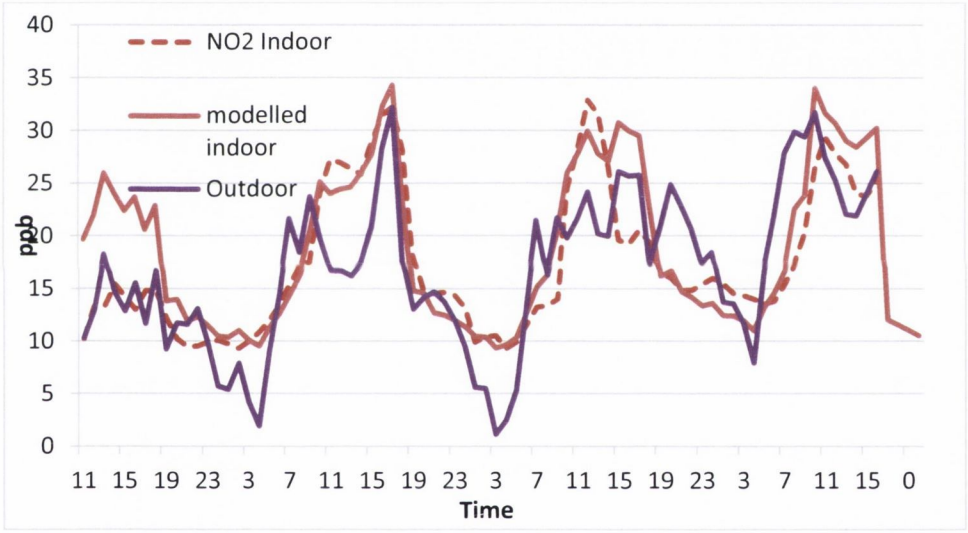

Figure B. 2 Indoor, modelled and outdoor concentrations for Site 1 run 2

Table B. 1Variable parameters for best fit model Site 1 run 2

Parameter	Value	Source	Time
V_d	0.0003		
V_d night	0.011	3.5	11
A/V	0.9000	4	12
k day	0.0003	4.5	13
k night	0.01	5	14
F_{inf}	0.67012	4.5	15
F_{inf} night	0.46263	4	16
F_{inf} early morning	0.25101	3.5	17
Source day	9.3805	3	18
Source night	7.76114	2.5	19
Source early morning	9.64441	2	20

ii) Best fit NO_2 model - Site 2

Site 2 showed a high correlation between indoor and outdoor concentrations and therefore the prediction involved increasing values during the day and the smoothing of some of the outdoor fluctuations as shown in Figure B. 3 and Figure B. 4. It should be noted that the only continuous data set available for Site 2 was at roof level next to the air intake, therefore the lag applied to street level data for mechanical ventilation is not necessary. Inputs for this best fit model are shown in Appendix C. A regression of modelled indoor concentrations of actual indoor concentrations gave an R^2 = 82.6 %, with a regression equation of: Indoor = 3.06 + (0.873 x Modelled). A 2-Sample T-test gives an estimate for the difference between modelled concentrations and actual indoor concentrations as (-2.27,2.50) with a T value of 0.10 and P value of 0.924.

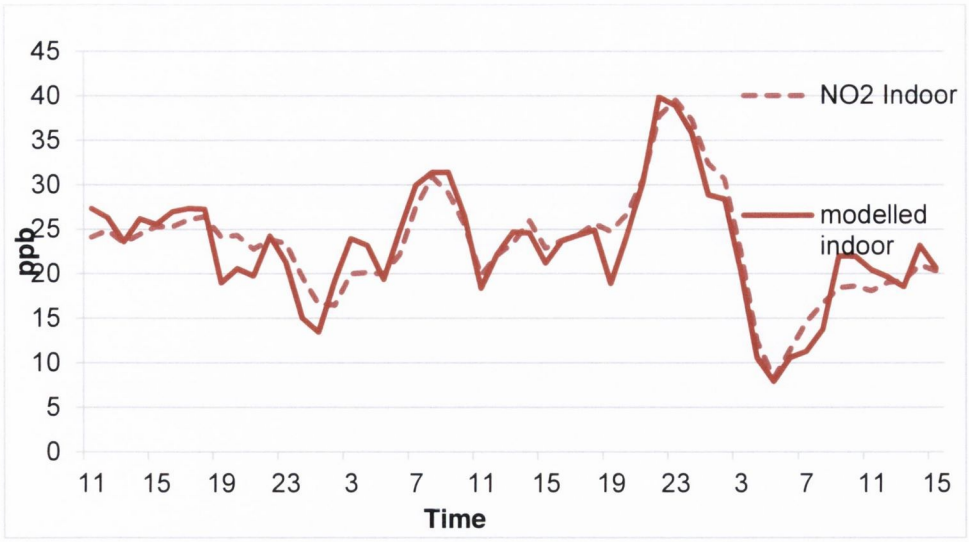

Figure B. 3 Indoor and modelled concentrations for Site 2 run 2

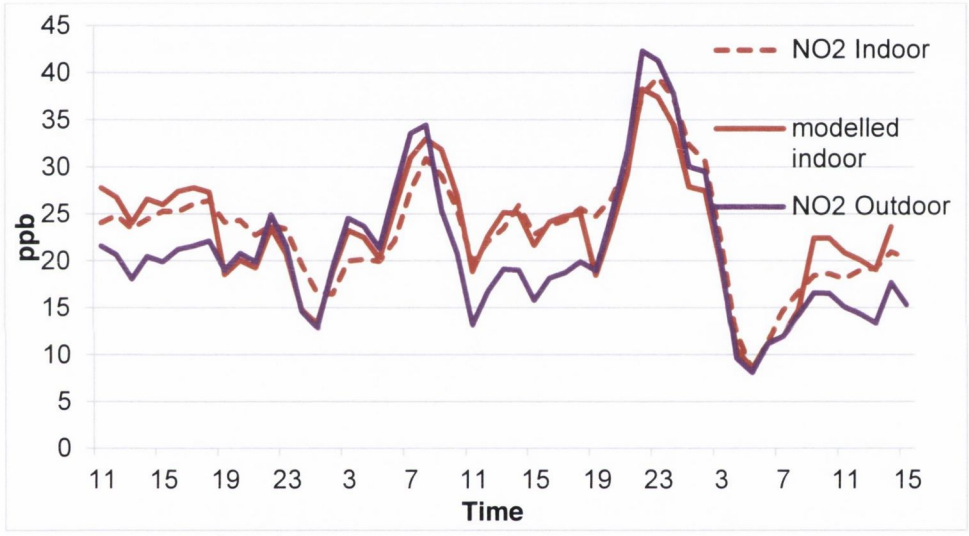

Figure B. 4 Indoor, modelled and outdoor concentrations for Site 2 run 2

As there was little smoothing necessary and the infiltration factor is the highest seen for any site, an additional source was added to account for the use of the gas cooker during working hours. This source decreases during the night-time period when cooking is not being actively carried out.

Table B. 2 Variable parameters for best fit model

Parameter	Value
V_d	0.0003
V_d night	0.0110
A/V	0.50
k day	0.00060
k night	0.02200
F_{inf}	0.87
F_{inf} night	0.70
F_{inf} early morning	0.73
Source day	5.00
Source night	2.00
Source early morning	3.00

iii) Best fit NO_2 model - Site 3

Site 3 was a mechanically ventilated office located in sports complex. The office was small with a large amount of items in it, therefore providing a large surface area for reactions and deposition. Indoor concentrations followed the same trend as outdoor but with smaller peaks and troughs as shown in Figure B. 5 and Figure B. 6. A regression of modelled indoor concentrations of actual indoor concentrations gave an R^2 = 57.2 %, and regression equation of: Indoor = 2.72 + 0.892 Modelled. A 2-Sample T-test gives an estimate for the difference between modelled concentrations and actual indoor concentrations as (-5.40, 1.977) with an estimate of a difference of 0.718 ppb a T-Value = 1.13, P-Value = 0.262 and DF = 186. This indicates that with 95 % confidence the means of indoor modelled and measured indoor are statistically indifferent. The user inputs which describe Site 3 are given in Appendix C and the input parameters calculated from these users provided inputs as well as those calculated via the regression of outdoor on indoor concentrations as detailed in Table B. 3.

Infiltration factors were low at this site which was necessary to smooth the peaks and troughs, but in order to maintain the baseline levels of 12 ppb indoors it was necessary to include a source. In this case the source represented the mean increase necessary to counter act the reduction in concentrations due to smoothing rather than a direct indoor source.

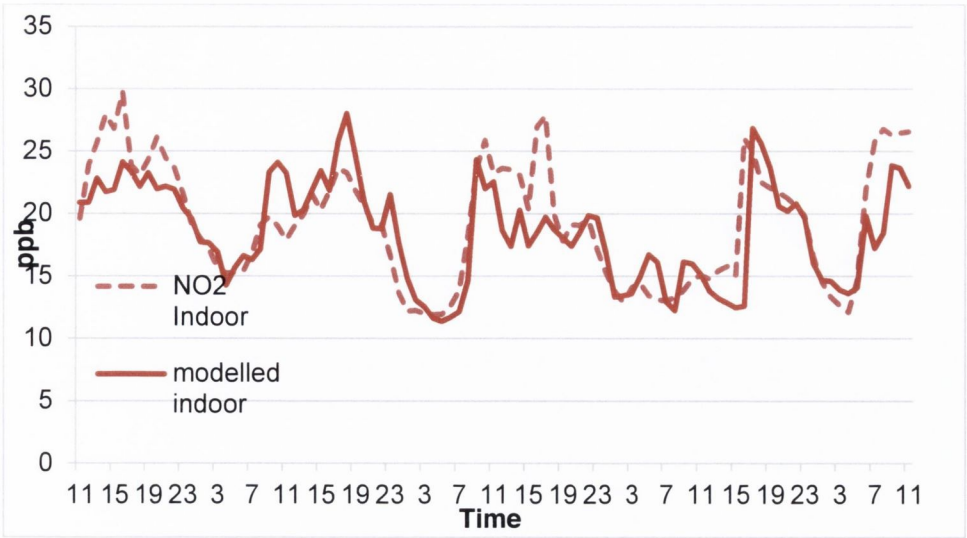

Figure B. 5 Indoor and modelled concentrations for Site 3 run 2

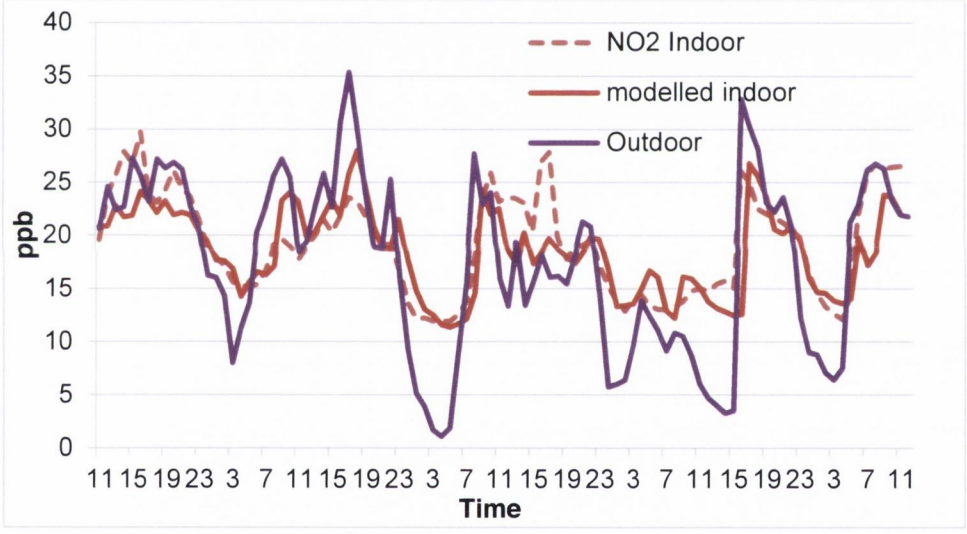

Figure B. 6 Indoor, modelled and outdoor concentrations for Site 3 run 2

Table B. 3 Variable parameters for best fit model for Site 3 run 2

Parameter	Value
V_d	0.0003
V_d night	0.011
A/V	2
k day	0.0006
k night	0.022
F_{inf}	0.35
F_{inf} night	0.3
F_{inf} early morning	0.25
Source day	12
Source night	10.48
Source early morning	12.5

iv) Best fit NO_2 model - Site 4

Site 4 is a mechanically ventilated gallery space which showed values with similar levels to outdoors during run 2. The inputs which represent this site are shown in Table B. 4 and details the results of the regression carried out using indoor and outdoor concentrations as well as the variables chosen as a result of the inputs. The site saw reasonable infiltration factors which did not vary greatly between working and non-working hours. The hours when mechanical ventilation was turned on i.e. 8 am to 8 pm were accounted for with an increased number of air changes within the model.

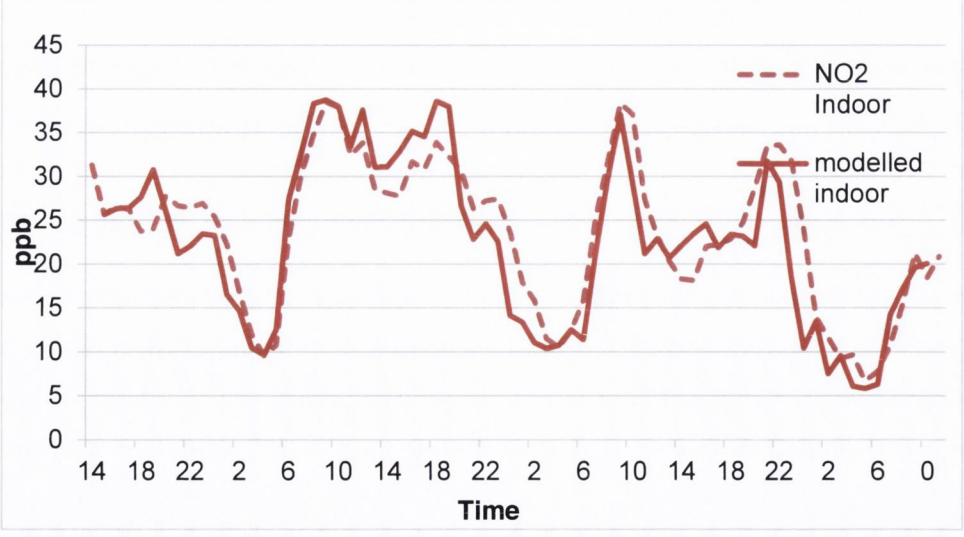

Figure B. 7 Indoor and modelled concentrations for Site 4 run 2

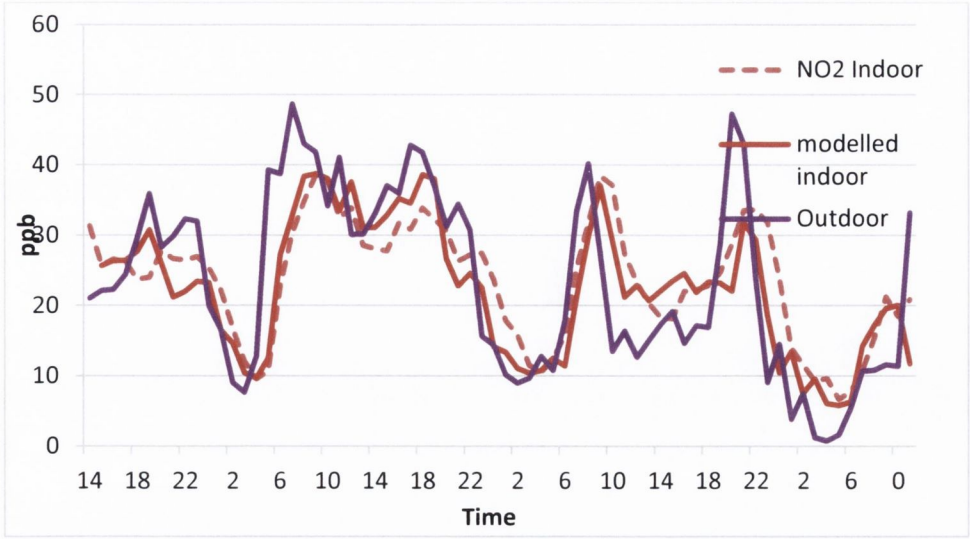

Figure B. 8 Indoor, modelled and outdoor concentrations for Site 4 run 2

A regression of modelled indoor concentrations of actual indoor concentrations gave an R^2 = 52.2 %, and regression equation of: Indoor = 9 + (0.651 x modelled). While this is quite low it can be seen in Figure B. 7 and Figure B. 8 that there appears to be a reasonable correlation between the actual indoor and modelled indoor concentrations. A 2-Sample T-test gives an estimate for the difference between modelled concentrations and actual indoor concentrations as (-1.78, 4.1) with an estimate of a difference of 1.16 ppb a T-Value = 0.78, P Value = 0.435 and DF = 136.

Table B. 4 Site 4 run 2

Parameter	Value Run 2
V_d	0.0003
V_d night	0.0110
A/V	0.50
k day	0.00015
k night	0.00550
F_{inf}	0.45
F_{inf} night	0.42
F_{inf} early morning	0.42
Source day	13.28
Source night	11.8
Source early morning	6

v) Best fit NO_2 model - Site 5

Site 5 showed two very different behaviours for the 1st half and 2nd half of the week, which made it difficult to produce a single model giving a good fit for both parts of the monitoring run. Inputs for this best fit model are shown in Appendix C.The resultant R^2 = 66.30 % with a regression equation of: Indoor = 1.11 - 0.912modelled. The model over predicts for the final night of monitoring due to the changed relationship to previous evenings where an increase in concentrations had occurred at this time, as shown in Figure B. 9 and Figure B. 10. A higher infiltration factor was seen during the day when office workers were moving around the site opening doors and allowing in outdoor air. While windows were present in this office, staff recorded no opening of these during monitoring, which was conducted in January. The site as a whole was well sealed being constructed as a high energy efficiency building less than 5 years previously.

A 2 Sample T-test gives a range for the difference between modelled concentrations and actual indoor concentrations for the run of (-0.622, 1.305) with an estimate of a difference of 0.342 ppb a T-Value = 0.70, P-Value = 0.485 and DF = 144. These values indicate that the test is 95 % confident that there is no statistical difference between actual indoor and modelled indoor concentrations.

If figures were adjusted a better fit for either the first of the second half of indoor/outdoor behaviour could be found but in order to adjust for both behaviours a compromise using the variables in Table B. 5 was settled upon.

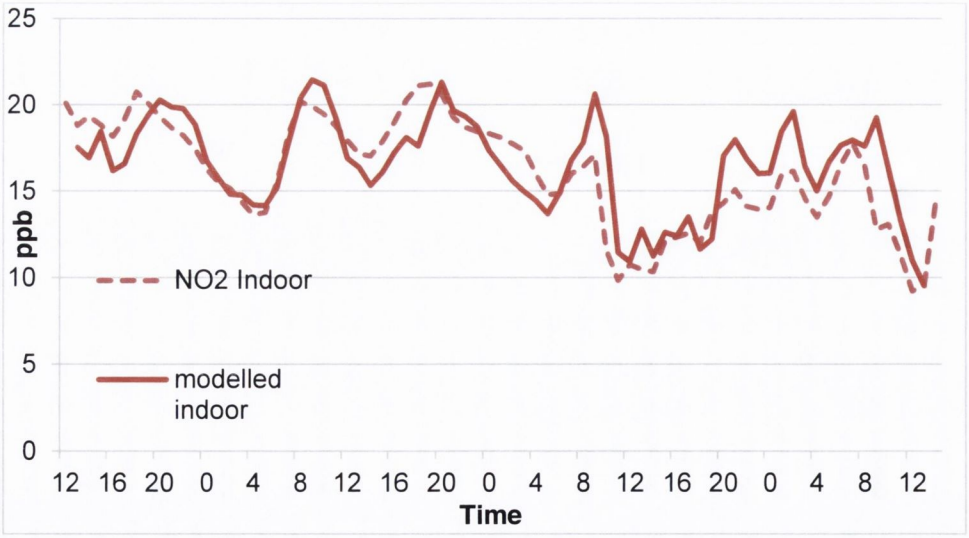

Figure B. 9 Indoor and modelled concentrations for Site 5 run 1

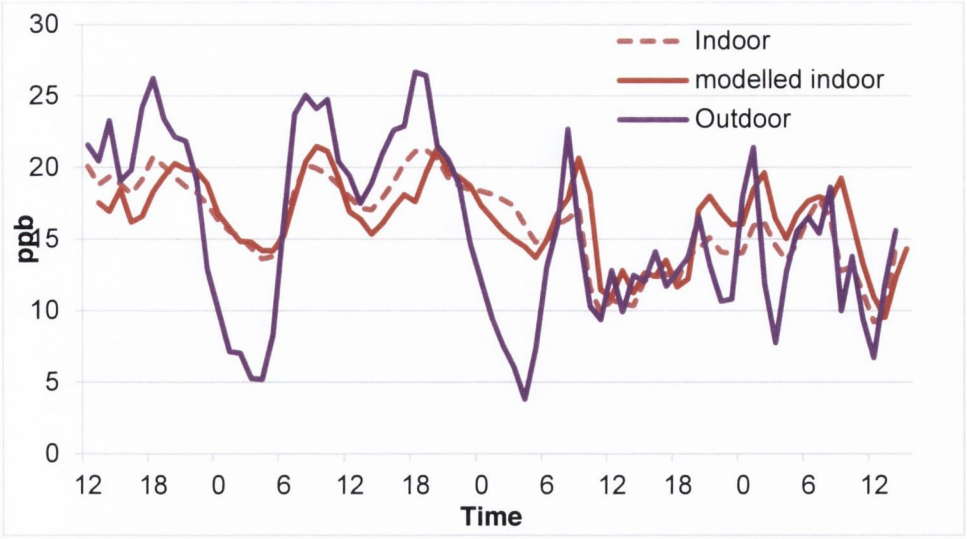

Figure B. 10 Indoor, modelled and outdoor concentrations for Site 5 run 1

Table B. 5 Varying parameters Site 5 run 1

Parameter	Value
V_d	0.0003
V_d night	0.011
A/V	0.9
k day	0.00027
k night	0.00990
F_{inf}	0.40
F_{inf} night	0.22
F_{inf} early morning	0.22
Source day	7.00
Source night	14.00
Source early morning	14.00

vi) Best fit NO_2 model - Site 6

This naturally ventilated office, located in an older building, inputs for this best fit model are shown in Appendix C. while the variables due to the regression to find f_{inf} and source values and the inputs are contained within Table B. 6. Site 6 showed significant reductions in NO_2 compared to outdoors. After much thought the most likely cause of this was attributed to heterogeneous reactions which were increased due to damp found in the building. These reactions were accounted for by low infiltration factors and high reaction rates. Sites with lower air changes allow a longer time for pollutants to

react on surfaces. As staff members in this building repeatedly complained about how the building felt poorly ventilated and damp, such low air changes can be assumed. This situation would be ideal for high levels of heterogeneous reactions, as reaction rates increase with increasing moisture and low ach provides NO_2 with extended time for these reactions to occur. Plots showing the time series of indoor, outdoor and modelled concentrations can be seen in Figure B. 11 and Figure B. 12.

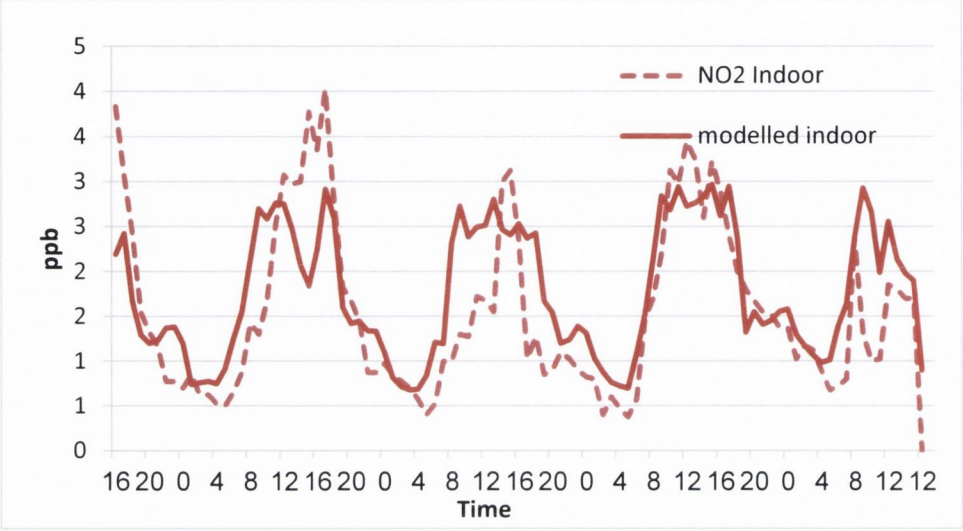

Figure B. 11 Indoor and modelled concentrations for Site 6 run 2

A regression of actual indoor concentrations versus modelled concentrations gave low results of R^2 = 53.3 %, while low, this is significantly higher than the regression of indoor and outdoor concentrations which gave a R^2 of 20.0 %. The range of the indoor concentrations is very small. A 2 sample T-Test gave a 95 % confidence interval for the difference between modelled and indoor concentrations of (-0.446, 0.030) and an estimate for the difference of -0.208 ppb.

