Spatial-Temporal Analysis of Traffic-Related Ground Level Ozone

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DECLARATION OF AUTHORSHIP

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

The following 4 journal publications were jointly authored:
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The above journal and conference papers were written as part of the candidate PhD thesis. The candidate came up with the original idea, performed statistical analysis and wrote the papers; however the co-authors supervised the candidate and provided help as and when required. These papers are part of Chapters 5, 6, 7, 9, and 10.

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ABSTRACT

Prolonged exposure to elevated levels of ozone (O_3) has been proven to adversely affect human health, agricultural crops and building materials. Therefore, ground level O_3 is currently regarded as one of the most harmful air pollutants, and identified as a priority pollutant in almost all national and international air quality legislations. Historically, O_3 has been regarded as a rural issue because relatively high levels of O_3-depleting species like NO from traffic and other combustion sources have helped to reduce its impact in urban area. However, more recently, and most likely as the result of increasingly more aggressive and effective management of NOx, urban O_3 levels have begun to rise much more rapidly than 'background O_3' in rural areas. As a result O_3 pollution is becoming an increasing important urban issue.

Therefore, the main aim of this PhD project is to characterise the temporal - spatial variability of ground level ozone. As in other studies, rural time-series of O_3 and meteorological data and spatial parameters are considered as part of the analysis. However, here the analysis is extended using recently collected urban data, most notably co-located O_3 and traffic related pollutant time-series and road traffic characteristics (from double loop counters), to provide more insight into the mechanisms driving traffic-related O_3 trends. Traditionally, many researchers have used linear, mean-centred (and parametric) statistical methods to ozone. However, here, in light of the non-linear association between ozone and its potential covariates, the focus has been on non-parametric methods. In particular two methods have been extensively used, namely Quantile Regression and Generalised Additive Modelling. Such approaches provide a much more comprehensive description of O_3 trends because they are better able to represent the distinctly different behaviour of O_3 at concentration extremes.

Statistical analysis shows that on average ozone concentrations are about 26 % higher in rural areas than in urban areas. The urban decrement varies at different quantiles of ozone concentrations and ranges from 10.5 $\mu g/m^3$ (25%) to 21.56 $\mu g/m^3$ (30%) at quantile 0.1 and 0.99, respectively. The results of quantile regression model show that up to 90 % of ozone variations between rural and urban sites can be explained with the help of road traffic characteristics. It is shown that the strength and nature (positive or negative) of the association between ozone and its covariates change at different levels of ozone. The model result shows that ozone levels increase towards north and decrease towards east in the UK. Ozone concentration appears to be negatively correlated with the distance from the coast within a range of 0 to 60 km, a trend associated with relatively less dry deposition of ozone molecules on water surfaces. Furthermore, there is a positive association between the altitude of monitoring site and ozone level, most likely due to local topographical effects. Ozone temporal trends show significant variability at different statistical metrics (e.g., mean, median, maximum and selected quantiles). Urban and rural trends have different rates and indicate that urban decrement has been decreasing over the period. Ozone trends during 1993 to 2011 and 2004 to 2011 showed different patterns, i.e., average ozone trends at both urban and rural sites are positive for the former and negative for the latter case. NOx trends have been stabilised during the last 8 years in urban areas and could have caused the ozone trends to change from positive to negative.

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CHAPTER 1: INTRODUCTION

1.1 Motivation

Tropospheric or ground level ozone (O_3) is one of the most harmful air pollutants. Ozone is not directly emitted by combustion processes or any other sources of air pollutants; rather it is formed photochemically from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NOx) in the atmosphere (AQEG, 2009). Ozone is a reactive compound and reacts with biological materials causing various health problems as well as damage to a wide range of biological and man-made materials, with most concern currently focused on agricultural crops and urban infrastructure (WHO, 2008; Bell and Treshow, 2008). Furthermore, ground level ozone is considered an important greenhouse gas and a principal source of the hydroxyl radical (IPCC, 2001), which is vital for the atmospheric reactivity. Due to interactions with other air pollutants, most notably NOx, VOCs and particulates, ozone plays a vital role in atmospheric chemistry. Despite the traditional focus of ozone as a rural or background pollutant that is managed on a national level, its impact is actually most acute in urban areas where the interaction between sources and sinks is most dynamic and complex. It is, therefore vital to characterise the variability of ground-level ozone in both time and space from urban perspective, which will help better understand ozone behaviour, and prepare a management and control strategy for ozone related urban air quality.

It is reported (e.g., Jenkin, 2008) that peak short term (e.g., hourly average) ozone levels generated in summer time photochemical episodes associated with periods of anticyclonic hot weather have reduced due to reduction in NOx and VOCs emissions in Europe. In the late 1970s and early 1980s during photochemical ozone episodes, ozone concentration were in the range of 350 – 400 µg/m^3 and reached to 516 µg/m^3 in the 1976 episode. In contrast, during the very hot summer of 2003, the peak hourly ozone level recorded in the UK was 279 µg/m^3 (Williams, 2007). However, there is evidence that annual mean ozone levels are increasing mainly because of the NOx titration effect, where reducing NOx levels lowers the local destruction of ozone near to sources of NOx and thus leads to increases in mean ozone levels. This is particularly pronounced in urban areas in the UK