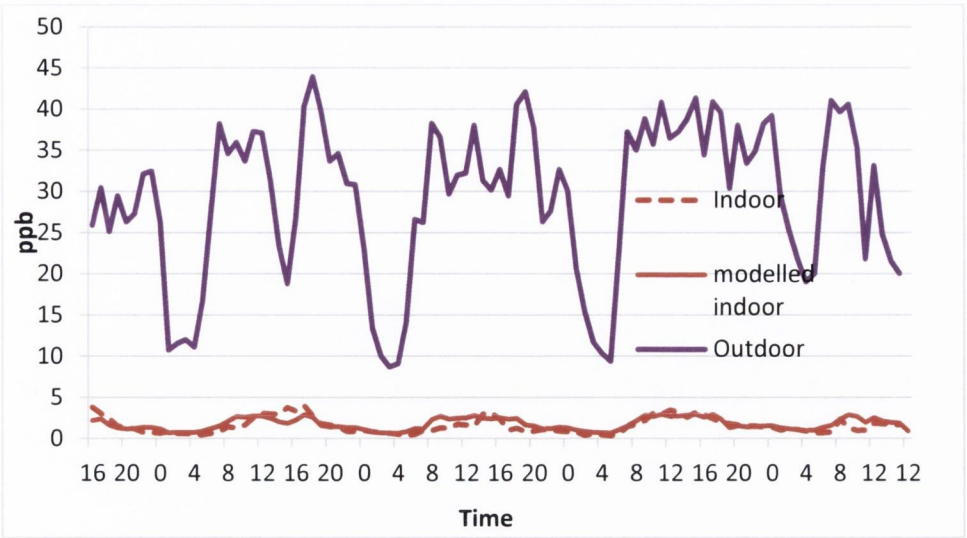

Figure B. 12 Indoor, modelled and outdoor concentrations for Site 6 run 2

Table B. 6 Varying parameters Site 6 run 2

Parameter	Value
V_d	0.0003
V_d night	0.011
A/V	0.9
k day	0.00027
k night	0.00990
F_{inf}	0.05
F_{inf} night	0.03
F_{inf} early morning	0.03
Source day	2.00
Source night	2.00
Source early morning	2.00

vii) Best fit NO_2 model - Site 7

Site 7 is a naturally ventilated catering supply shop located on a heavily trafficked street in Dublin city centre. Inputs for this best fit model are shown in Table B. 7 and the source and f_{inf} values generated due to the regression equation. The regression of indoor and outdoor concentrations showed low f_{inf} factors with high sources which acted to smooth the data and then increase the mean values in order to get modelled concentrations to emulate the actual indoor concentrations. The f_{inf} was higher in the morning when concentrations increased sharply upon opening of the shop. Also, as mentioned previously, the back door to the shop was often left open during the morning

hours which coincided with sharp rises outdoors leading to sharp rises in concentrations indoors. The outdoor concentrations show a greater standard deviation (10.90) compared to modelled (4.382) and indoor concentrations (5.457), mean values for the three times series were 22.05 ppb, 20.048 ppb and 19.90 ppb for outdoor, indoor and modelled respectively. A time series plot of the indoor, outdoor and modelled concentrations is shown in Figure B. 13 and Figure B. 14. When 2-Sample T-tests are carried out it showed that indoor and modelled concentrations with 95 % confidence were statistically significantly indifferent and therefore there is no reason to suspect that modelled does not predict mean indoor concentrations well (-1.184, 1.575), with a T value of 0.28 and P value of 0.780. The estimate for the difference is 0.195 ppb.

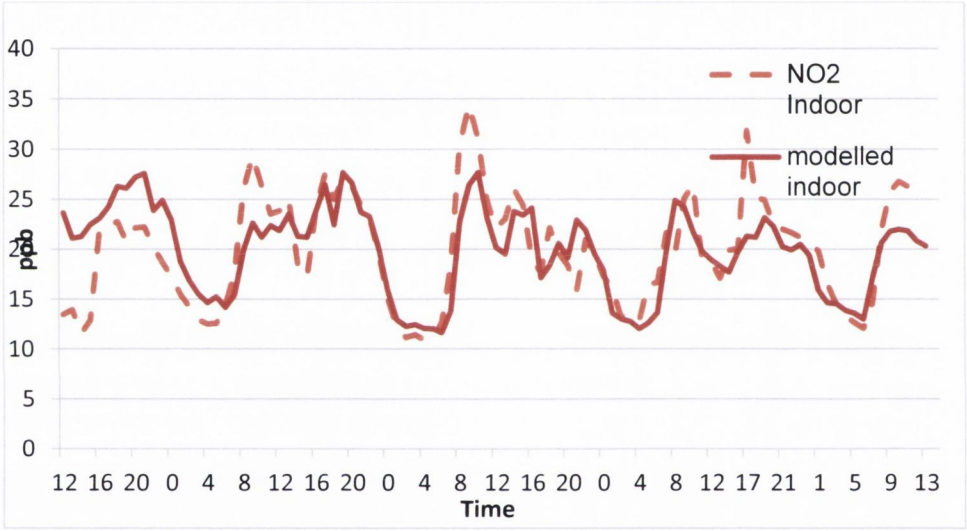

Figure B. 13 Indoor and modelled concentrations for Site 7 run 1

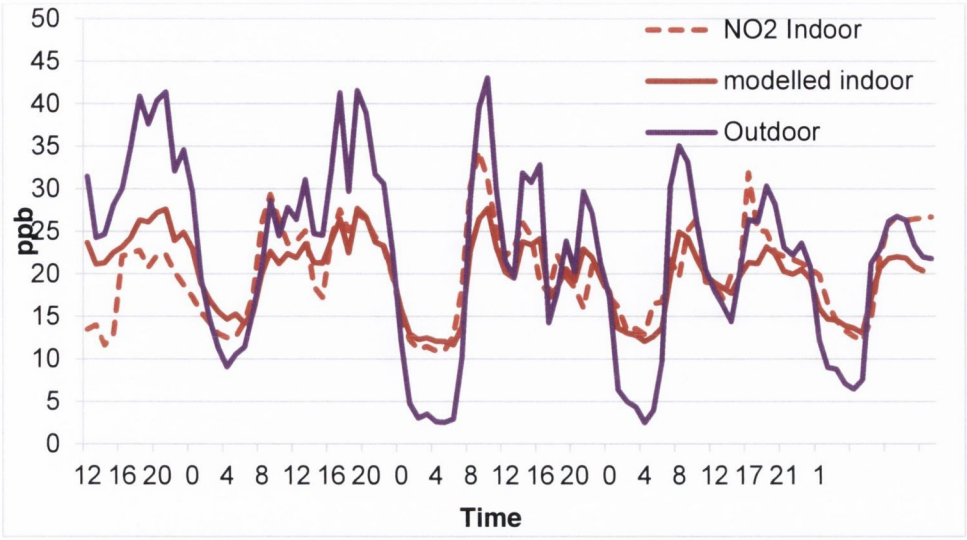

Figure B. 14 Indoor, modelled and outdoor concentrations for Site 7 run 1

Fluctuations indoor and outdoor differed significantly at this site with indoor concentrations not reaching the same peaks or troughs that the outdoor concentrations did. Regression shows a reasonable correlation (R^2 = 62.7 %) between indoor and modelled concentrations, with a regression equation of: Indoor = 2.305 + 0.892 x Modelled.

Table B. 7 Variable parameters for best fit model Site 7 run 1

Parameter	Value
V_d	0.0003
V_d night	0.0110
A/V	0.90
k day	0.00027
k night	0.00990
F_{inf}	0.34852
F_{inf} night	0.30225
F_{inf} early morning	0.40432
Source day	12.8194
Source night	11.3805
Source early morning	11.6596

viii) Best fit NO_2 model - Site 8

The relationship between indoor and outdoor for Site 8 was very unusual with a R^2 of 0.1 % and little interaction between the two as shown in Figure B. 16 this lead to

difficultly attaining the parameters to be used for the model in order to achieve the indoor modelled concentrations as shown in Figure B. 15.

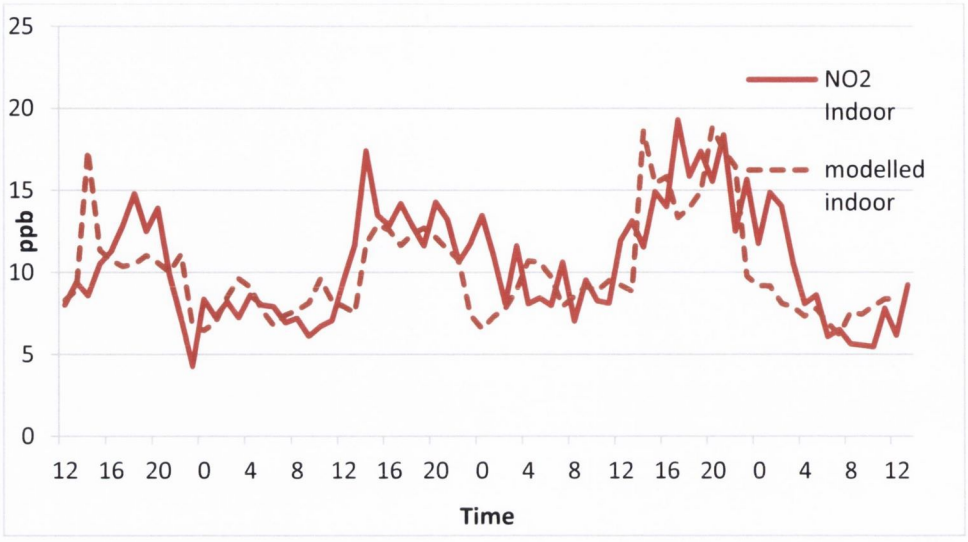

Figure B. 15 Indoor and modelled concentrations for Site 8 run 1

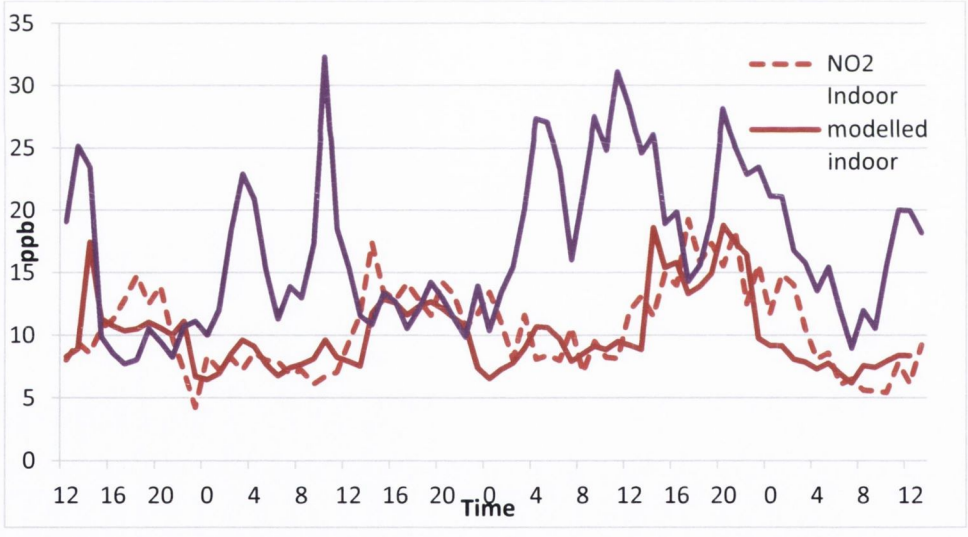

Figure B. 16 Indoor, modelled and outdoor concentrations for Site 8 run 1

The regression analysis of indoor verses outdoor concentrations which was used at other sites to find f_{inf} and source returned f_{inf} values below 0.04 due to the poor interaction. This site required trial and error inputs of parameters until a suitable modelled indoor value was achieved. These parameters are noted in Table B. 8 with the lowest infiltration seen for the morning. Input parameters detailed in Appendix C including the opening hours of the shop and characteristics of the building.

Due to the behaviour of the indoor concentrations at this site the hours for using the three sources and f_{inf} factors needed adjusting - for all other sites these were calculated using the opening hours and known behaviours of outdoor concentrations. The model showed very low infiltration until near midday when concentrations indoors begun to rise due to a presumed indoor source. The outdoor concentrations had seen increases from midnight with no connected increase indoors. Indoor concentrations peaked in the early evening, near closing time. At the same time outdoor concentrations were at a minimum for the day. This indicated an indoor source present during the working day which slowly reduces overnight. This reduction is likely to be due to chemical degradation of NO_2 as during the time when indoor concentrations decrease indoor concentrations rise sharply. The infiltration factor is highest in the afternoon and early evening while the concentrations are rising, the source indoors is also highest at this time.

Table B. 8 Variable parameters for best fit model Site 8 run 1

Parameter	Value
V_d	0.0003
V_d night	0.0110
A/V	0.9
k day	0.0006
k night	0.022
F_{inf}	0.45
F_{inf} night	0.25
F_{inf} early morning	0.1
Source day	8
Source night	7.5
Source early morning	5.6

ix) Best fit NO2 model - Site 9

Site 9 has a smoothed version of the outdoor concentrations which is shown in Figure B. 17 and Figure B. 18. This was achieved by a low infiltration rate provided by the regression calculated using the indoor and outdoor concentrations. A high R^2 = 78.1 % was calculated between actual indoor and modelled indoor concentrations with a regression equation of Indoor = 2.31 + 0.858 Modelled. When 2-Sample T-tests are carried out it is found that indoor and modelled concentrations with 95 % confidence

are statistically significantly indifferent and therefore there is no reason to suspect that modelled does not predict indoor concentrations well (-2.102, 0.672) with a T-Value = -1.02, P-Value = 0.311 and DF = 191. The estimate for the difference is 0.715 ppb.

The input variables given by the user are available in Appendix C while the variables which these inputs generated and the results of the regression equation to find the most applicable F_{inf} and source value are listen in Table B. 9

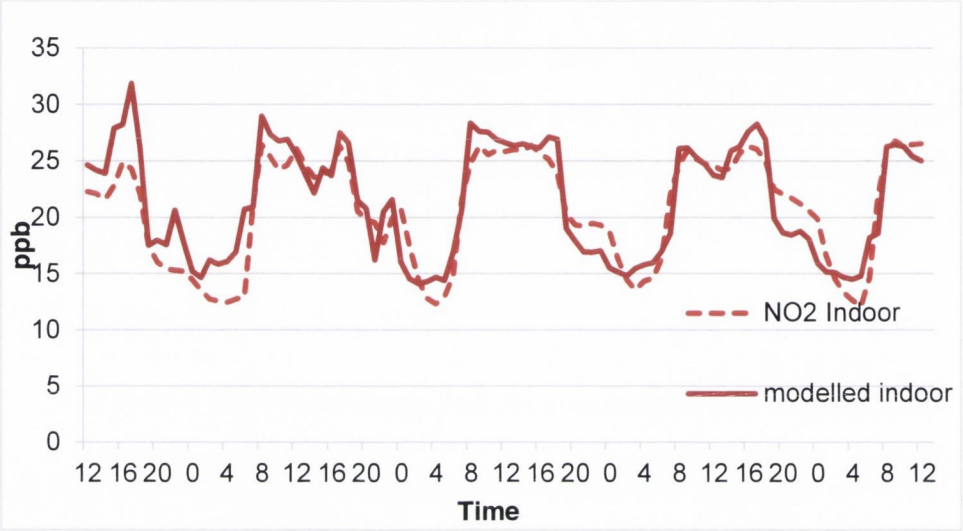

Figure B. 17 Indoor and modelled concentrations for Site 9 run 2

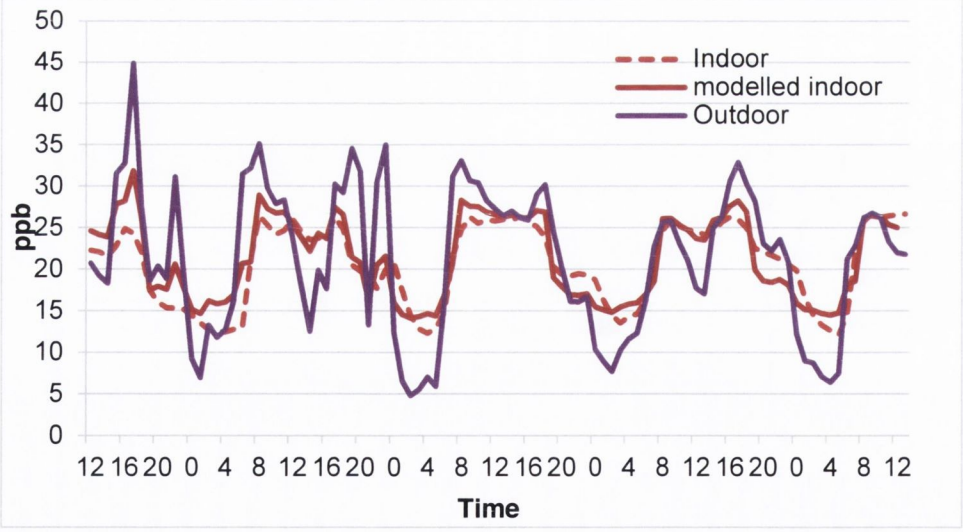

Figure B. 18 Indoor, modelled and outdoor concentrations for Site 9 run 2

Table B. 9 Variable parameters for best fit model Site 9 run 2

Parameter	Value
V_d	0.0003
V_d night	0.011
A/V	0.9
k day	0.00027
k night	0.0099
F_{inf}	0.3
F_{inf} night	0.3
F_{inf} early morning	0.25
Source day	20
Source night	15
Source early morning	15

x) Best fit NO_2 model - Site 10

Site 10 was a mechanically ventilated office which saw a greater influence from street level traffic than the ventilation intake at the roof. When a regression of indoor versus modelled concentrations are R^2 = 74.9 % with a regression equation of Indoor = 2.22 + 0.894 Modelled. A 2 sample T-Test reports a 95 % confidence interval of (-1.304, 1.420) and an estimate for the difference of 0.058 ppb. T-Value = 0.08 P-Value = 0.933 DF = 187. This indicates that statistically there is no reason to believe that there is a difference between the means of actual indoor and modelled indoor concentrations.

The input variables for achieving these results are shown in Appendix C. Infiltrations during day were partially low as indicated via the regression of indoor versus outdoor concentrations. This is likely to be due to the steady concentrations during working hours which were not greatly affected by outdoor concentrations. During non-working hours the influence of street level concentrations fluxes is greater with infiltration playing a larger role. Again, as with many other mechanically ventilated sites a baseline overnight lever was viewed at this site below which NO_2 concentrations did not drop below.

Best fit $PM_{2.5}$ regressions

xi) Best fit $PM_{2.5}$ model - Site 1

Indoor and outdoor $PM_{2.5}$ concentrations at Site 1 showed a R^2 of 1.6 %, see , indicating there is little prediction value of indoor variations using outdoor

concentration. The best fit model is shown in Figure B. 19 and Figure B. 20 for Site 1; this model found a marginally higher R^2 = 5.1 %. Values of this level indicate that the modelled indoor data was not able to account for indoor fluctuations in the $PM_{2.5}$ concentration. The model however did achieve a 95 % confidence interval (CI) for the estimate of the difference between actual indoor and modelled indoor concentrations which contained the null hypothesis that the differences were 0. The 95 % CI estimate was found via a 2 sample T-test with results of (-1.211, 0.885) and an estimate of the difference of 0.163 $\mu g\ m^{-3}$ T-Value = -0.31, P-Value = 0.758 and DF = 92. The smoother modelled data shows a slight diurnal trend. The parameters used in this model are listed in Table B. 10.

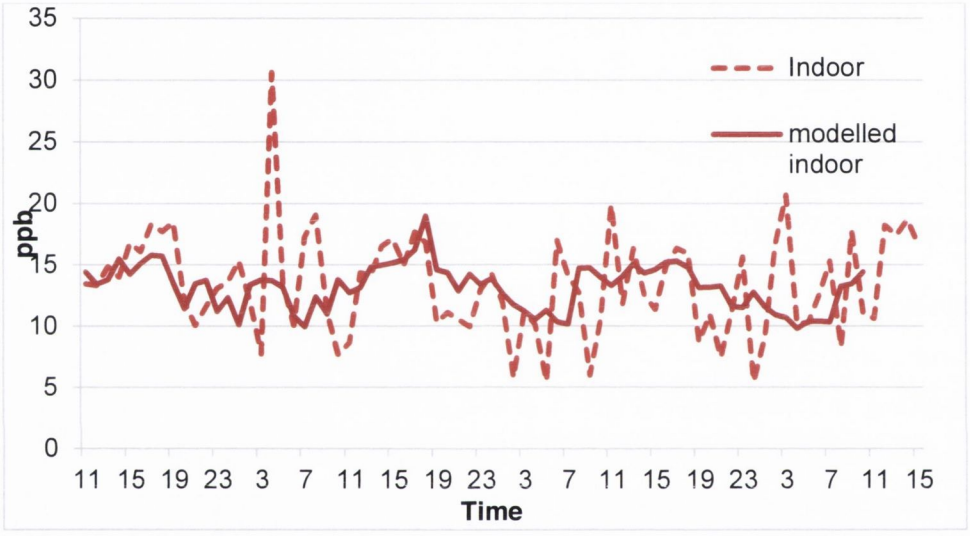

Figure B. 19 Indoor and modelled concentrations for Site 1 run 2

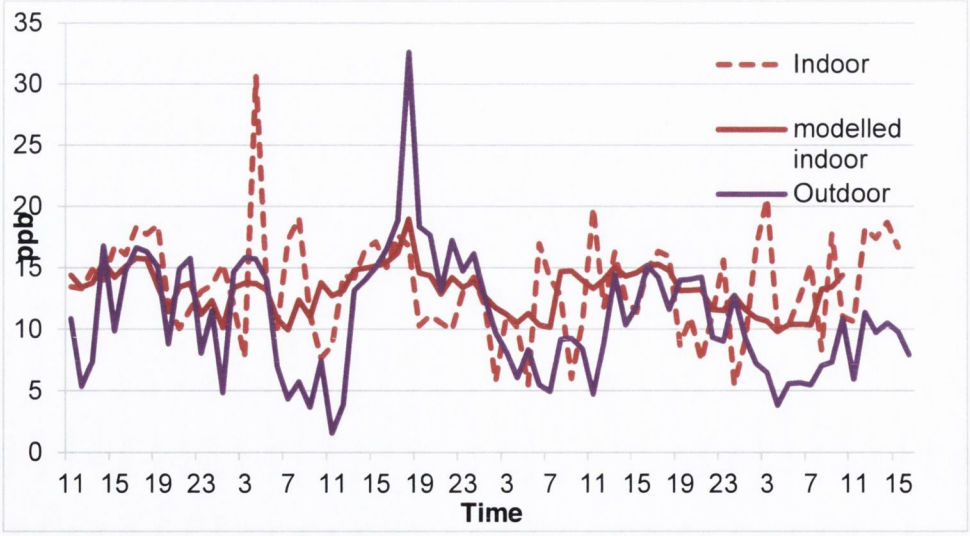

Figure B. 20 Indoor, outdoor and modelled concentrations for Site 1 run 2

Table B. 10 Parameters for individual best fit Site 1

Parameter	Value
V_d	0.05
V_d night	0.0003
A/V	0.9
k day	0.10000
k night	0.00060
F_{inf}	0.20
F_{inf} night	0.33
F_{inf} early morning	0.67
Source day	12.48
Source night	8.56
Source early morning	8.56

xii) Best fit $PM_{2.5}$ model - Site 2

Site 2 again showed a low R^2 value (4.5 %) for actual indoor and modelled indoor concentrations with a 2 sample T-test producing a 95% CI for difference between the two of (-0.175, 1.237) and an estimate for difference of 0.531 μg m^{-3}, T-Value = 1.49, P-Value = 0.139 and DF = 121. The correlation between outdoor and indoor values was 1.4 % indicating that fluctuations outdoors do not predict indoor changes in concentrations well. While the fluctuations were difficult to predict it was possible to show general trends and achieve a statistically indifferent exposure concentration using the model as shown in Figure B. 21 and Figure B. 22. The inputs used are shown in Table B. 11, these differed from the figures calculated via the regression with a great f_{inf} and lower source during working hours. These gave a better estimate for the difference and R^2 than use of the original data.

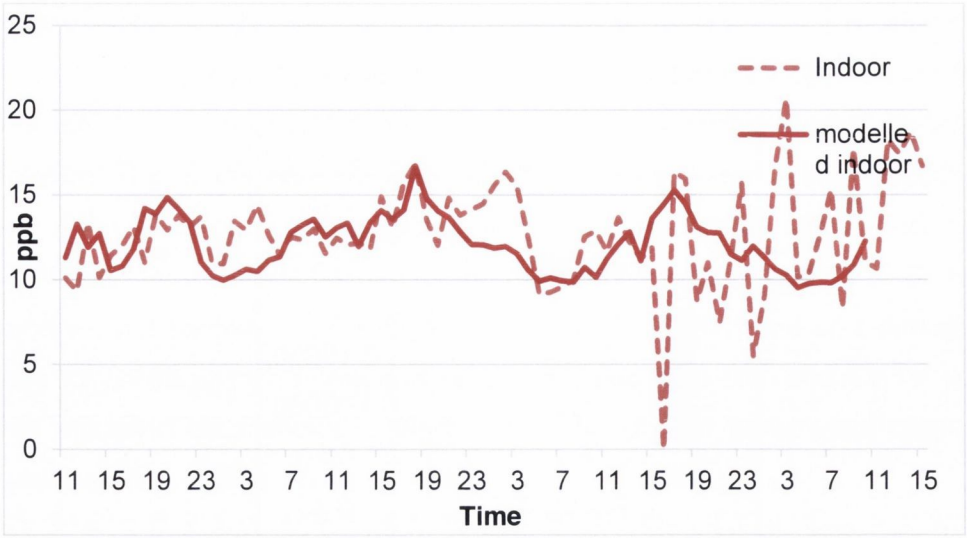

Figure B. 21 Indoor and modelled concentrations for Site 2 run 2

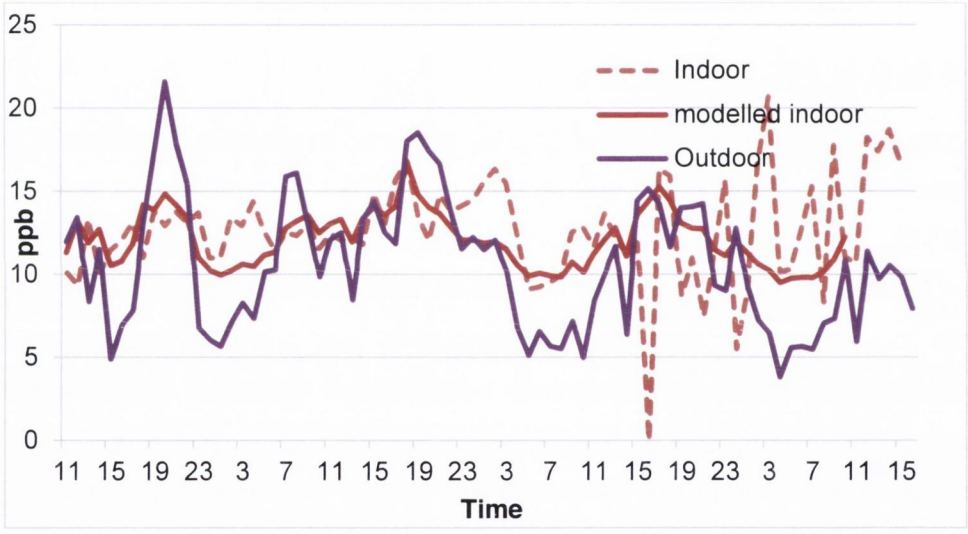

Figure B. 22 Indoor, outdoor and modelled concentrations for Site 2 run 2

Table B. 11 Parameters for individual best fit Site 2

Parameter	Value
V_d	0.05
V_d night	0.0003
A/V	0.9
k day	0.1
k night	0.0006
F_{inf}	0.2
F_{inf} night	0.05
F_{inf} early morning	0.05
Source day	6
Source night	6
Source early morning	6

xiii) Best fit $PM_{2.5}$ model - Site 3

Site 3 has the highest R^2 (11.4 %) between indoor and outdoor concentrations out of the first 3 sites see Figure B. 24. The results of this is the achievement of a higher R^2 = 21.1 % between actual indoor and modelled data. Again modelled indoor data was found using a 2 sample T-test to be statistically indifferent (-0.114, 1.702) from indoor data with 95 % confidence, with an estimate of the difference of 0.794 $\mu g\ m^{-3}$, T-Value = 1.73, P-Value = 0.086 and DF = 99. The plot shown in Figure B. 23 shows the relationship between actual indoor and modelled indoor concentrations, and again the outdoor concentrations which are shown in Figure B. 23 display a great diurnal trend than indoors. Two large peaks on day 1 and 2 are not detected by the model and during these periods inhabitants of the monitored building would experience greater indoor exposure than suggested by the model.

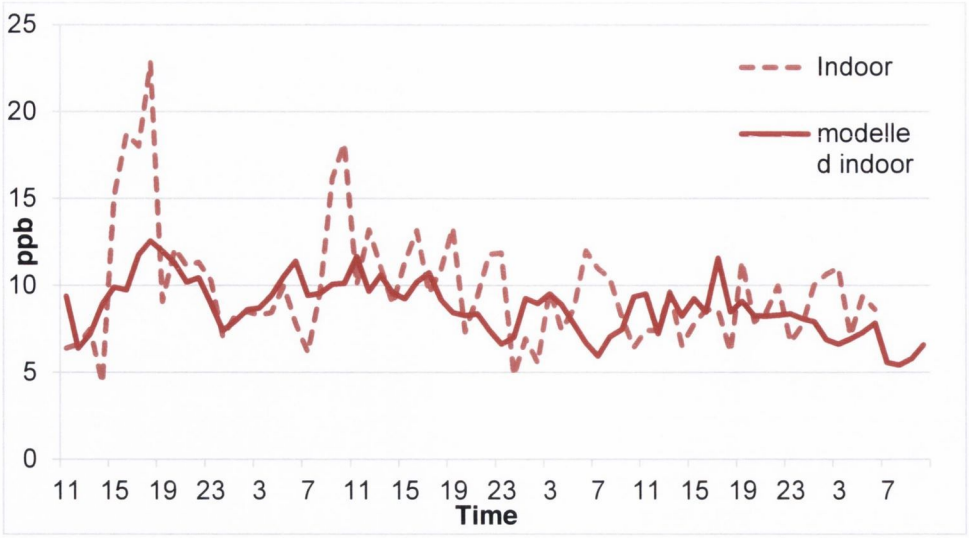

Figure B. 23 Indoor and modelled concentrations for Site 3 run 2

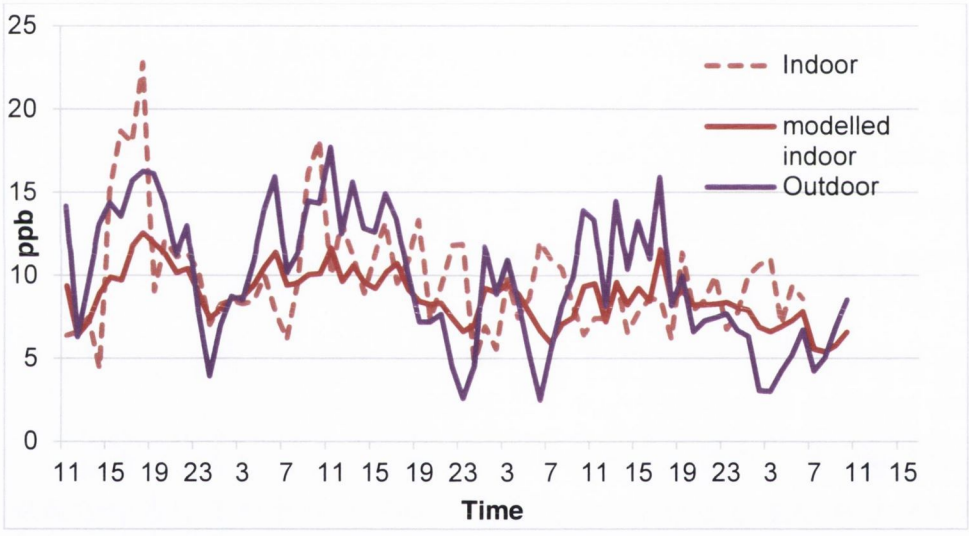

Figure B. 24 Indoor, outdoor and modelled concentrations for Site 3 run 2

Table B. 12 Parameters for individual best fit Site 3

Parameter	Value
V_d	0.05
V_d night	0.0003
A/V	2
k day	0.1
k night	0.0006
F_{inf}	0.3
F_{inf} night	0.1
F_{inf} early morning	-0.12
Source day	1.5
Source night	3
Source early morning	4

xiv) Best fit $PM_{2.5}$ model - Site 4

Site 4 run 1 showed a R^2 of 0 % between indoor and outdoor concentrations, with the relationship seen in Figure B. 25. For NO_2 the relationship between indoor and outdoor was an R^2 = 51 %, considerably higher than the value found for $PM_{2.5.}$ The modelled indoor concentrations achieved a R^2 = 5 % (T-Value =- -0.92, P-Value = 0.359) and produced an estimate of the difference between actual indoor and modelled indoor of 1.096 $\mu g\ m^{-3}$ lying marginally outside the 95 % confidence interval of a 2 sample T-test T-Value = 4.35, P-Value = 0.000 and DF = 114. Indoor concentrations range between 15 -20 $\mu g\ m^{-3}$ with outdoor concentrations having a very weak influence, as indicated in the R^2 of 0. This lead to difficulty calculating the indoor concentrations via the model, f_{inf} values remained small and accounted for some variations but mean modelled concentrations required a large source to reach the range as indoor concentrations. Modelled concentrations ran on the low side for the 1st night into the second morning as indoor concentrations produced lower concentrations; reducing the f_{inf} further did not produce better results.

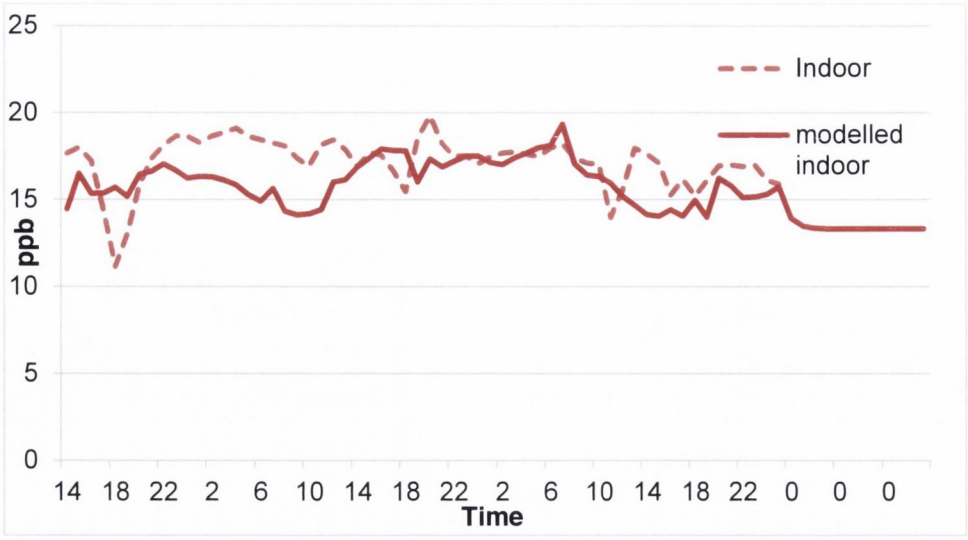

Figure B. 25 Indoor and modelled concentrations for Site 4 run 1

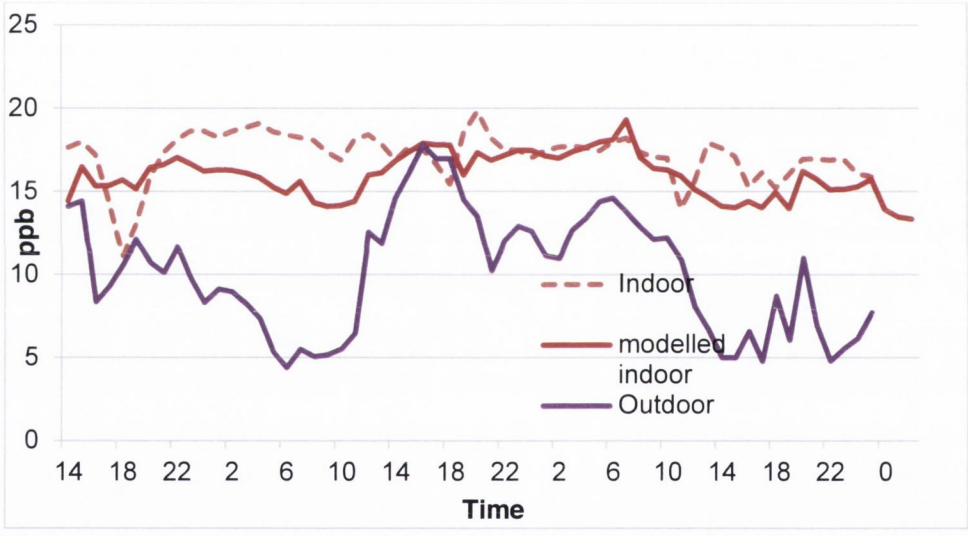

Figure B. 26 Indoor, outdoor and modelled concentrations for Site 4 run 1

Table B. 13 Parameters for individual best fit Site 4

Parameter	Value
V_d	0.1
V_d night	0.0003
A/V	0.5
k day	0.2
k night	0.0006
F_{inf}	0.15
F_{inf} night	0.05
F_{inf} early morning	0.15
Source day	10
Source night	12
Source early morning	10

xv) Best fit $PM_{2.5}$ model - Site 5

The results at site 5 of the best fit model for $PM_{2.5}$ showed an increased R^2 from 0.7 % between indoor and outdoor concentrations up to 31.4 % for actual indoor and modelled indoor concentrations. R-Sq = 31.4%. The site showed an estimate of the difference of 1.56 μg m^{-3} with modelling concentrations showing the higher values on average and again very marginally outside the 95 % CI for a 2 sample T-test (-2.535, -0.777), T-Value = -3.73, P-Value = 0.000 and DF = 133. This is due to a decrease occurring indoors on the last day of monitoring which was not accounted for within the model as the f_{inf} factor is very low. The times that these reductions did occur did not correlate to outdoor data. The low f_{inf} was generated through the regression equations described previously and occurs as the relationship between indoor and outdoor is very poor (R^2=0.7 %) and for the fluctuations outdoors that do influence the indoor concentrations they do so with varying lag and level of influence, therefore no set relationship can be determined.

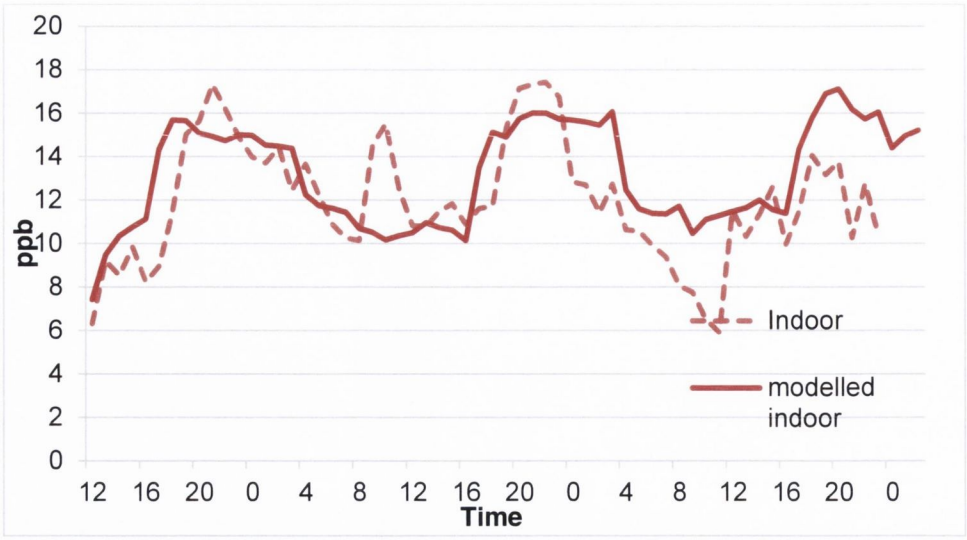

Figure B. 27 Indoor and modelled concentrations for Site 5 run 1

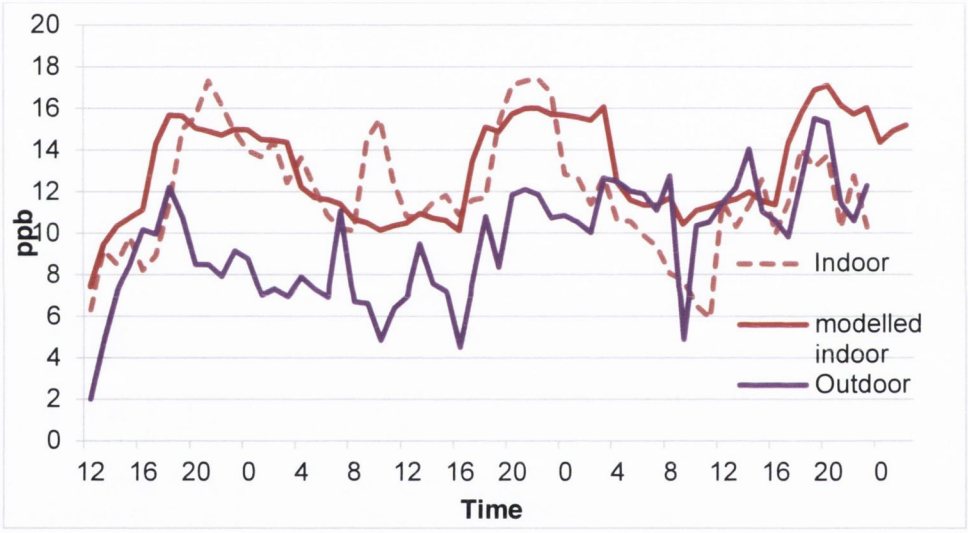

Figure B. 28 Indoor, outdoor and modelled concentrations for Site 5 run 1

Table B. 14 Parameters for individual best fit Site 5

Parameter	Value
V_d	0.05
V_d night	0.00
A/V	0.90
k day	0.10
k night	0.00
F_{inf}	0.01
F_{inf} night	0.06
F_{inf} early morning	-0.24
Source day	7.00
Source night	9.00
Source early morning	9.00

xvi) Best fit $PM_{2.5}$ model - Site 6

The modelled $PM_{2.5}$ data at Site 6 follows the trend within indoor data but does not account for the fluctuations. Similar to most other sites, the $PM_{2.5}$ indoor and outdoor concentrations vary around a mean value but do not show connected peaks. For this reason the model returned a smoothed trend for indoors which shows an R^2 between actual indoor and modelled indoor of 10 %. However, if the exposure level is considered the mean values are tested using a 2 sample T-test the difference of the means lies within the 95 % CI (-0.039, 1.246) with an estimate of the difference of 0.603 $\mu g\ m^{-3}$, T-Value = 1.86, P-Value = 0.066 and DF = 128

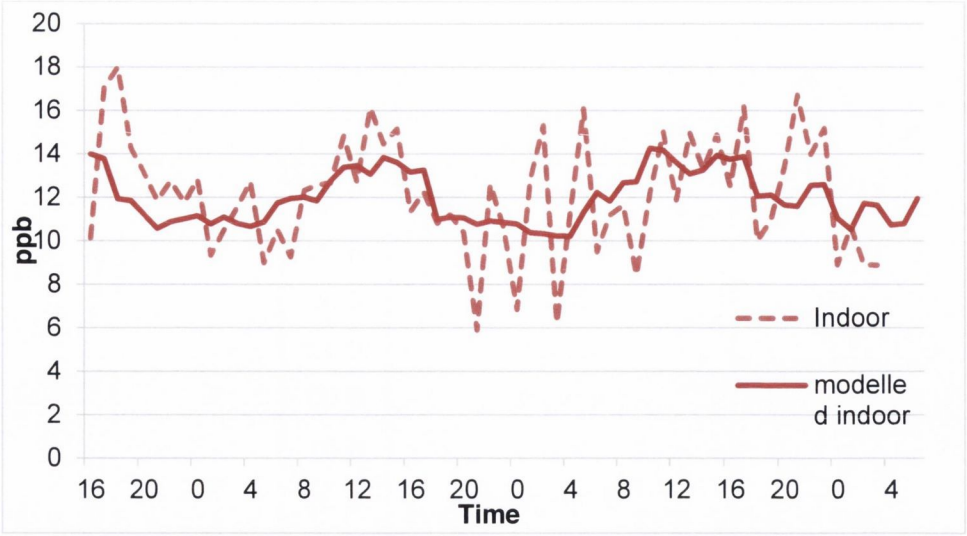

Figure B. 29 Indoor and modelled concentrations for Site 6 run 2

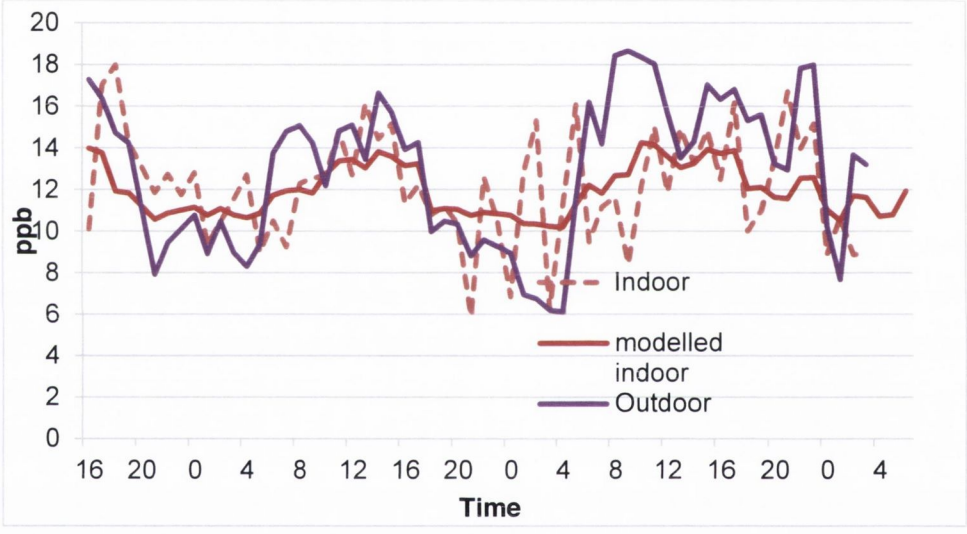

Figure B. 30 Indoor, outdoor and modelled concentrations for Site 6 run 2

Table B. 15 Parameters for individual best fit Site 6

Parameter	Value
V_d	0.0500
V_d night	0.0003
A/V	2.00
k day	0.10
k night	0.0006
F_{inf}	0.27
F_{inf} night	0.20
F_{inf} early morning	0.20
Source day	9.76
Source night	9.00
Source early morning	9.00

xvii) Best fit $PM_{2.5}$ model - Site 7

Site 7 did not show as many short term fluctuations indoors or outdoors as many of the other sites. Two large indoor peaks were shown inside (see Figure B. 31 and Figure B. 32) that did not show any connected outdoor peaks. As the model uses outdoor concentrations to calculate indoor concentrations it does not account for unexpected indoor peaks. If this peak is removed in order to calculate a 2 sample T-test of the difference of the means between actual indoor and modelled indoor data the result returns an estimate of the difference of 0.166 μg m^{-3}. The 95% CI (-0.762, 1.095) includes 0 therefore we cannot be confident (at the 95% level) that these data show any difference between actual indoor and modelled indoor data; T-Value = 1.50, P-Value = 0.137 and DF = 74. The f_{inf} for working hours for this site is the highest calculated, as shown in Table B. 16 indicating that there was a strong connection between indoor and outdoor data and a high number of air changes and high penetration factor.

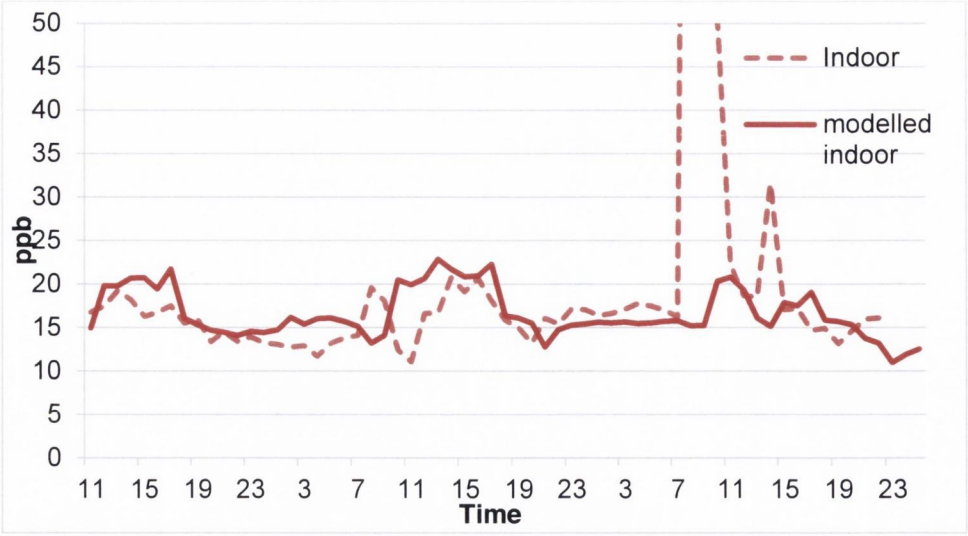

Figure B. 31 Indoor and modelled concentrations for Site 7 run 1

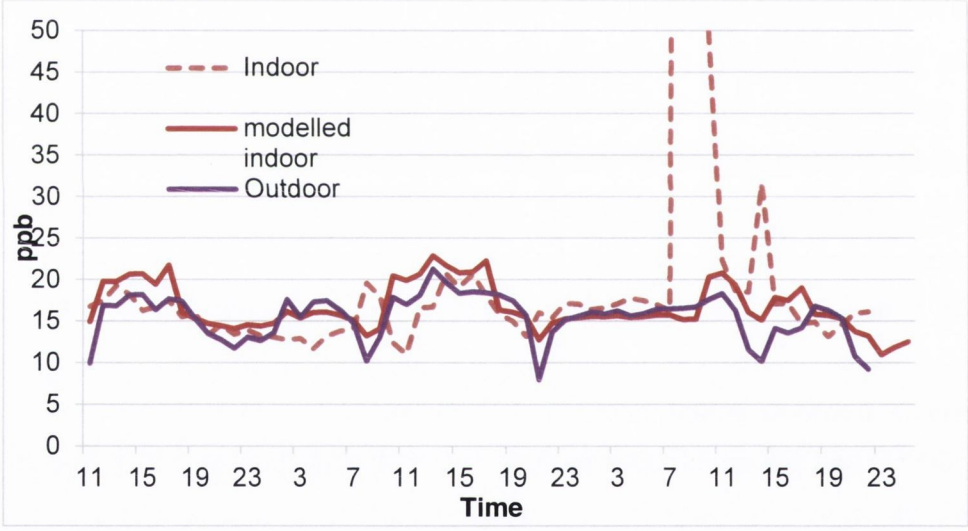

Figure B. 32 Indoor, outdoor and modelled concentrations for Site 7 run 1

Table B. 16 Parameters for individual best fit Site 7

Parameter	Value
V_d	0.0500
V_d night	0.0003
A/V	2.00
k day	0.10
k night	0.0006
F_{inf}	0.78
F_{inf} night	0.35
F_{inf} early morning	0.35
Source day	8.00
Source night	10.00
Source early morning	10.00

xviii) Best fit $PM_{2.5}$ model - Site 8

In general indoor and outdoor data showed a low correlation with an R^2= 3 % for Site 8, with both sites showing variation around a mean value of about 11.5 µg m^{-3}. While the model was not able to achieve correlation with fluctuations indoors due to the low prediction ability of outdoor data, it did produce a 95% CI (-0.863, 0.274) which included 0, therefore we cannot be confident that there is a difference between actual indoor and modelled indoor data; T-Value = -1.02, P-Value = 0.307 and DF = 163. The estimate of the difference was 0.295 µg m^{-3} showing modelled indoor concentrations marginally higher than actual indoor concentrations.

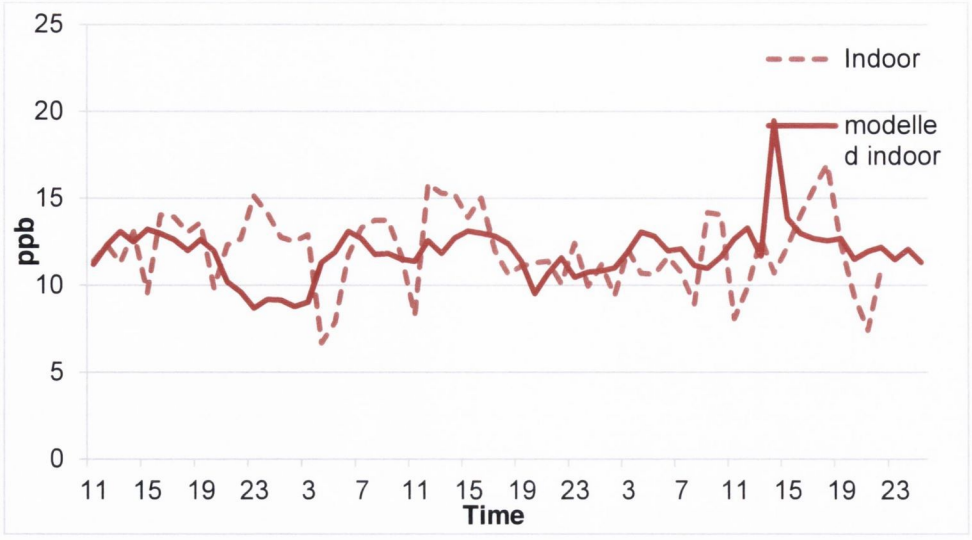

Figure B. 33 Indoor and modelled concentrations for Site 8 run 1

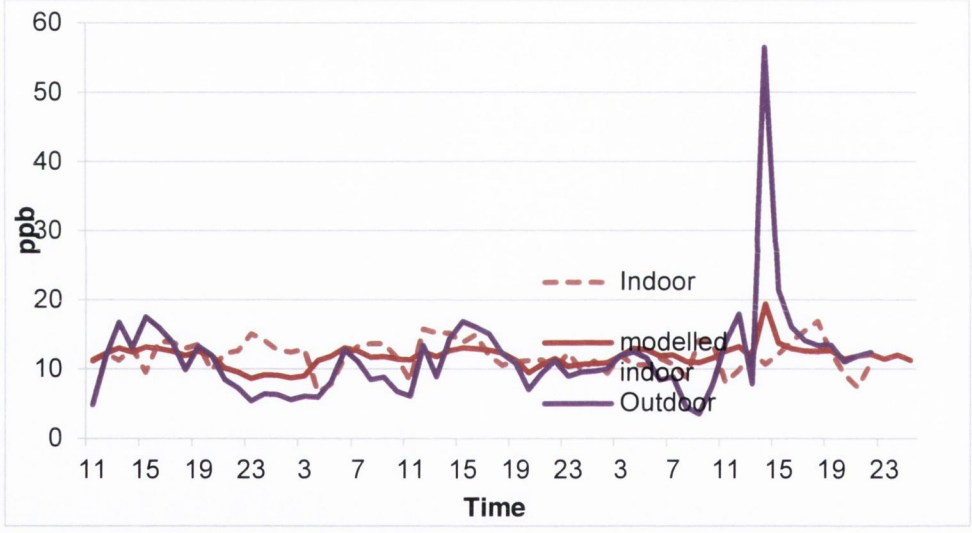

Figure B. 34 Indoor, outdoor and modelled concentrations for Site 8 run 1

Table B. 17 Parameters for individual best fit Site 8

Parameter	Value
V_d	0.1000
V_d night	0.0003
A/V	0.50
k day	0.20
k night	0.0006
F_{inf}	0.20
F_{inf} night	0.50
F_{inf} early morning	0.26
Source day	10.41
Source night	9.74
Source early morning	5.97

xix) Best fit $PM_{2.5}$ model - Site 9

Indoor concentrations were significantly greater than outdoor concentrations at Site 9 for $PM_{2.5}$, with slight indications of negatively correlated trends, but generally little correlation (R^2= 5.6 %). When user data was inputted, the model gave parameters as shown in Table B. 18 and the produced modelled indoor concentrations can be seen in Figure B. 35 and Figure B. 36. The estimate for the difference in actual indoor and modelled indoor concentrations when a 2 sample T-test is carried out is 0.159 μg m^{-3} with a 95 % CI for the difference between the actual indoor and modelled indoor of (-0.305, 0.624), T-Value = 0.68, P-Value = 0.498 and DF = 107.

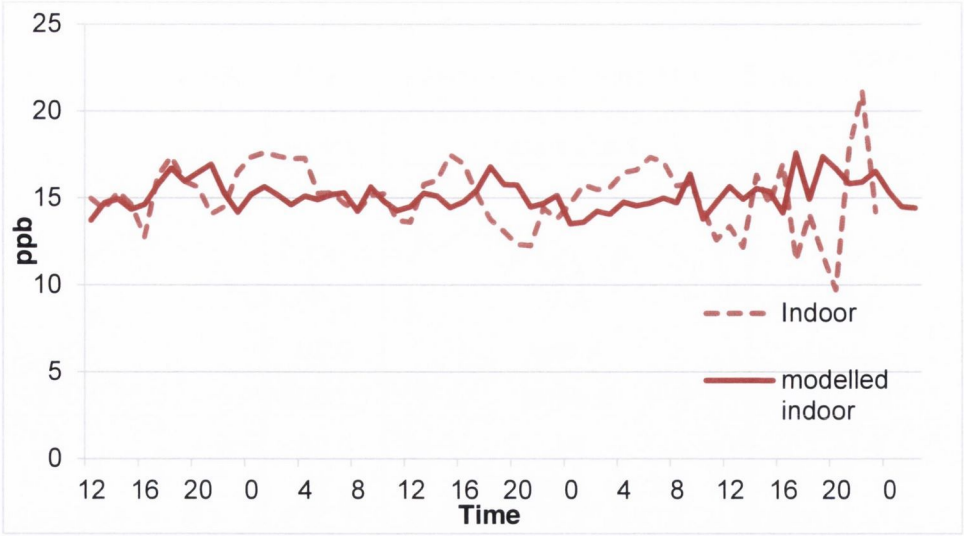

Figure B. 35 Indoor and modelled concentrations for Site 9 run 1

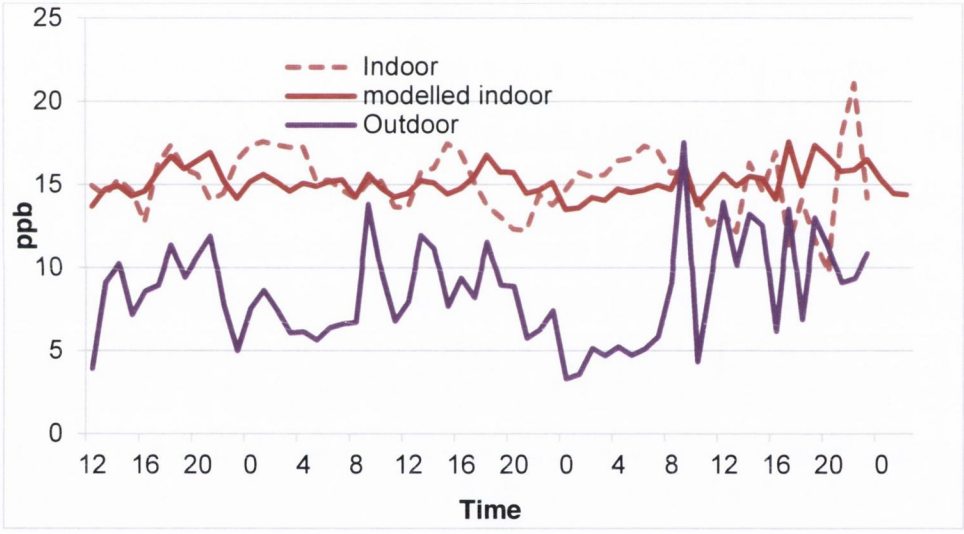

Figure B. 36 Indoor, outdoor and modelled concentrations for Site 9 run 1

Table B. 18 Parameters for individual best fit Site 9

Parameter	Value
V_d	0.0500
V_d night	0.0003
A/V	0.90
k day	0.10
k night	0.0006
F_{inf}	0.22
F_{inf} night	0.40
F_{inf} early morning	0.40
Source day	12.95
Source night	12.65
Source early morning	12.18

xx) Best fit $PM_{2.5}$ model - Site 10

Site 10 shows a correlation between indoor and outdoor data of 2.9 %, with indoor concentrations having generally higher concentrations as shown in Figure B. 37 and Figure B. 38. Due to the low correlations between the outdoor and indoor data there are also low correlations of the modelled indoor data and actual indoor data as modelled data is produced from the outdoor concentrations. While the model does not predict the fluctuations well it does provide a perfectly matching mean value, with a 2 sample T-Test producing an estimate of the difference between actual indoor and modelled indoor data of 0 $\mu g\ m^{-3}$, the 95 % CI for the mean differences is (-1.043, 1.043) and T-Value = -0.00 P-Value = 1.000 DF = 149.

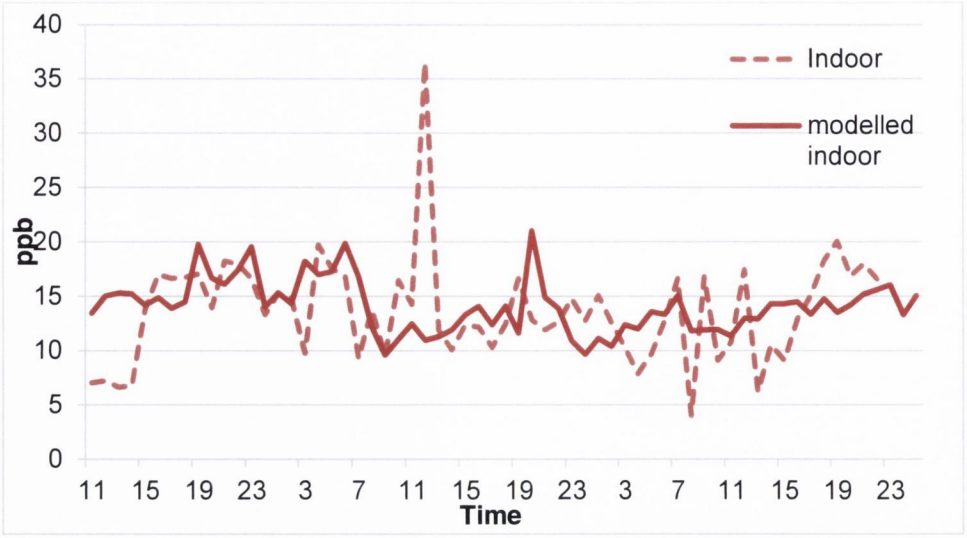

Figure B. 37 Indoor and modelled concentrations for Site 10 run 1

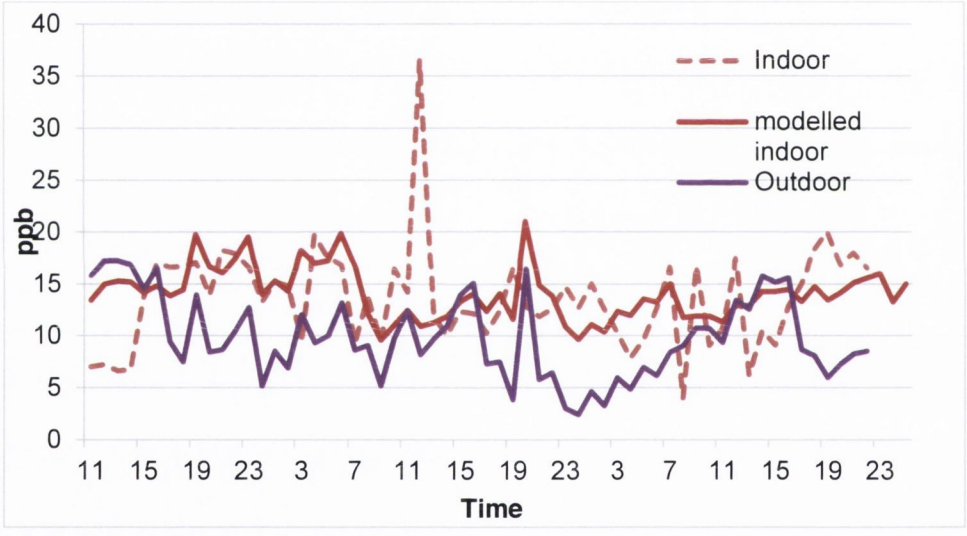

Figure B. 38 Parameters for individual best fit Site10

Table B. 19 Parameters for individual best fit Site 9

Parameter	Value
V_d	0.1000
V_d night	0.0003
A/V	0.50
k day	0.20
k night	0.0006
F_{inf}	0.34
F_{inf} night	0.60
F_{inf} early morning	0.60
Source day	5.00
Source night	5.00
Source early morning	5.00

Appendix C. Input Parameters for Mass Balance Model

Answer	What statement best describes your building:
Site2 Run2	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
3	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
3	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
18	What time does mechanical ventilation turn off evening (24hour clock),0 if none
1	What best describes the room: (1)An open space (2) normal (3) cluttered
0	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
1	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site3 Run2	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
2	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
18	What time does mechanical ventilation turn off evening (24hour clock),0 if none
3	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
1	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site3 Run2	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
2	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
18	What time does mechanical ventilation turn off evening (24hour clock),0 if none
3	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
1	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site4 Run2	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
2	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
20	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
20	What time does mechanical ventilation turn off evening (24hour clock),0 if none
1	What best describes the room: (1)An open space (2) normal (3) cluttered
0	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site 5 Run1	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
1	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
1	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
17	What time does building close in evening (24hour clock)
8	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
17	What time does mechanical ventilation turn off evening (24hour clock),0 if none
1	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site 6 Run2	What is this site name?
0	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
3	Is the building energy efficient: (1) very (2) normal (3) not efficient
10	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
-	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
-	What time does mechanical ventilation turn off evening (24hour clock),0 if none
3	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
1	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)

0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site 7 Run1	What is this site name?
0	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
3	Is the building energy efficient: (1) very (2) normal (3) not efficient
10	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
-	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
-	What time does mechanical ventilation turn off evening (24hour clock),0 if none
3	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
1	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site 8 Run1	What is this site name?
0	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
3	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
19	What time does building close in evening (24hour clock)
-	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
-	What time does mechanical ventilation turn off evening (24hour clock),0 if none
2	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site9 Run2	What is this site name?
0	Is the building Mechanically (1) or naturally (0) ventilated
3	Are the window/doors in the room closed (1), half open (2), Fully open (3)
2	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
3	Is the building energy efficient: (1) very (2) normal (3) not efficient
9	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
-	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
-	What time does mechanical ventilation turn off evening (24hour clock),0 if none
3	What best describes the room: (1)An open space (2) normal (3) cluttered
1	Does the room have carpeting: yes (1) no (0)
1	Is the building showing any signs of damp: yes (1) no (0)
0	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Answer	What statement best describes your building:
Site10 Run1	What is this site name?
1	Is the building Mechanically (1) or naturally (0) ventilated
1	Are the window/doors in the room closed (1), half open (2), Fully open (3)
1	Is the building: Air tight (1) very air tight (2) normal (3) leaky building
2	Is the building energy efficient: (1) very (2) normal (3) not efficient
8	What time does building open in morning (24hour clock)
18	What time does building close in evening (24hour clock)
23	What time does mechanical ventilation turn on in morning (24hour clock),0 if none
0	What time does mechanical ventilation turn off evening (24hour clock),0 if none
1	What best describes the room: (1)An open space (2) normal (3) cluttered
0	Does the room have carpeting: yes (1) no (0)
0	Is the building showing any signs of damp: yes (1) no (0)
1	Does the room have a false ceiling: yes (1) no (0)
0	Does the building have a gas cooker e.g. in a canteen yes (1) no (0)

Appendix D: Artificial Neural Networks

NO_2 artificial neural network model performance

Site 1 (Naturally ventilated shop)

The time series of neural network training for NO_2 is shown in Figure D. 2. The errors are less than 12 % of the range of the data with the errors occurring at times of sharp changes between one data point and another. For instance, the large first error of about – 4 which occurs at Time = 6 on the x axis (contained within the circle), is 11.7 % range of the output data but it fits closely to the plot of the target data set. If this large error point, which was calculated while training the data set, was used rather than the known target data the effect on output would be marginal as it does not vary the time series trend. The same can be said for all other error points throughout the data set.

The data set provides an R value of 0.967 for the testing of the trained data set using the target values provided as can be seen in Figure D. 1.

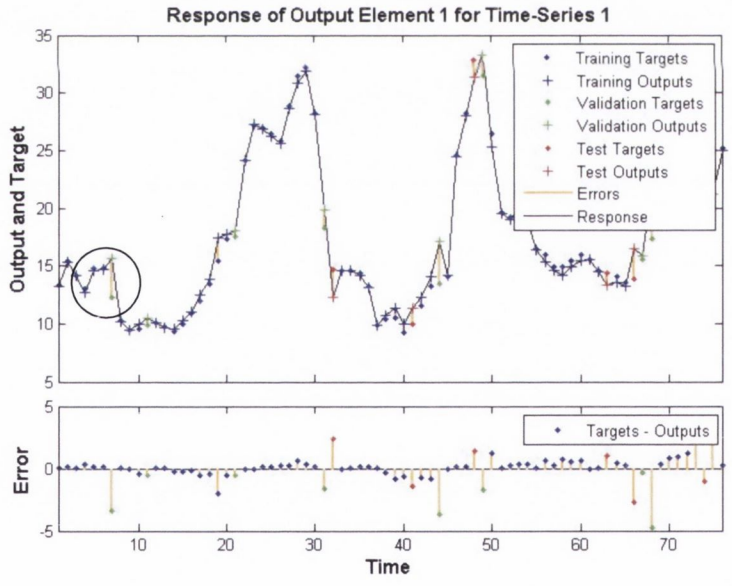

Figure D. 1 Time series of neural network training Site 1 run 2 NO_2

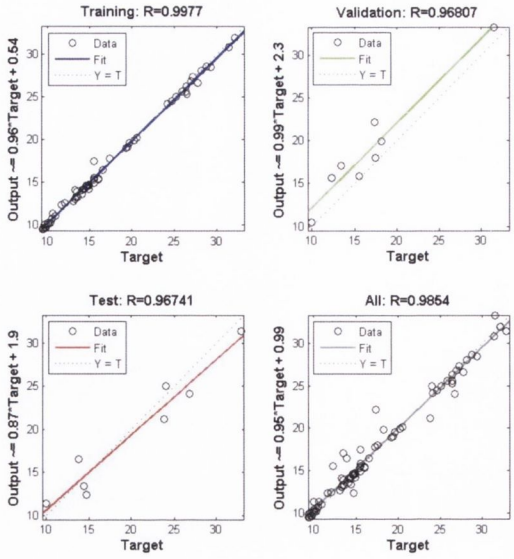

Figure D. 2 Site 1 run 2 NO_2 Regression of trained output data set

Site 2 (Mechanically ventilated Office)

The data collected at Site 2 produces a very strong trained network with very few errors all of which are less than 3 ppb as can be seen in Figure D. 3. The error histogram for this Neural Network shows the errors to range between -2.55 to 2.48 although only 5 instances occur outside the range of -0.434 to 0.890. The regression plot for the testing of the trained Neural Network shows a good R value of 0.939 as seen in Figure D. 4.

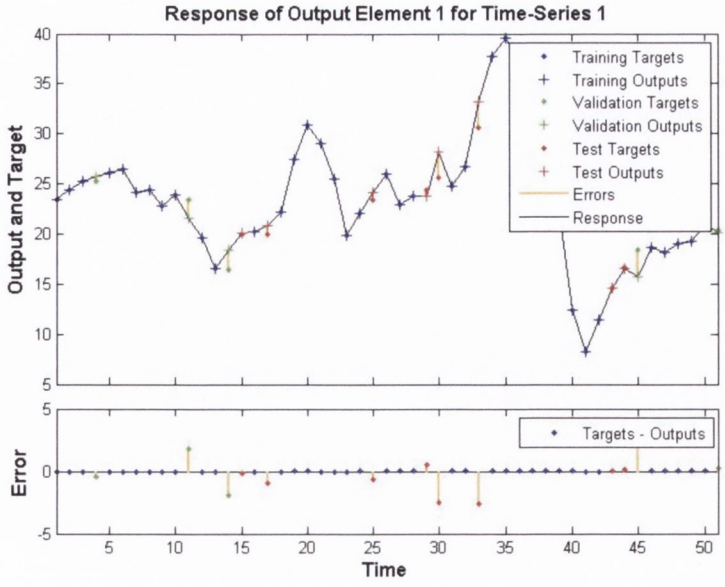

Figure D. 3 Time series of neural network training Site 2 run 2 NO_2

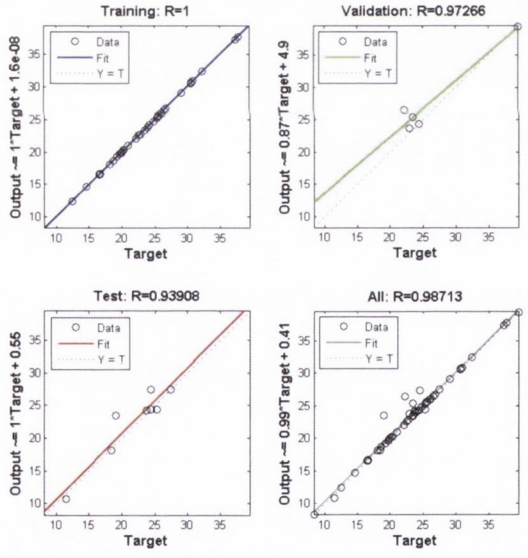

Figure D. 4 Site 2 run 2 NO_2 regression of trained output data set

Site 3 (Mechanically ventilated Office)

The trained data set for Site 3 produces another strong R value of 0.967 for testing, with an overall R of 0.990 for the testing, validation and training periods, see Figure D. 6. The time series of training, validation and test data shown in Figure D. 5 again shows the errors occurring at points which make little difference to the trend-line between the previous and proceeding data point.

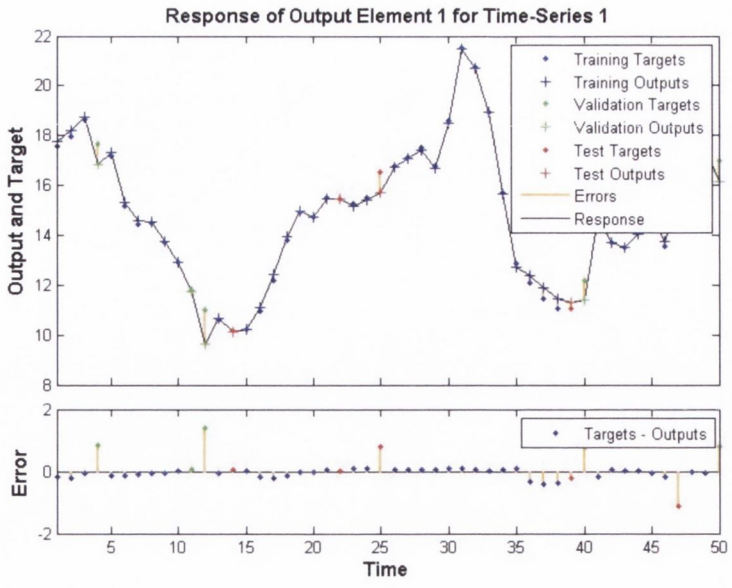

Figure D. 5 Time series of neural network training Site 3 run 1 NO_2

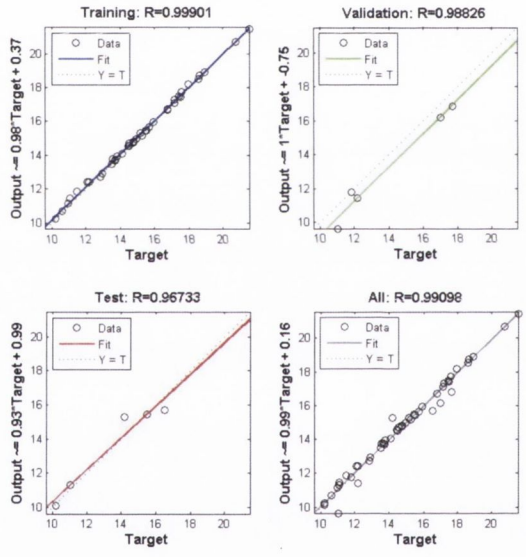

Figure D. 6 Site 3 run 1 NO_2 regression of trained output data set

Site 3 run 2 shows only 2 errors above 1 ppb, the highest of which occurs at Time = 52 ,(i.e. 52 hours into the data set). As seen in previously generated networks this error point occurred when a sharp unexpected rise occurred in the data set. While the error is high (spanning nearly 33 % of the range of the target data) it does not significantly change the trend-line for the data series. R = 0.961 for testing of the newly trained network, with a perfect fit for the training period data. Best subset regressions had found R^2 values above 80 % without using the hidden networks which neural networks

uses for training data sets, hence its ability to find such high R values for the modelled data.

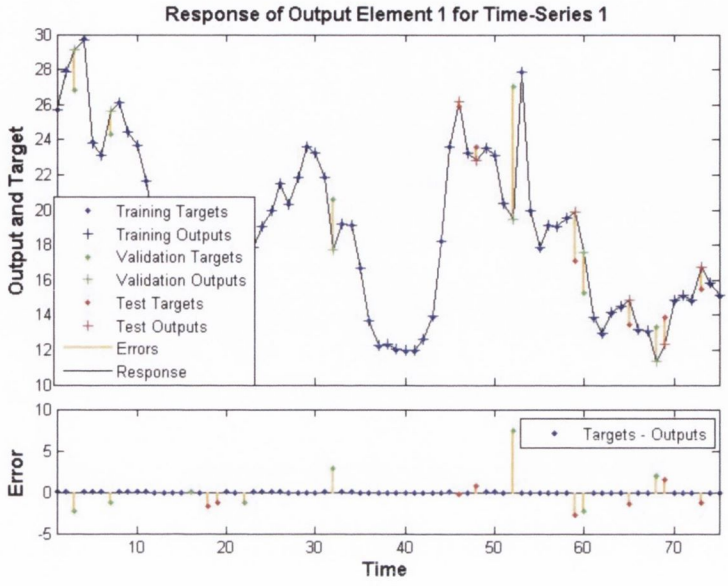

Figure D. 7 Time series of neural network training Site 3 run 2 NO_2

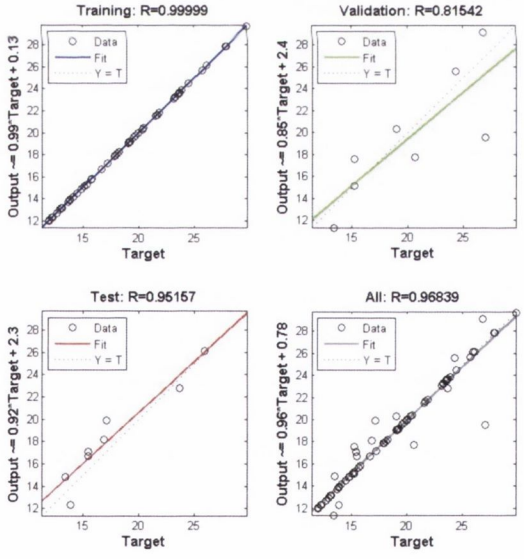

Figure D. 8 Site 3 run 2 NO_2 regression of trained output data set

Site 4 (Mechanically ventilated Gallery Space)

The errors for Site 4 run 1 are in the range of 1 ppb (Figure D. 9), with a high test data set R value of 0.988 (Figure D. 10) showing that a well-trained Neural Network was developed using the meteorological variables and outdoor concentrations of NO_2 to predict indoor concentrations. Best subset regressions showed high R^2 values of 79.9% when the same variables are used. The hidden interactions or neurons help the trained Neural Network to predict the indoor concentrations. During training the affect of meteorological factors and outdoor concentrations on indoor concentrations will create these hidden interactions that may not be seen through simple regressions.

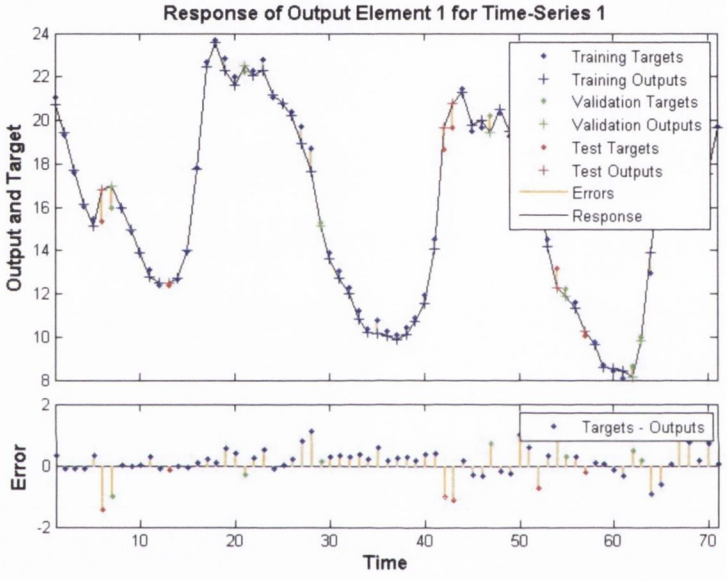

Figure D. 9 Time series of neural network training Site 4 run 1 NO_2

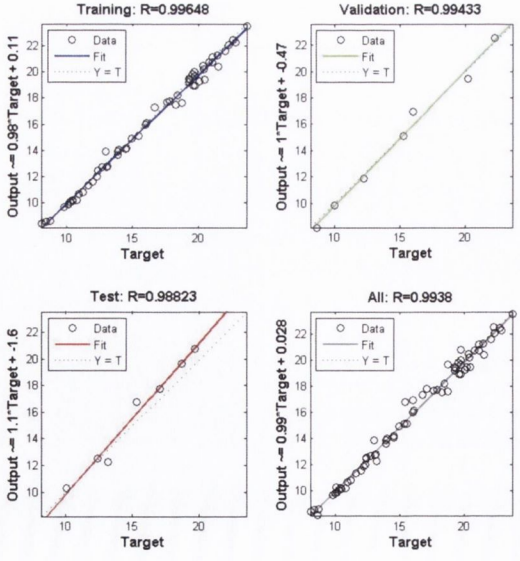

Figure D. 10 Site 4 run 1 NO_2 regression of trained output data set

Like run 1, run 2 also shows a very well trained Neural Network with few errors. The training targets show almost no error while some errors up to 6 ppb can be seen for validation and test data. These errors do not have high leverage to the data set and although they may seem high, little difference is made to the data series trend-line if the trained point was used rather than the inputted target variable. For an example of this, the error occurring at Time = 42 in Figure D. 11(circled) while being large is only marginally away from the trend-line of the data and if used would not significantly affect this trend-line due to the positioning of the previous and proceeding data points. Figure D. 12 shows the regression of the training, validation and test data, with test data showing an R = 0.964 for Site 4 run 2.

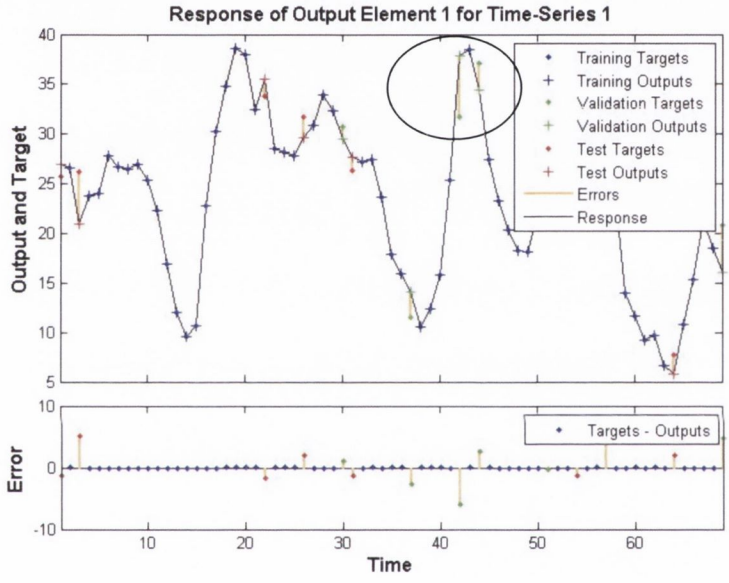

Figure D. 11 Time series of neural network training Site 4 run 2 NO_2

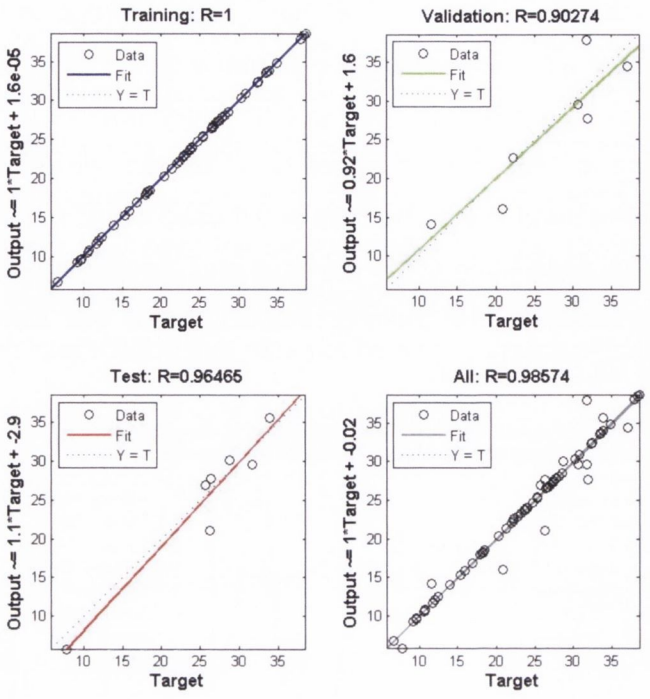

Figure D. 12 Site 4 run 2 NO_2 regression of trained output data set

Site 5 (Mechanically ventilated Office)

Site 5 produces slightly over estimated training targets for much of the time series plot although these are of magnitude of less than 1 ppb (Figure D. 13). The second half of the data set shows some larger errors, but none of magnitude more than 2 ppb. The R value for test data is strong at 0.977 with a lower R value seen for the validation points 0.850, as shown in Figure D. 13. Studying the time series, many of the larger errors can be seen to be represented by green dots indicating that they occurred during the validation phase.

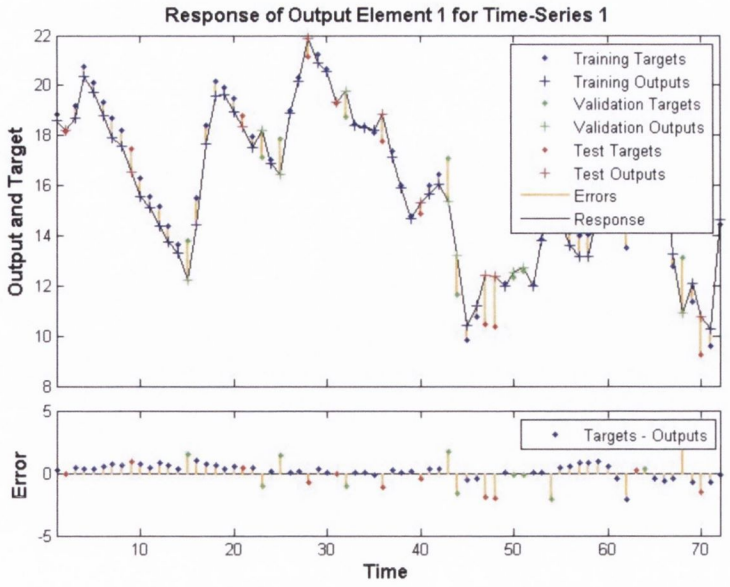

Figure D. 13 Time series of neural network training Site 5 run 1 NO_2

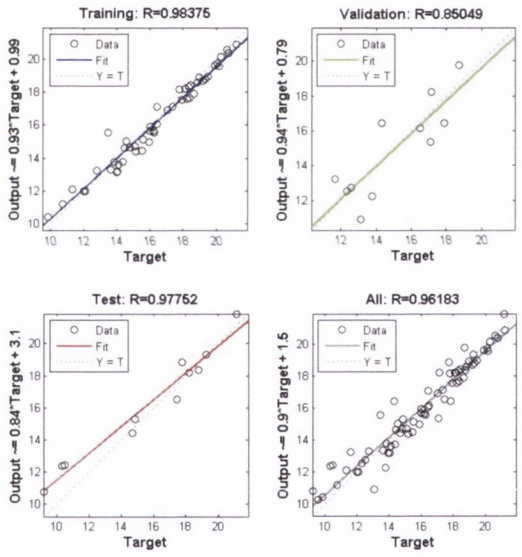

Figure D. 14 Site 5 run 1 NO_2 regression of trained output data set

Site 6 (Naturally ventilated Office)

The difference between indoor and outdoor concentrations for Site 6 was significant during both runs, due to an unknown process, (suspected to be heterogeneous reactions) significantly influencing the data set. These reactions caused very low indoor concentrations of less than 9 ppb during run 1. Only 1 error above 1 ppb occurs on the second morning near hour 25, see Figure D. 16. This error occurred at a point of a sharp spike, and similar to previous sites does not affect the trend-line. Errors occurring

between the hours of 35 and 50 however do drag the trend-line down by 1 ppb which is a considerable error as the range here is only between 3 ppb and 9 ppb. Figure D. 16 gives an R of 0.956 for the testing of the trained neural network through the validation period.

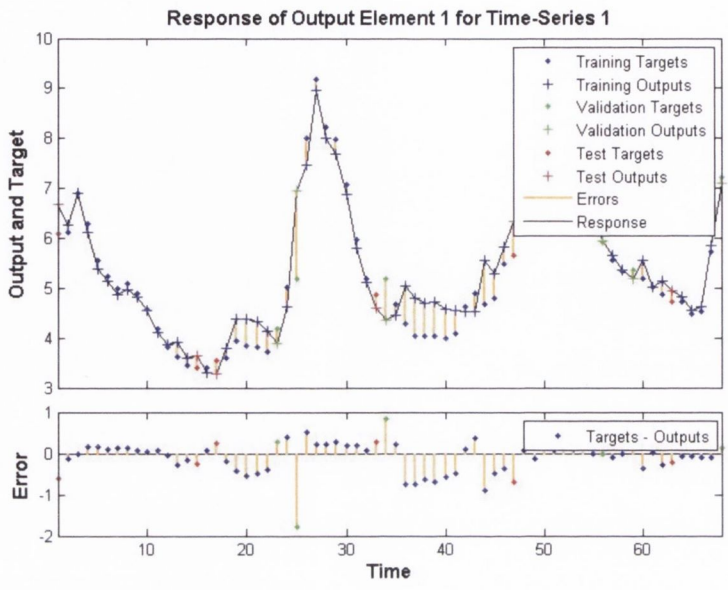

Figure D. 15 Time series of neural network training Site 6 run 1 NO_2

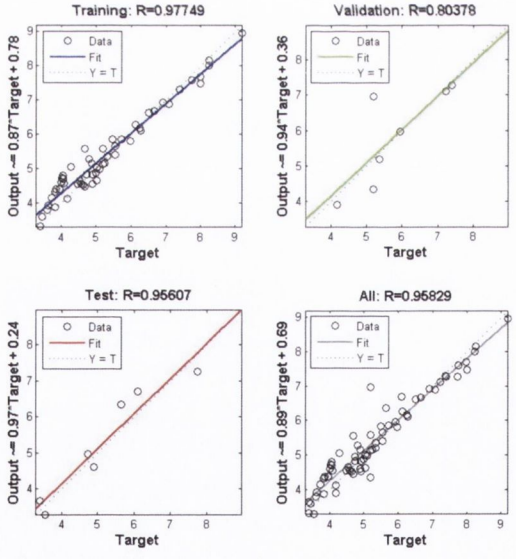

Figure D. 16 Site 6 run 1 NO_2 regression of trained output data set

The errors for run 2 are much less frequent than during run 1. The range of data during this run was 0.5 to 4 ppb and so therefore even errors of 0.5 ppb are significant. In reviewing the individual errors, they occurred at times when sharp spikes in data

occurred and have little influence on the trend-line of the data set. Figure D. 18 shows the regression analysis of the training, validation and test data, with an overall R = 0.990 and R = 0.81 for the testing phase.

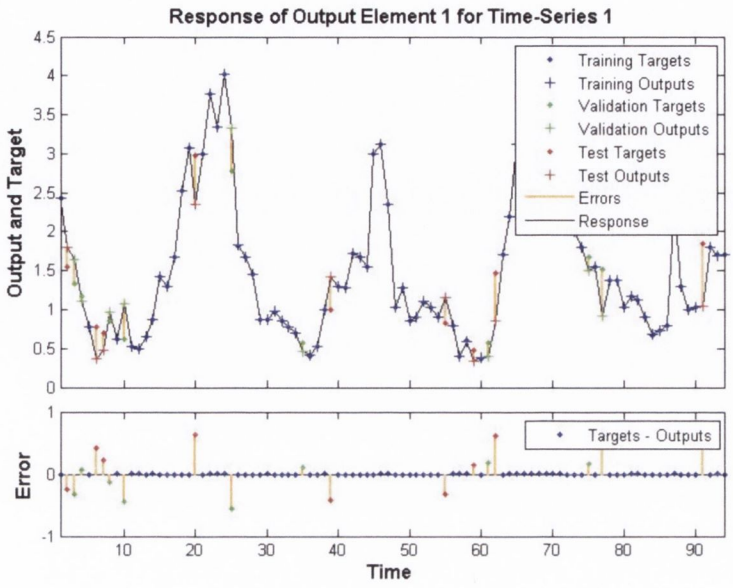

Figure D. 17 Time series of neural network training Site 6 run 2 NO_2

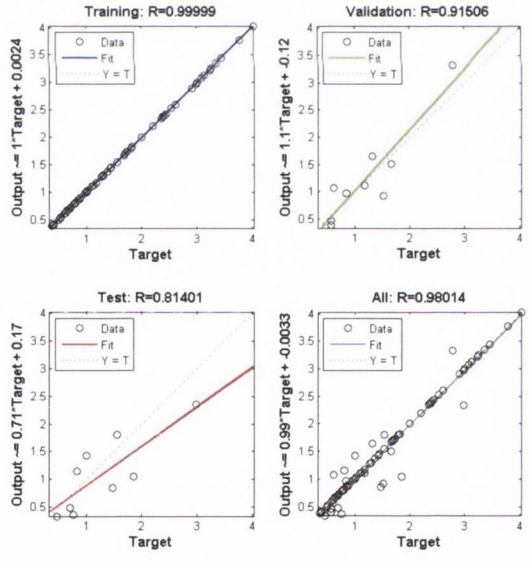

Figure D. 18 Site 6 run 2 NO_2 regression of trained output data set

Site 7 (Naturally ventilated Shop)

The errors at Site 7 range from – 4.8 to 6.5 ppb, the largest of these occurring at points of high spikes in the data, where they do little to influence the trend-line of the time series. Several errors, including the one circled in Figure D. 19, occur at what should have been a peak in the time series, and act to reduce the peaks by 4 ppb. The regression analysis of the training, validation and testing data shows a good overall R value of 0.980 but the R for test data is lower at 0.814. A single high leverage point drags the R value downwards

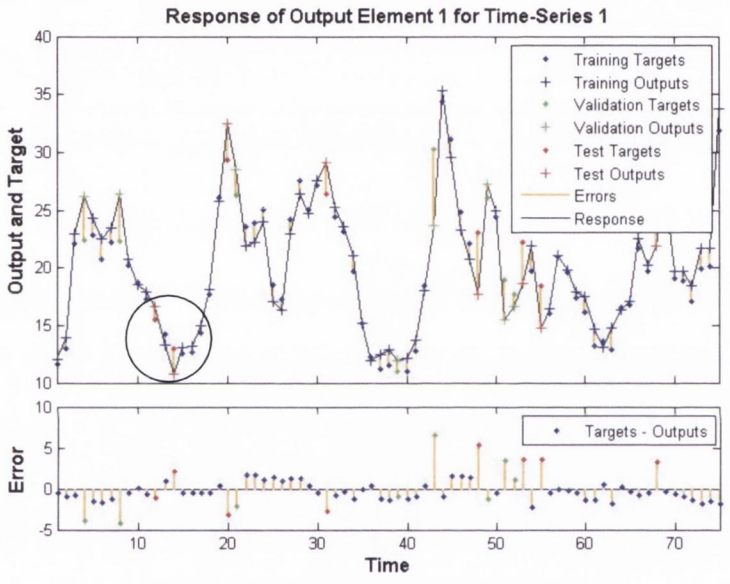

Figure D. 19 Time series of neural network training Site 7 run 1 NO_2

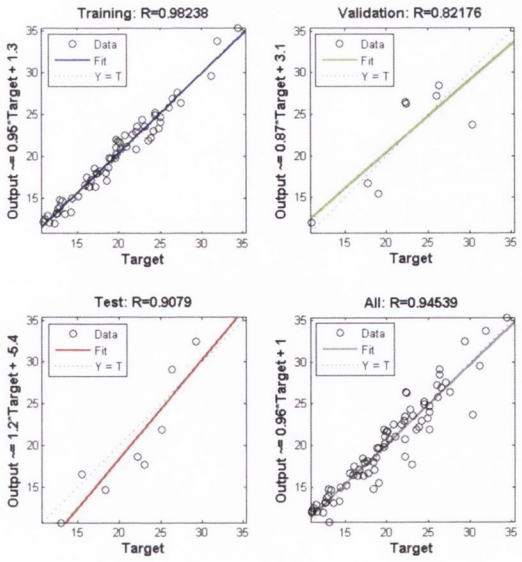

Figure D. 20 Site 7 run 1 NO_2 regression of trained output data set

Site 8 (Naturally ventilated Shop)

This data set begins at 8am on the second day of monitoring as an issue with electricity supply during the first night of monitoring resulted in no outdoor data being collected for NO_2 for this night. The range of the indoor data set is between 15 and 6 ppb. 2 errors of 5 ppb were seen at hour 36 (circled) and 49 as seen in Figure D. 22. Although not as high as the error at 36 hours, errors at 4, 8, 23 and 34 hours all have high leverage to the trend-line; 4 out of 5 of the points would cause increases in the trend-line or peaks, which are not actually present, to be predicted. The 5th point, occurring at 8 hours, pulls a trough in the data from about 7.5 ppb down to just above 4 ppb. The regression analysis carried out on the data allocated for testing of the trained neural network, see Figure D.1, shows a good R = 0.967. The validation data for this site shows a much lower R = 0.669, which are a consequence of the errors seen in Figure D. 21.

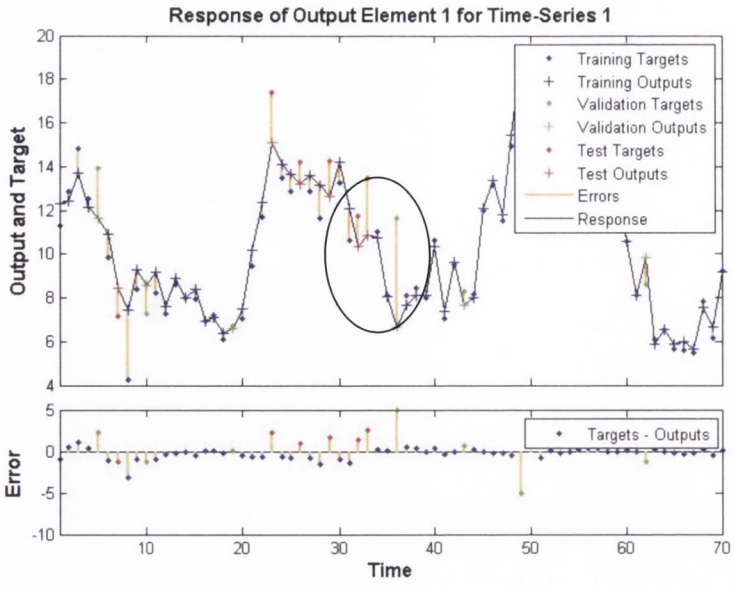

Figure D. 21 Time series of neural network training Site 8 run 1 NO_2

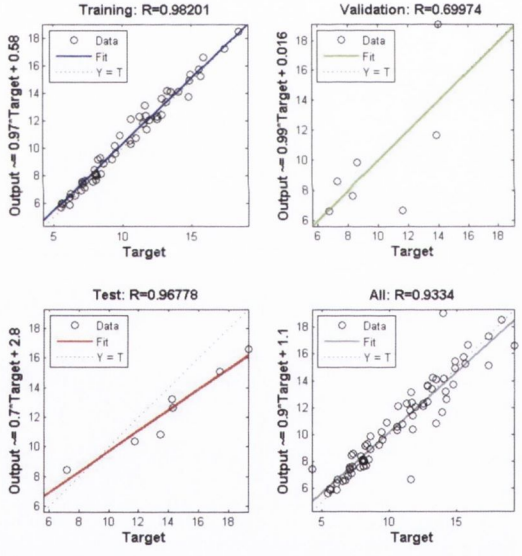

Figure D.1 Site 8 run 1 NO_2 regression of trained output data set

Site 9 (Naturally ventilated Office)

Site 9 shows very few errors above 0.5 ppb, with only 1 above 1 ppb, as shown in Figure D. 23. This site showed low indoor NO2 concentrations and therefore even these small errors can influence the trend-line. Some of these errors are circled in the time series of training, validation and test data. The circled errors, at hours 60 - 65 are small at less than 0.5 ppb but drag down the data removing the small peak creating a

flat plateau instead. R = 0.951 was found for the testing of the trained neural network with an overall R = 0.948 for training, testing and validation of the network.

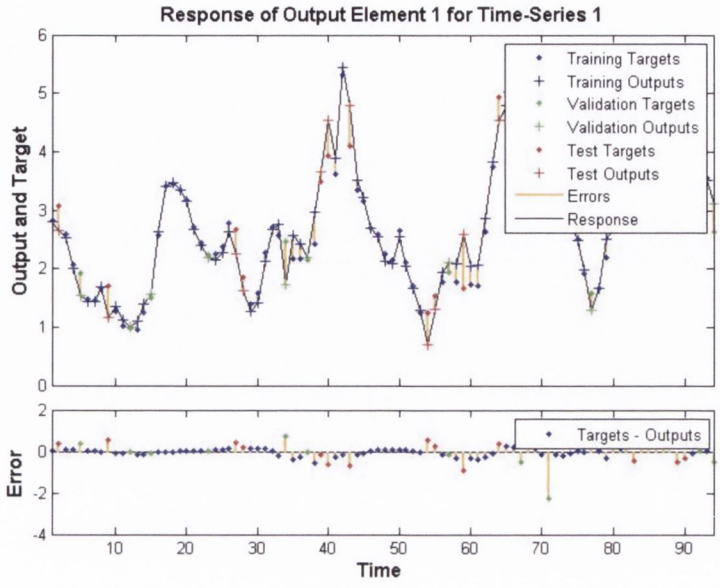

Figure D. 22 Time series of neural network training Site 9 run 1 NO_2

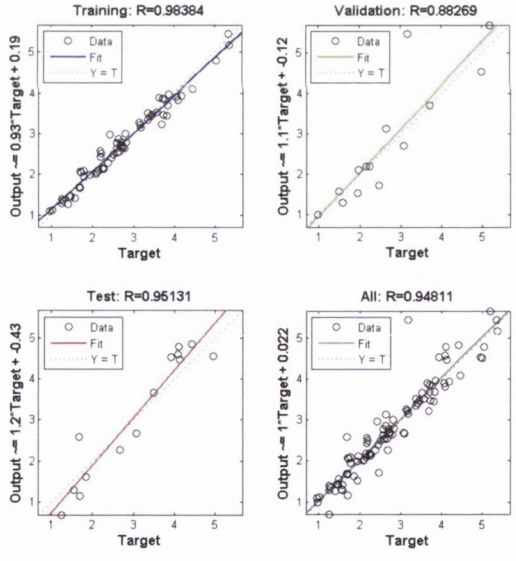

Figure D. 23 Site 9 run 1 NO_2 regression of trained output data set

Apart from some errors of 1.26 ppb in the first 7 hours of monitoring, Site 9 run 2 shows a strongly trained neural network in Figure D. 25 and Figure D. 26. Regression analysis returns R values of training, test and validation data or R = 0.992, R = 0.948 and R = 0.950 respectively.

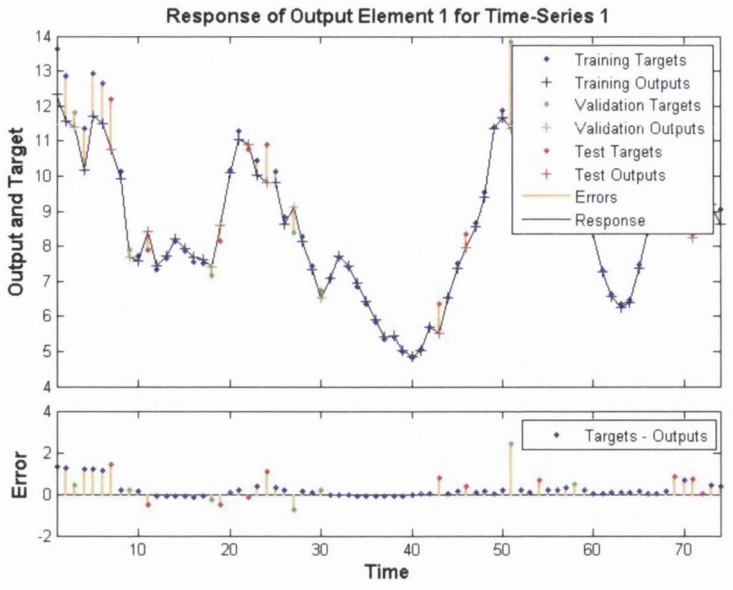

Figure D. 24 Time series of neural network training Site 9 run 2 NO_2

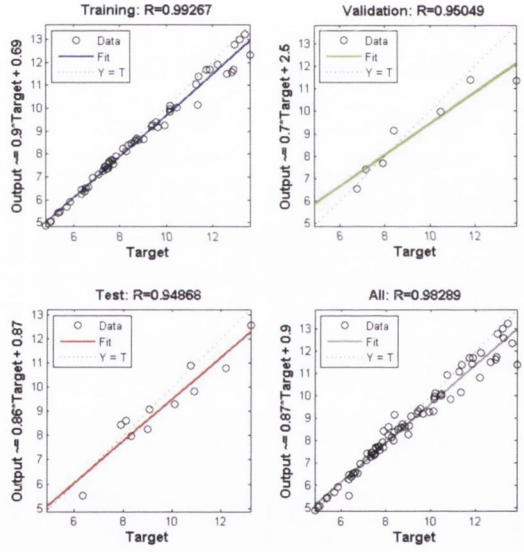

Figure D. 25 Site 9 run 2 NO_2 regression of trained output data set

Site 10 (Mechanically ventilated Office)

Training data points show very little error for Site 10 run 1 with errors only occurring for validation and testing points in Figure D. 27. These errors are in the range of -2.7 to 1.8 ppb, with the highest of these errors occurring at 24 hours into monitoring where the neural network expects a peak in data where none is present. Figure D. 28 shows strong regression values of R = 0.944 for testing of the trained data and R = 0.991 for the combination of test, training and validation data sets.

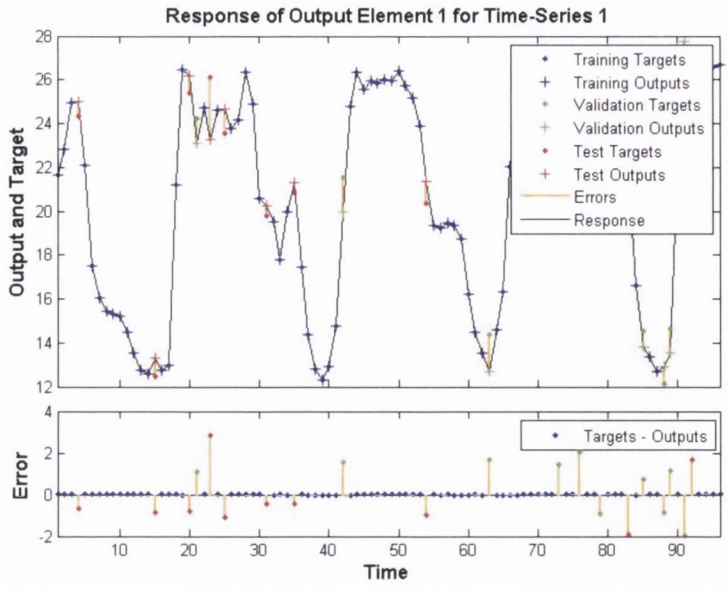

Figure D. 26 Time series of neural network training Site 10 run 1 NO_2

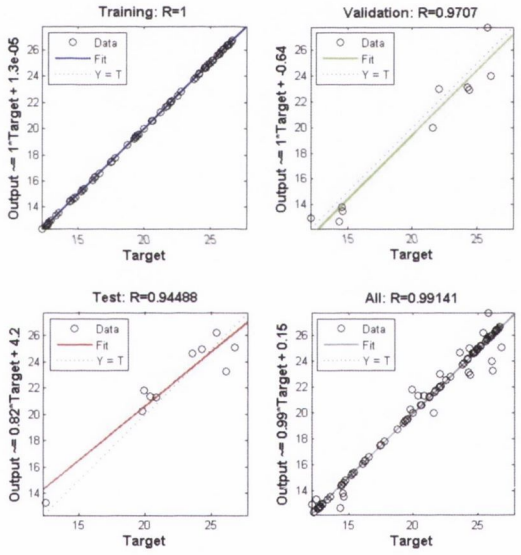

Figure D. 27 Site 10 run 1 NO_2 regression of trained output data set

The second run at Site 10 shows very little error with only 5 error points above 1 ppb (see Figure D. 30), which is less significant at this site that others such as Site 6 due to the larger data range (12 to 30 ppb). The error which occurs at 53 hours into the time series would cause the trough in the data not to be present in the neural network. Regression analysis found good R values for testing of the data with R = 0.926 and an overall R = 0.974 for testing, validation and training of the data set.

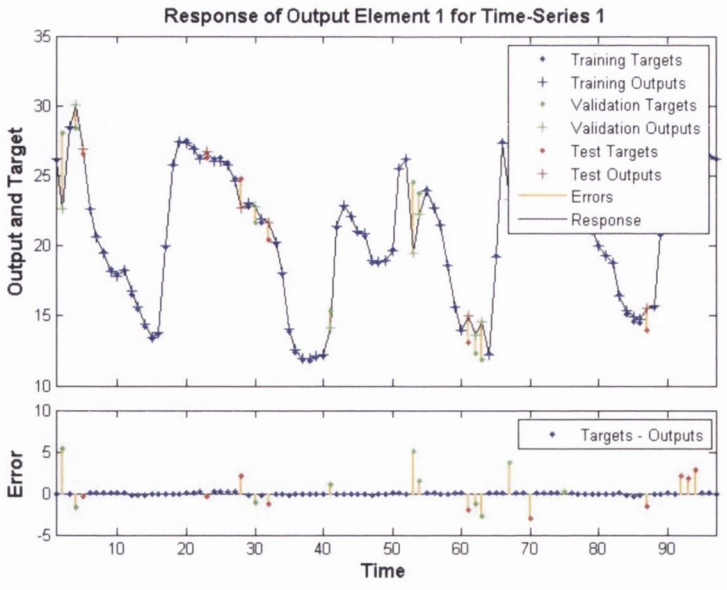

Figure D. 28 Time series of neural network training Site 10 run 2 NO_2

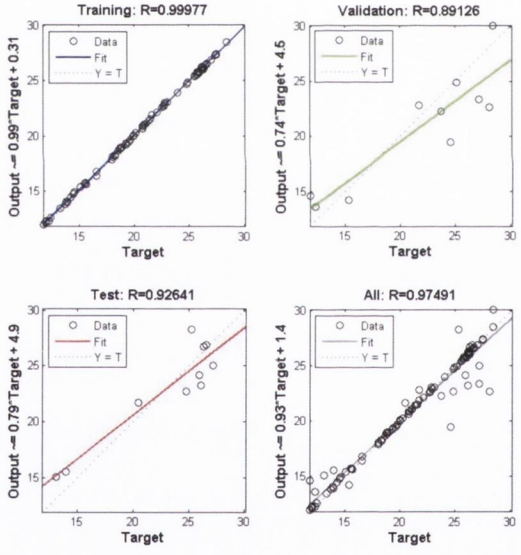

Figure D. 29 Site 10 run 2 NO_2 regression of trained output data set

$PM_{2.5}$ artificial neural network model performance

Site 1 (Naturally ventilated Shop)

Site 1 run 2 for $PM_{2.5}$ shows errors ranging from -10.91 to 8.899 although out of the 77 error points only 5 lie outside the range of -2.571 to 6.814. The largest error (10.91) occurs at Time = 15 hours and is circled in Figure D. 31. This error causes the peak at

15 hours to be significantly increased and therefore affects the trend-line of the time series. Regression analysis shows a good Pearson's R for training data (R = 0.996) but reduced correlation between target and validation data as well as target and test data. The R value for validation is low at 0.485 due to a number of high leverage points. The same occurs for testing with the point at Time = 15 hours pulling the line of best fit downwards from 20 to 22 $\mu g\ m^{-3}$.

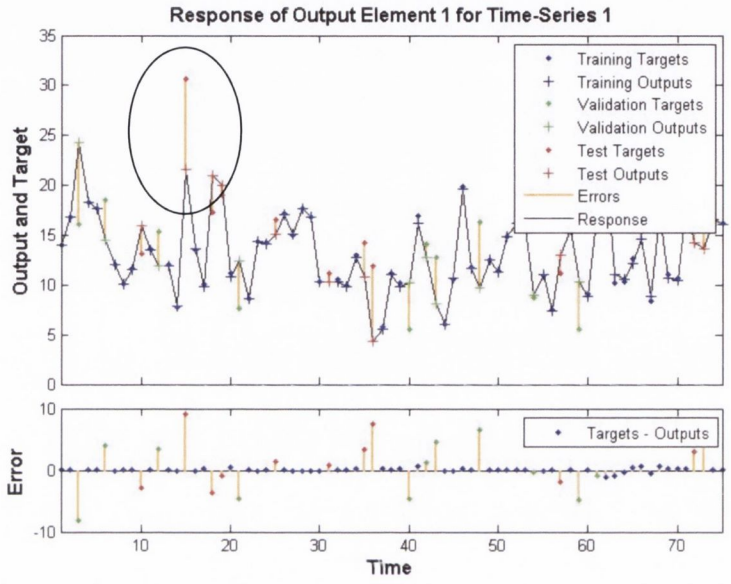

Figure D. 30 Time series of neural network training Site 1 run 2 $PM_{2.5}$

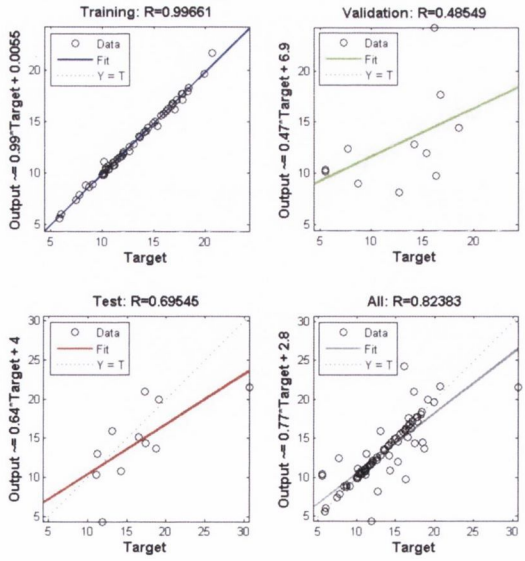

Figure D. 31 Site 1 run 2 $PM_{2.5}$ regression of trained output data set

Site 2 (Mechanically ventilated Office)

9 errors in the range of -2.018 to 2.231 μg m^{-3} were found for Site 2 run 2, a number of these which would cause inaccurate readings of the time series if used, as shown in Figure D. 32. For instance one peak at Time = 5 on the x-axis creates an inaccurate peak in the data set, whilst other errors such as the one which occurs at Time = 29 does not influence the tread-line of the data set meaningfully. Regression analysis of the trained neural network test points shows an R of 0.717 and an R of 0.994 for training data points, see Figure D. 33. The validation R has a low value of C.489 this is due to many of the validation point having large errors. Reviewing the indoor and outdoor time series a correlation of only R^2 of 0.38 was found between indoor and outdoor $PM_{2.5}$. The correlation was low due to indoor fluctuations not related to outdoor concentrations and meteorological variables, e.g. cooking sources and therefore high errors were also expected in the trained network.

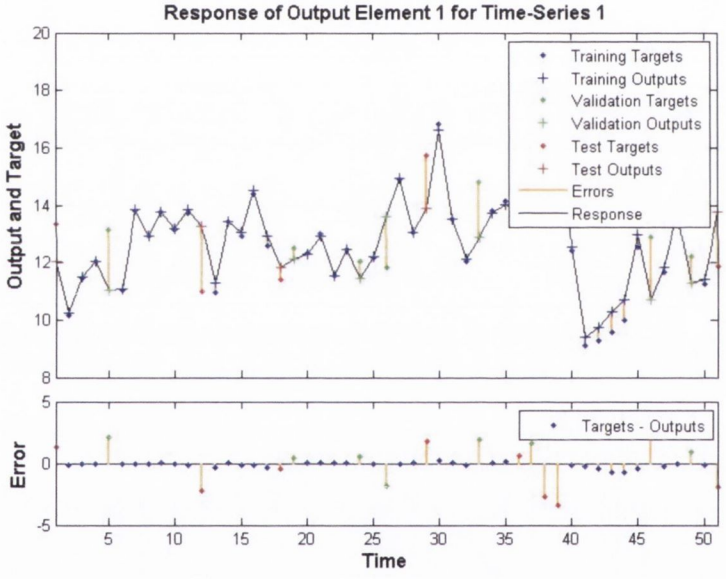

Figure D. 32 Time series of neural network training Site 2 run 2 $PM_{2.5}$

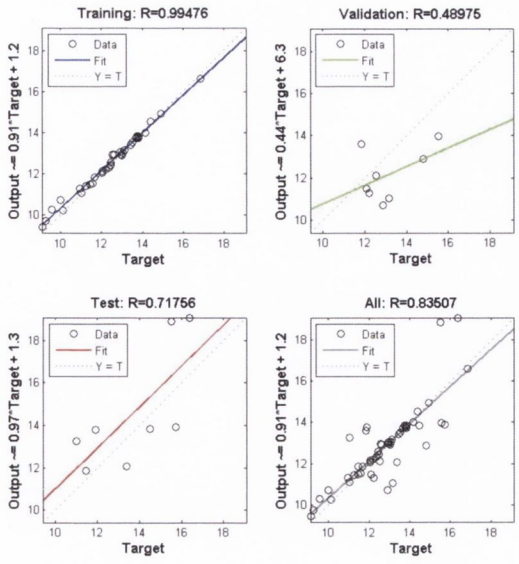

Figure D. 33 Site 2 run 2 $PM_{2.5}$ regression of trained output data set

Site 3 (Mechanically ventilated Office)

Site 3 shows some large errors for the $PM_{2.5}$ neural network, see Figure D. 34. Run 1 was conducted at the ventilation intake level and the room where indoor monitoring took place had a direct feed to this air intake. Errors for this site range from – 8.09 to 4.93 μg m^{-3}. Unlike all other data sets up to this point the errors shown here significantly influence the time series over an extended period of time, over-predicting for certain time periods and under-predicting for others. The errors are largest for the validation and training data with only 1 test error point lying outside the range of -1.23 to 0.819 μg m^{-3}. The regression analysis of the neural network shows poor R values of 0.647, 0.234 and 0.708 for training, validation and testing respectively. Similar to Site 2 a low correlation was found between indoor and outdoor concentrations when a regression was carried out prior to training of the Neural Network. This regression found an R^2 = 0.2, indicating that there is little interaction between indoor and outdoor concentrations. While the use of Neural networks improved the prediction for testing the poor R for validation does not give confidence in the ability of the neural network to predict future indoor concentrations.

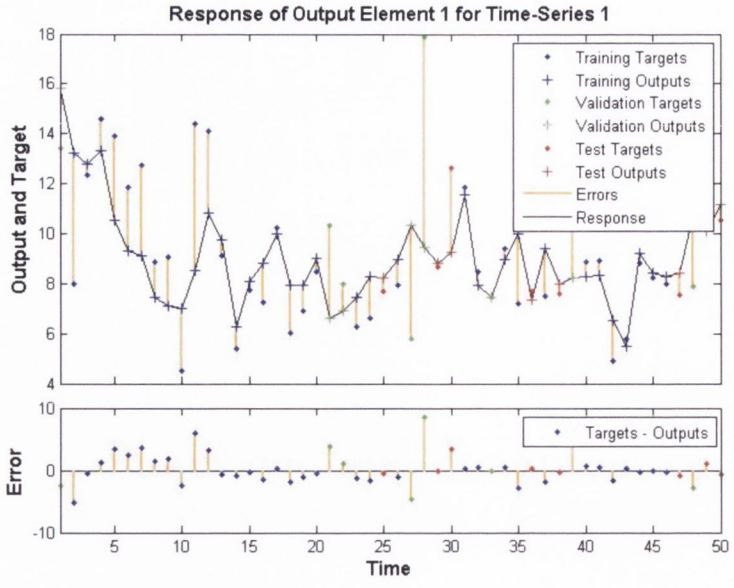

Figure D. 34 Time series of neural network training Site 3 run 1 $PM_{2.5}$

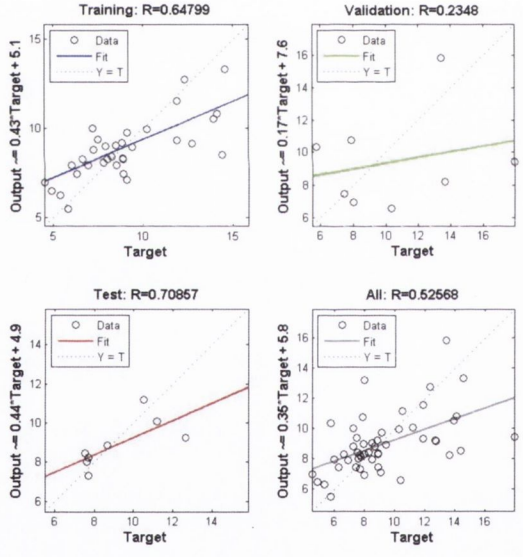

Figure D. 35 Site 3 run 1 $PM_{2.5}$ regression of trained output data set

Site 3 run 2 produces a much stronger trained Neural Network than run 1, as shown in Figure D. 36. This data was recorded at ground level and the better trained network may be due to the longer time that meteorological conditions have to influence the concentrations and therefore are more useful predictors. Or, it may simply indicate as seen in previous investigations in Chapters 4 and 5 that ground level concentrations have a greater influence on indoor fluctuations than the roof level concentrations. The

regression analysis shows better R values for training (R = 0.984), validation (R = 0.780) and testing (R = 0.776) than for run 1, see Figure D. 37. These predictions were strong compared to the original regression done between indoor and outdoor values which had an R^2 = 0.11. Errors ranged from -6.855 to 4.62 μg m^{-3} although all expect for 6 were within the range of -2.02 and 2.20.

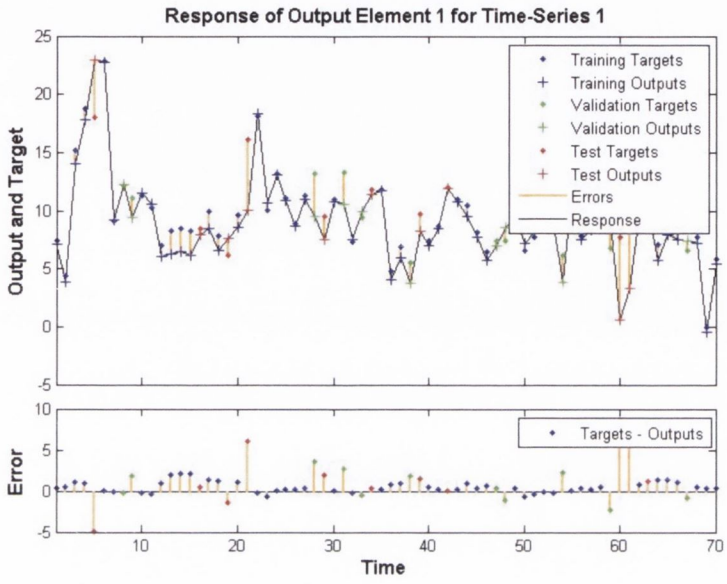

Figure D. 36 Time series of neural network training Site 3 run 2 $PM_{2.5}$

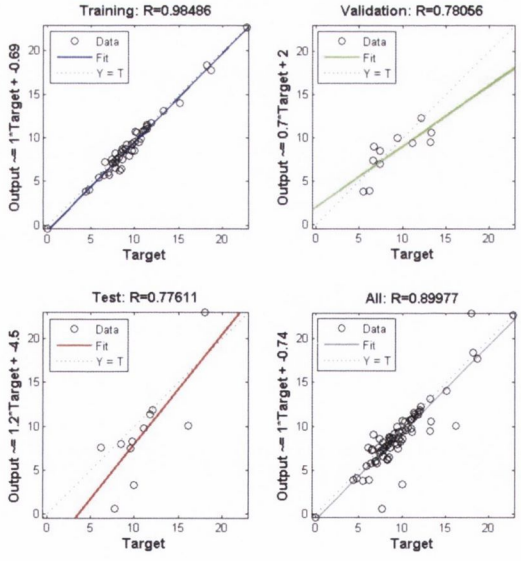

Figure D. 37 Site 3 run 2 $PM_{2.5}$ regression of trained output data set

Site 4 (Mechanically ventilated Gallery space)

Errors for Site 4 run 1 range between -2.729 to 7.366, although only 5 points are seen outside the range of -1.135 to 1.522, as shown in Figure D. 38. Many of the errors occur at peaks or troughs in the time series and therefore cause these to be extenuated or dampened. For instance the error at Time = 2 is extenuated while the peak at Time = 23 hours is reduced, smoothing the time series. The regression analysis on the Neural Network data in Figure D. 39 shows R values for training, validation and testing of 0.953, -0.011 and 0.864 respectively. The poor validation regression is mainly due to 1 high leverage error, other than this 1 error validation points produce a relatively good prediction.

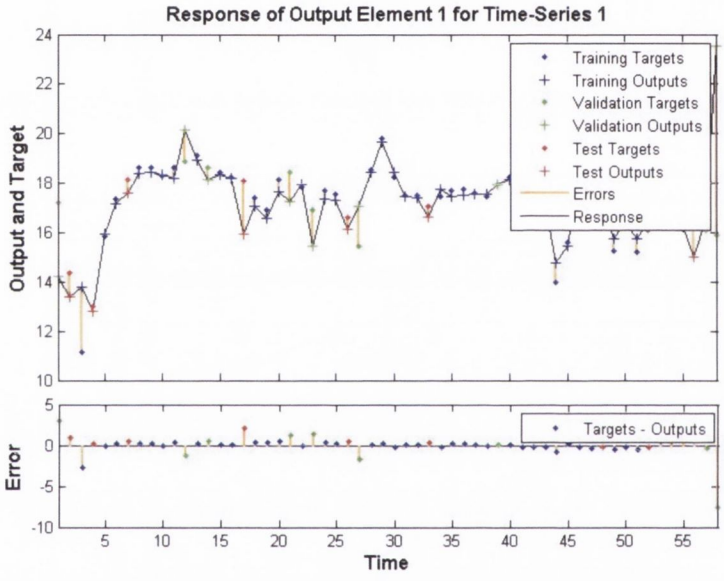

Figure D. 38 Time series of neural network training Site 4 run 1 $PM_{2.5}$

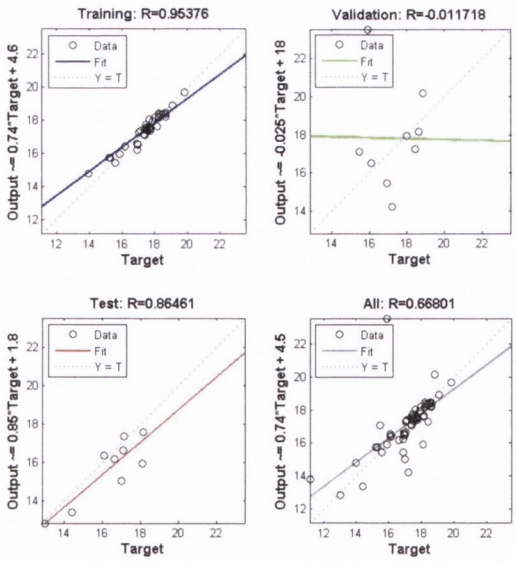

Figure D. 39 Site 4 run 1 $PM_{2.5}$ regression of trained output data set

During run 2, $PM_{2.5}$ at Site 4 was monitored simultaneously at roof level, ground level and indoors and therefore presented a unique opportunity to compare and see if the extra data i.e. from both ground and roof level at once improved the ANN performance. The performance of the 3 different ANNs to predict the indoor data will be assessed. The input data for these 3 ANNs are; meteorological and ground level data, meteorological and roof level data and finally meteorological, roof level and ground level data.

Site 4 run 2 Meteorological and street level outdoor

Run 2 provided a better R value for the regression of the modelled and target values than for run 1, particularly for the validation of the training data, see Figure D. 40. The errors for this run were higher than other runs to the greater range over which data is spread. The range was between -54.78 to 38.55 $\mu g\ m^{-3}$ although all instances except for 6 lie between -25.31 to 4.16 $\mu g\ m^{-3}$. Reviewing where these errors lie in the time series (Figure D. 41), it is seen that most lie around the sharp peaks seen early in the time series. These peaks were not seen in the street level data and therefore the ability of the meteorological variables to predict the increases indoors even with large errors is positive.

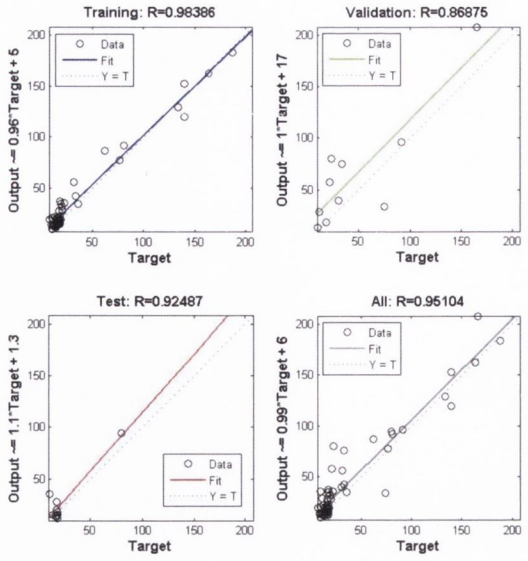

Figure D. 40 Site 4 run 2 (street) $PM_{2.5}$ regression of trained output data set

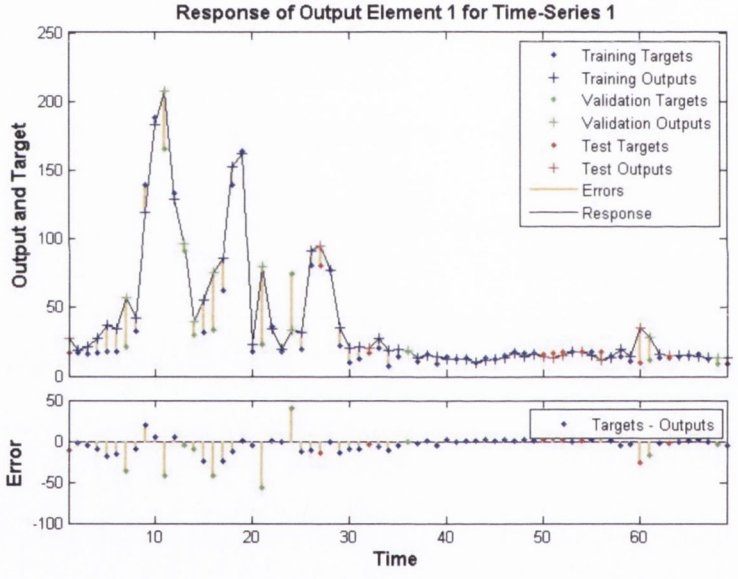

Figure D. 41 Time series of neural network training Site 4 run 2 (Street) $PM_{2.5}$

Site 4 run 2 Meteorological and roof level outdoor

The roof level data inputs showed a higher R value and fewer errors than the street level data as shown in Figure D. 42 and Figure D. 43. The errors were within the range of -25.67 to 61.02 μg m^{-3} but all bar 5 were in the range of -16.54 to 6.268 μg m^{-3}. Most of the larger errors again occur during the peaks, but the roof level data seems to account for a greater number of these than the street level data.

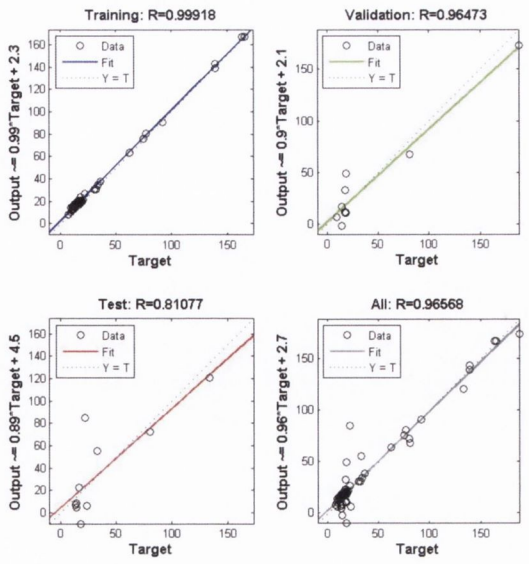

Figure D. 42 Site 4 run 2 (roof) $PM_{2.5}$ regression of trained output data set

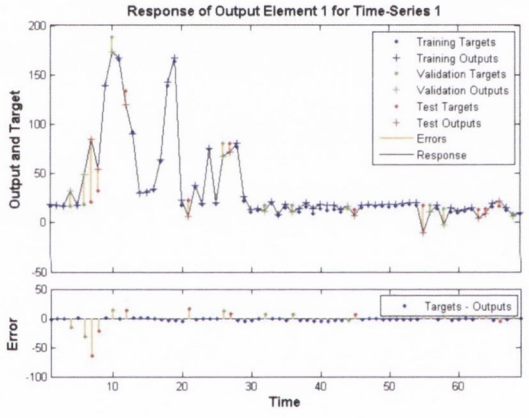

Figure D. 43 Time series of neural network training Site 4 run 2 (roof) $PM_{2.5}$

Site 4 run 2 Meteorological, Roof and street level outdoor

Site 4 run 2 produces a strong Neural Network from training using the target data but with high errors due to the significant spike that was seen for the first day and a half of monitoring (see Figure D. 44). These errors range from -30.05 to 30.95 $\mu g\ m^{-3}$ but all, bar 7, lie within the range of -14 and 8.47 $\mu g\ m^{-3}$. An extra input was included in this run as both ventilation intake, or roof level $PM_{2.5}$ data, and ground level data were included, unlike the two previous runs at this site. The inclusion of both roof and ground level data significantly reduced errors during the first day and a half of monitoring where a large increase in indoor concentrations were seen in Figure D. 44. The large spike at Time = 7 hours and magnitude –30.05 occurs for testing data, this error

creates a dip in the data between the previous and proceeding data points. Regression analysis for the training, validation and testing of the Neural Network versus the target data show high R values of 0.992, 0.973 and 0.957 respectively. The high R value for testing is due to a high leverage point. These points occurred due to testing and validation points being checked during the first two days, a time when unusually high peaks occurred. The R value seems reasonable if these high leverage points were removed.

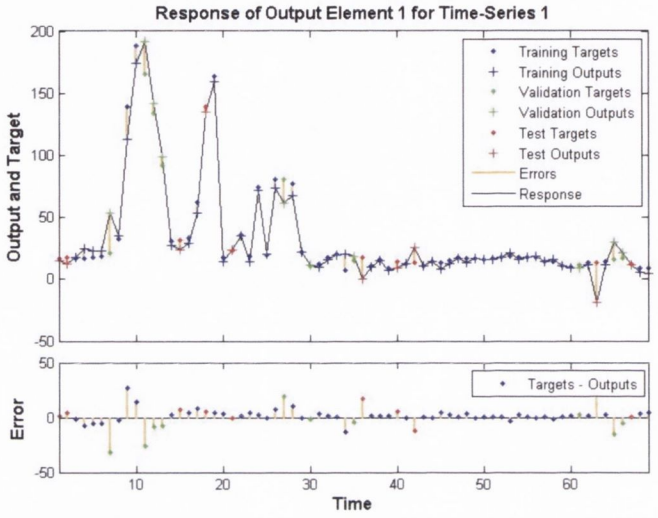

Figure D. 44 Time series of neural network training Site 4 run 2 $PM_{2.5}$

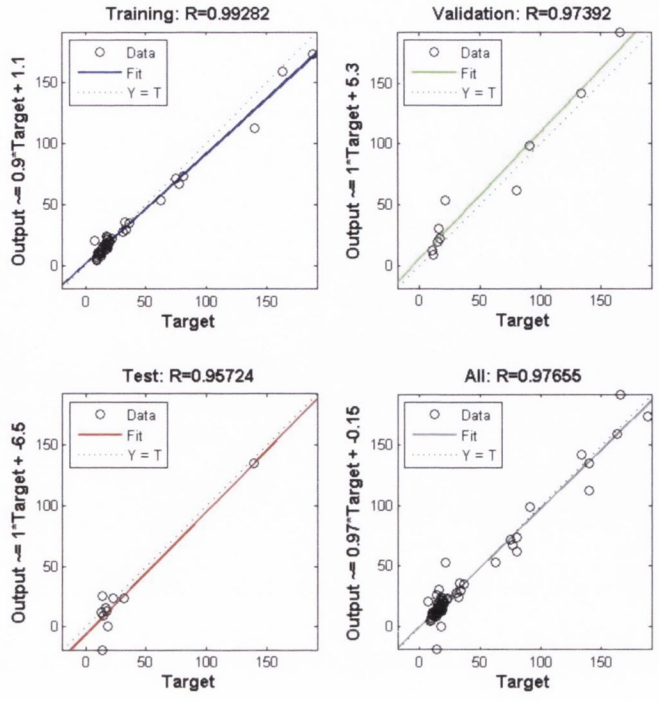

Figure D. 45 Site 4 run 2 $PM_{2.5}$ regression of trained output data set

Figure D. 46 shows a plot of the actual indoor data, or target, and the 3 neural networks trained using data containing roof level data, street level data and a combination of the two as well as meteorological data for each network. All 3 trained networks show strong prediction ability with R values above 0.95. The results of 2 sample T-Tests show estimates of the difference of 1.29, -5.51 and -1.04 between target and roof level, street level and a combination of the two respectively. The 2 sample T-Tests found that all three 95% confidence intervals contained zero, therefore, the predicted data using the trained networks for all three situations predicts outputs that have a mean value statistically indifferent from zero. Further the R values in Figure D. 40, Figure D. 42 and Figure D. 45 found that the target is best predicted by a combination of ground level data and roof level data R=0.976, a lower R=0.965 was found for roof level and finally the lowest R was found between street level and target data. While the combination of roof and ground level combined with meteorological data found the best prediction ability, both street level and roof level found good prediction ability individually.

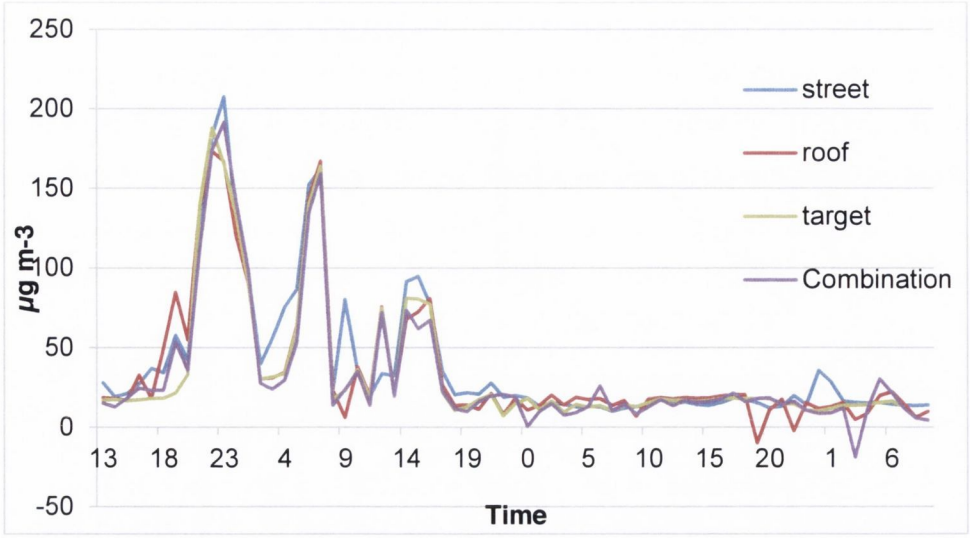

Figure D. 46 Time series of trained and actual indoor concentrations for Site 4 run 2

Site 5 (Mechanically ventilated Office)

Site 5 shows a large amount of over prediction of $PM_{2.5}$ data especially between the hours of 13 to 35 hours, see Figure D. 46. This over prediction occurs during a time of partially high relative humidity as a large amount of rain fell during this week. Not all this rainfall was recorded by Met Eireann but was by personal records of the metrological factors at the site. Figure D. 48 shows the regression analysis of the training, validation and testing of the newly developed Neural Network for this mechanically ventilated office building which yielded an R = 0.928 for testing and an overall R = 0.864 for all 3 phases.

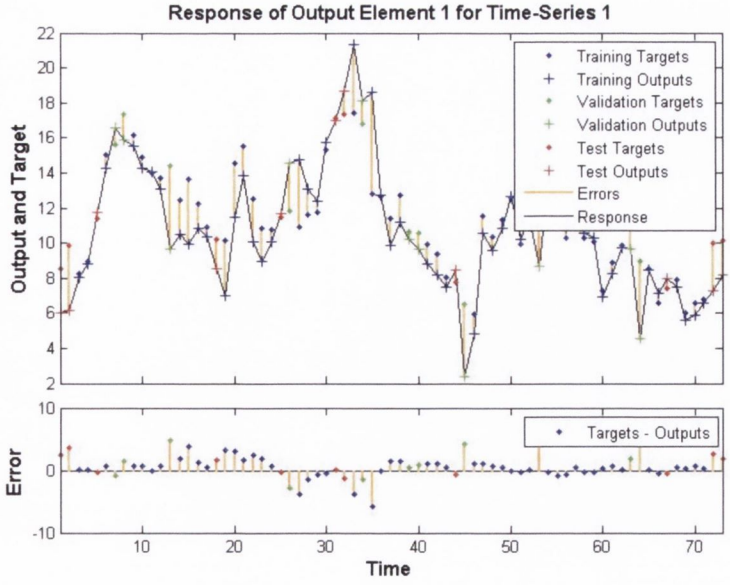

Figure D. 47 Time series of neural network training Site 5 run 1 $PM_{2.5}$

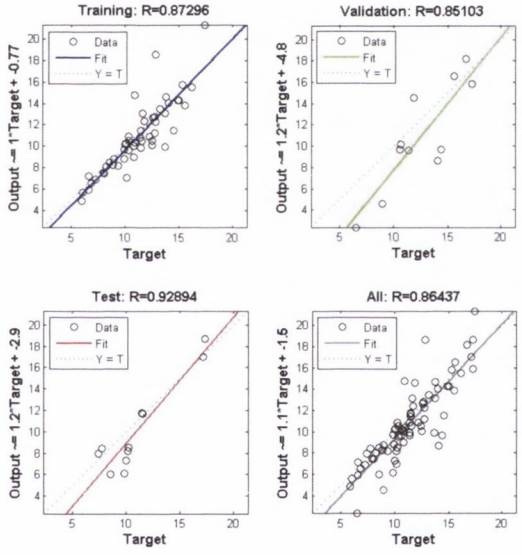

Figure D. 48 Site 5 run 1 $PM_{2.5}$ regression of trained output data set

Site 6 (Naturally ventilated Office)

Site 6 shows a reasonable output for the error during the time series as can be seen in Figure D. 50. Errors are between –6.85 and 4.62 μg m^{-3} although all but 5 of these error points lie between -2.022 and 2.20 μg m^{-3}. The errors generally do not have high leverage to the known trend-line of the data. The regression analysis carried out on the 15 % of target data set aside for testing shows an R = 0.984, the validation data shows a lower R = 0.630 and the testing data an R = 0.660. Outdoor data for this site saw

several unexplained peaks which were not seen indoors, this may have affected the prediction power of the Neural Network. Autocorrelation for this site was found to be within the bounds of confidence limits.

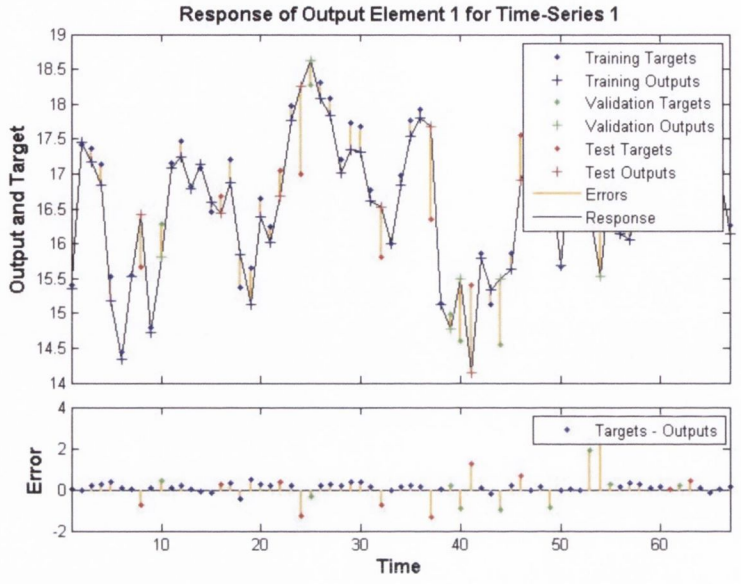

Figure D. 49 Time series of neural network training Site 6 run 1 $PM_{2.5}$

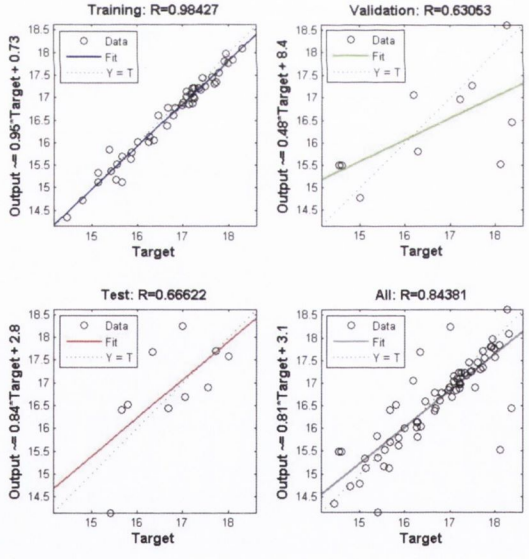

Figure D. 50 Site 6 run 1 $PM_{2.5}$ regression of trained output data set

Run 2 for Site 6 has a very noisy time series, as reflected with a larger number of errors due to the high number of fluctuations. The errors range from -7.21 to 5.034 as shown in the histogram of errors in Figure D. 52 which shows a Gaussian distribution.

Regression analysis shows a R =1 for training and a R = 0.936 for testing of the trained data, see Figure D. 53. A stronger R of 0.813 was also found compared to run 1.

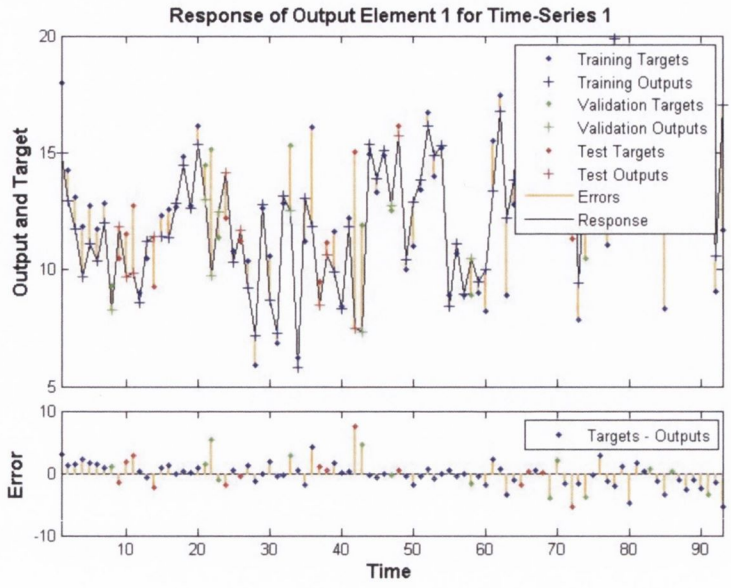

Figure D. 51 Time series of neural network training Site 6 run 2 $PM_{2.5}$

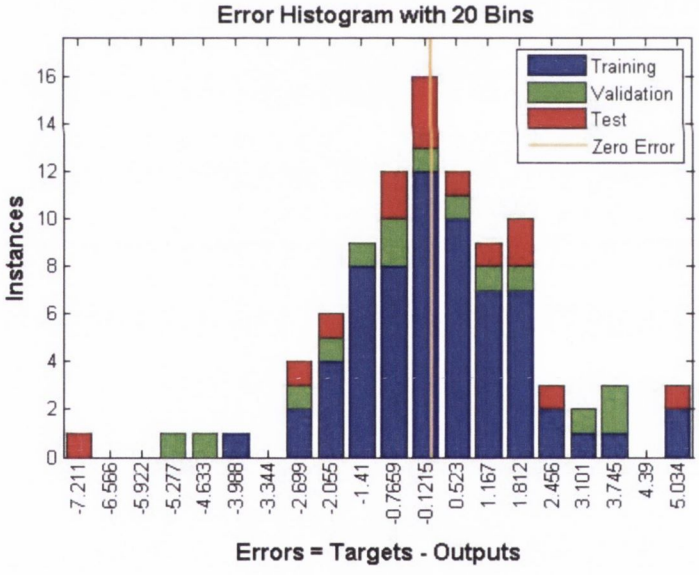

Figure D. 52 Error Histogram Site 6 run 2 $PM_{2.5}$

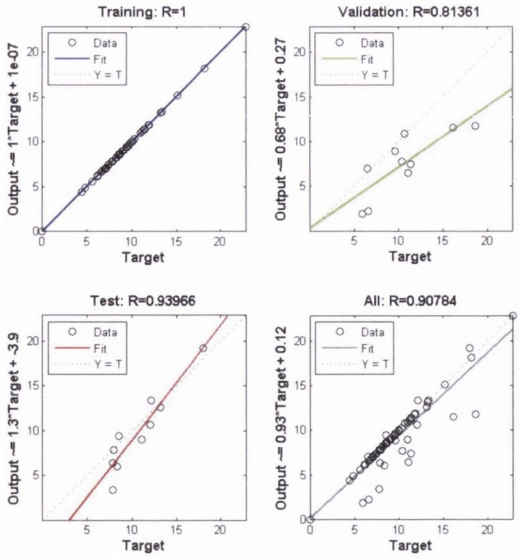

Figure D. 53 Site 6 run 2 $PM_{2.5}$ regression of trained output data set

Site 7 (Naturally ventilated Shop)

Site 7 developed a strongly trained Neural Network with only five errors which lie outside the range of -0.5302 and 2.790. The max of these was 6.779 which occurred at hour 33 into the time series and causes a large reduction in the data set which was not present in the actual data, see Figure D. 54. The regression analysis in Figure D. 55 shows strong correlation between the target and the training, validation and test data with R = 0.992, 0.701 and 0.837 respectively. With the large error point seen at hour 33, the R value for the regression of test data would be stronger.

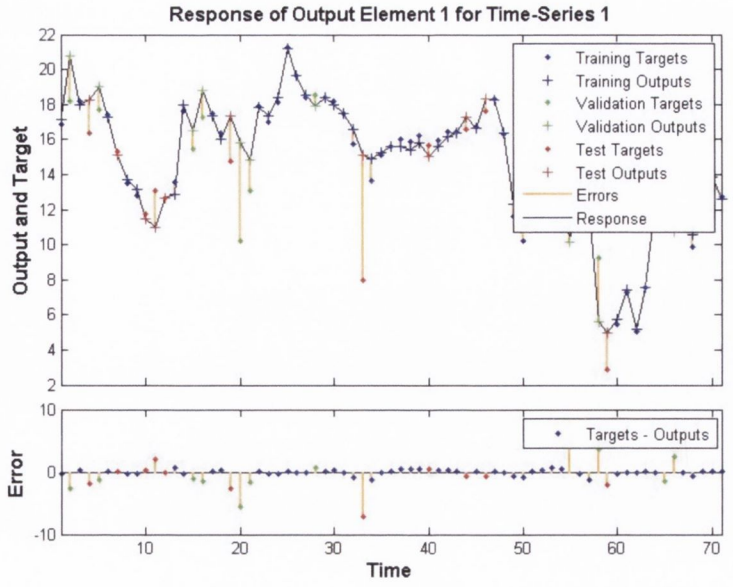

Figure D. 54 Time series of neural network training Site 7 run 1 $PM_{2.5}$

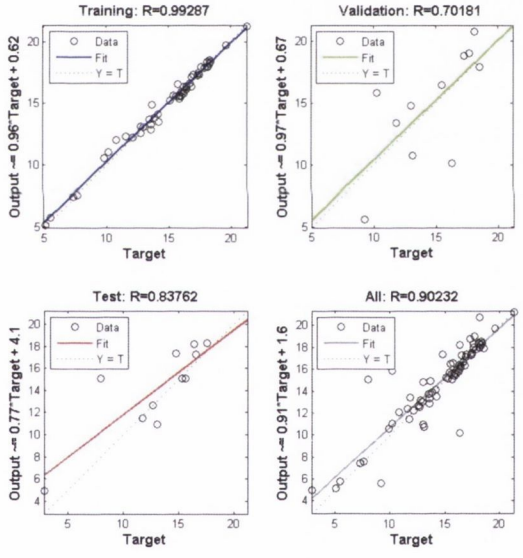

Figure D. 55 Site 7 run 1 $PM_{2.5}$ regression of trained output data set

Site 8 (Naturally ventilated Shop)

Site 8 shows errors between -7.132 to 9.108 but only five errors were outside the range of -2.854 to 1.41. One of these is a testing error point and is a particularly high leveraging point. This particular point is circled in Figure D. 56 and drags a peak value

downwards from near 24 μg m^{-3} to 15 μg m^{-3}, highly underestimating the peak seen at 53 hours into the time series. The regression analysis shows a good Pearson's R for testing of 0.9627 but lower R values for validation and testing of 0.602 and 0.643 respectively. The testing value is pulled downwards due to the previously mentioned high leveraging error

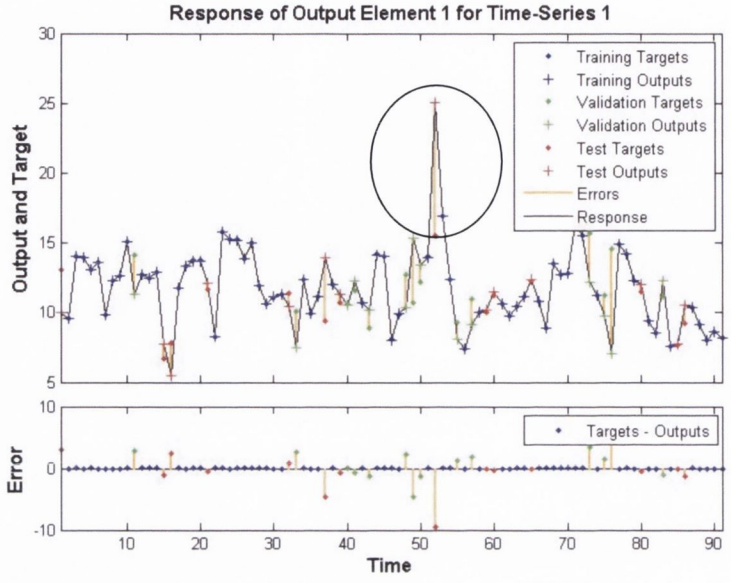

Figure D. 56 Time series of neural network training Site 8 run 1 $PM_{2.5}$

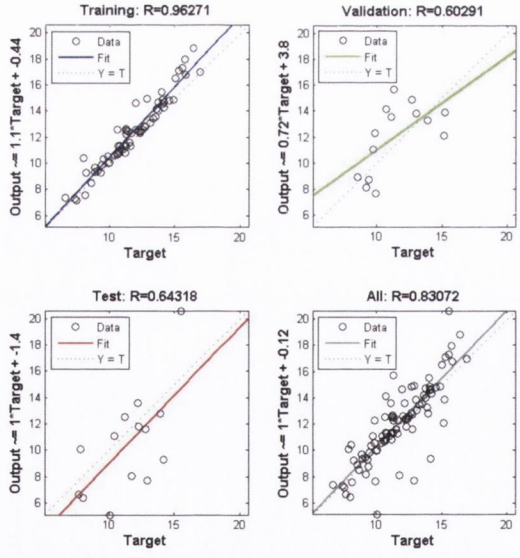

Figure D. 57 Site 8 run 1 $PM_{2.5}$ regression of trained output data set

Site 9 (Naturally ventilated Office)

A large number of small errors are seen for the first 22 hours of the time series in Figure D. 58 ranging from -2.088 to 2.16 μg m^{-3} which produces a Gaussian distribution

when plotted into an error histogram. The trained data in Figure D. 58 under predicts the first 22 hours of data by just over 1 but up to 2 μg m^{-3}. The regression analysis of the trained network shows that test data points show the highest R = 0.953 while training R was found to have a value of 0.872. This value would have been higher if not for one high leverage data point which pulls the line of best fit upwards. The regression scatter plots show data points mainly in the top right corner. The consolidation of data here is due to the scale being extended for the first few hours of monitoring which found lower indoor concentrations of 13 μg m^{-3}. After these initial concentrations the data stays within a range of 16 to 18 μg m^{-3}, resulting in the large amount of data points bunched in one area of the regression scatter plots.

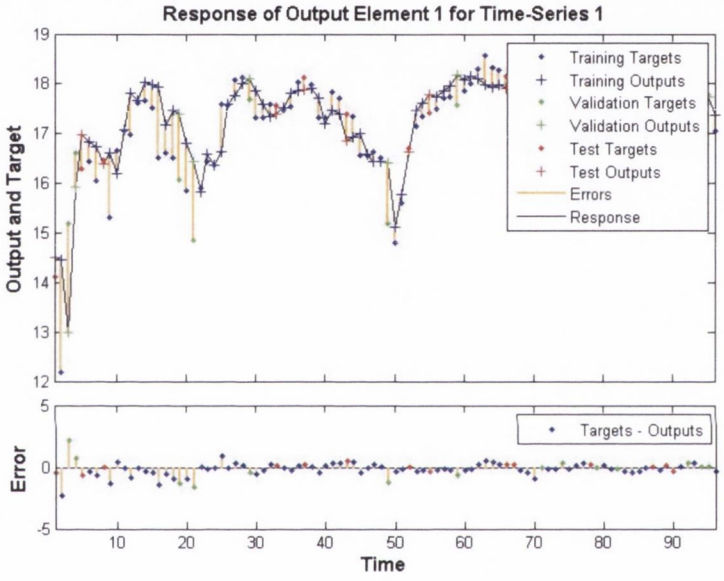

Figure D. 58 Time series of neural network training Site 9 run 1 $PM_{2.5}$

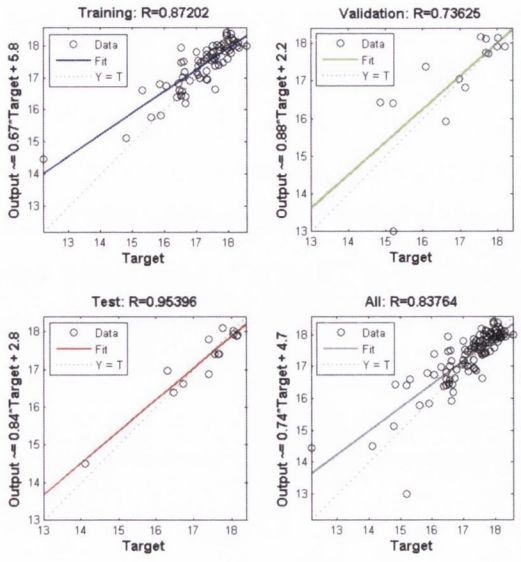

Figure D. 59 Site 9 run 1 $PM_{2.5}$ regression of trained output data set

Site 9 run 2 shows several high leverage errors which remove depressions in the data set, as shown in Figure D. 60. There are also instances where non-existent troughs and peaks in the data set are expected by the Neural Network. The errors range from 2.627 to 3.58, but the majority of them lie within the range of -1.97 to 1.62. In Figure D. 61 the training, validation and test data show reasonable relationships between target and Neural Network predicted data with R = 0.816, 0.875 and 0.645 respectively. The original regression of outdoor data predicting indoor, gave a significantly lower correlation of R^2 = 0.056 % therefore a considerable improvement is made by using the trained network to predict indoor or target concentrations.

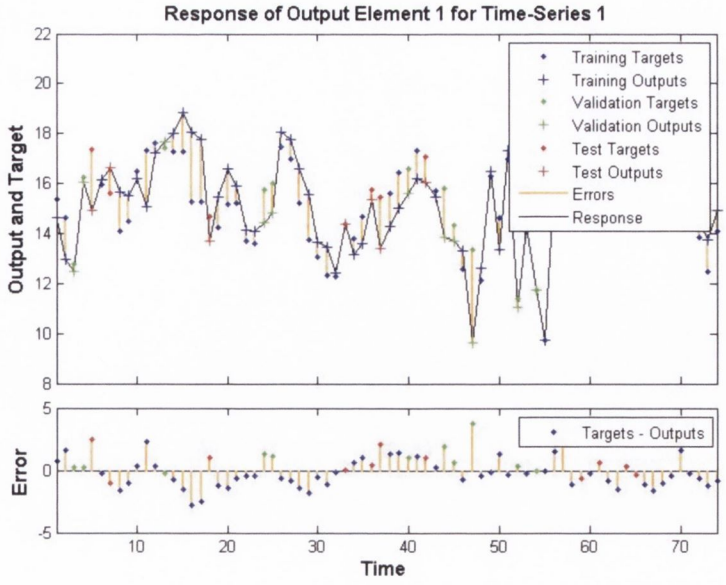

Figure D. 60 Time series of neural network training Site 9 run 2 $PM_{2.5}$

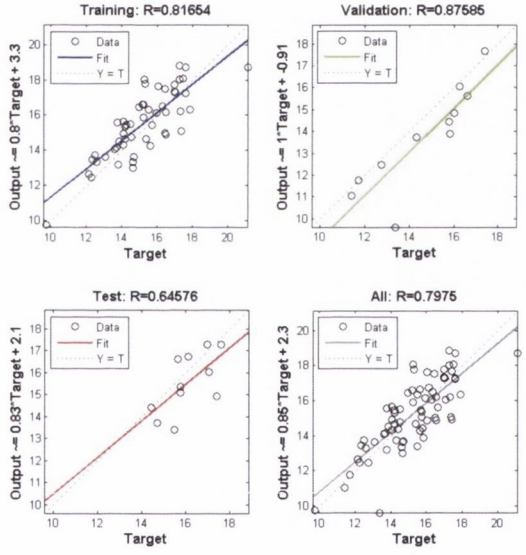

Figure D. 61 Site 9 run 2 $PM_{2.5}$ regression of trained output data set

Site 10 (Mechanically ventilated Office)

Site 10 showed a large amount of errors both over and under predicting the time series seen in Figure D. 62. The errors range between -7.867 to 7-976 although most are within the range of -4.528 and 3.808. The regression analysis shows a partially poor validation set of data points with a R = 0.332 although training and testing data points show much stronger correlations of R = 0.890 and R = 0.608 respectively in Figure D. 63.

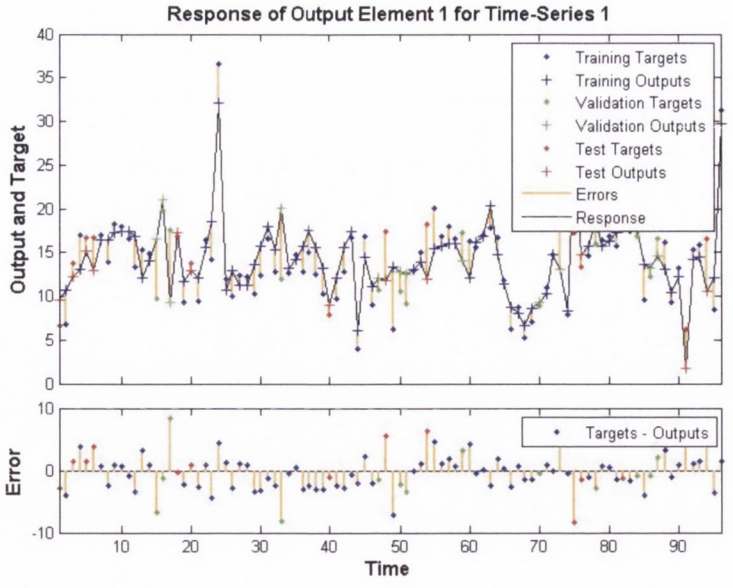

Figure D. 62 Time series of neural network training Site 10 run 1 $PM_{2.5}$

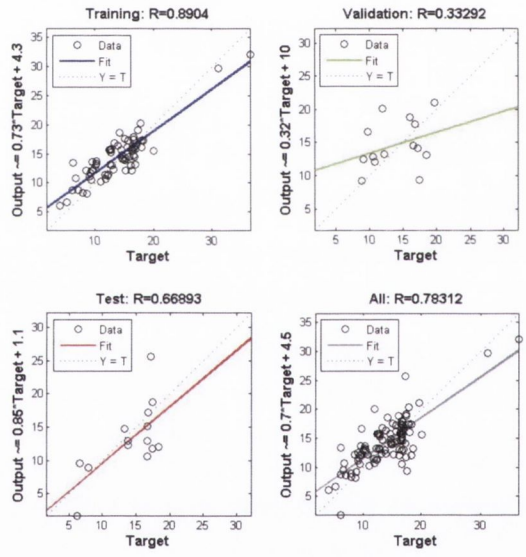

Figure D. 63 Site 10 run 1 $PM_{2.5}$ regression of trained output data set

Run 2 for Site 10 also shows a high level of error away from the validation indoor data although many of these points are non-leveraging and therefore do not significantly affect the time series trend-line in Figure D. 64. This site saw large levels of rainfall during the monitoring period, all of which is not accounted for in the Met Eireann data which may have been a cause for some of the failures in the prediction. Errors for training, testing and validation of this Neural Network generally lie between -2.15 and -1.153 although extremes lie at -4.902 and 5.557. Figure D. 65 shows a regression analysis of the ability of the Neural Network to predict the target data, the network

performs well in training (R= 0.967) and testing (R= 0.700) but not as well in Validation (R = 0.610).

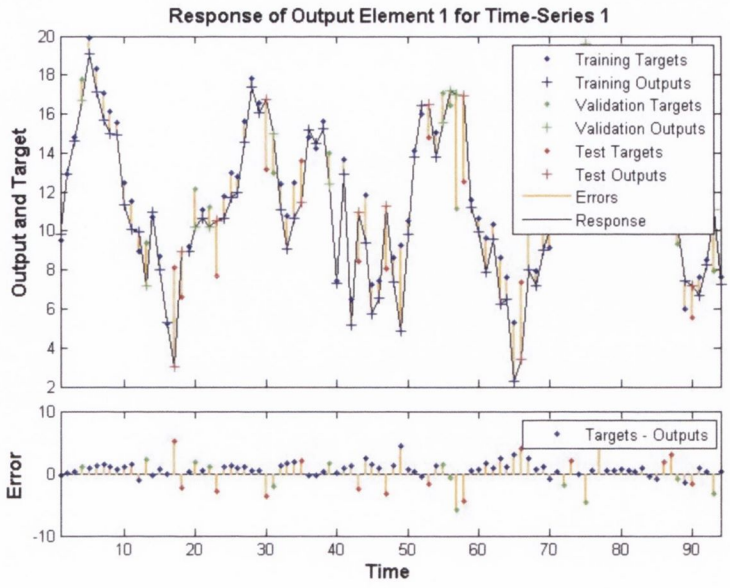

Figure D. 64 Time series of neural network training Site 10 run 2 $PM_{2.5}$

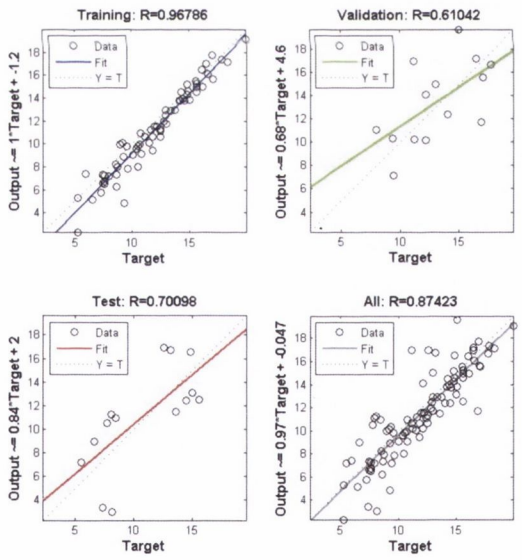

Figure D. 65 Site 10 run 1 PM2.5 regression of trained output data set

Appendix E: Neural Network Forward Predict Code

```
% This script assumes these variables are defined:

%   timeh - input time series.
%   input - feedback time series.

time = importdata('s4r1NO2.csv');
inputT = importdata('s4r1NO2 target.csv');
inputF = importdata('s4r2NO2.csv');
timeh = time;
input = inputT;
toPredict = inputF;
inputSeries = tonndata(timeh,true,false);
targetSeries = tonndata(input,true,false);
forecastSeries = tonndata(inputF,true,false);

% Create a Nonlinear Autoregressive Network with External Input
inputDelays = 1:2;
feedbackDelays = 1:2;
hiddenLayerSize = 12;
net = narxnet(inputDelays,feedbackDelays,hiddenLayerSize);

% Prepare the Data for Training and Simulation
% The function PREPARETS prepares timeseries data for a particular
network,
% shifting time by the minimum amount to fill input states and layer
states.
% Using PREPARETS allows you to keep your original time series data
unchanged, while
% easily customizing it for networks with differing numbers of delays,
with
% open loop or closed loop feedback modes.
[inputs,inputStates,layerStates,targets] =
preparets(net,inputSeries,{},targetSeries);

% Setup Division of Data for Training, Validation, Testing
net.divideParam.trainRatio = 70/100;
net.divideParam.valRatio = 15/100;
net.divideParam.testRatio = 15/100;

% Train the Network
[net,tr] = train(net,inputs,targets,inputStates,layerStates);

% Test the Network
outputs = net(inputs,inputStates,layerStates);
errors = gsubtract(targets,outputs);
performance = perform(net,targets,outputs) ;

% Plots

figure, plotregression(targets,outputs)
figure, plotresponse(targets,outputs)
```

```
% Closed Loop Network
% Use this network to do multi-step prediction.
% The function CLOSELOOP replaces the feedback input with a direct
% connection from the outout layer.
netc = closeloop(net);
netc.name = [net.name ' - Closed Loop'];

% Creating a new input series which has the time
% inputs for the second half of the time but also
% includes last 10 time steps from the previous
% timeSeries

newInputSeries = forecastSeries;

%Creating a new target with first 10 values which
%are the expected outputs network and the
%remaining targets are set to NAN, These values
%which are set to NAN will be predicted.
newTargetSet = nan(size(newInputSeries)) ;
newTargetSet = num2cell(newTargetSet ) ;
newTargetSet (1:70) = targetSeries(end-69:end) ;
[xc,xic,aic,tc] = preparets(netc,newInputSeries,{},newTargetSet);
yPredicted = sim(netc,xc,xic,aic);
typ=transpose(yPredicted);
figure, plotresponse(targets,yPredicted)
figure, plotregression(targets,yPredicted)

dlmwrite('forwardpred.csv',typ,'delimiter',',','precision', 8);

figure, plotresponse(targets,outputs)

%%%END CODE%%%
```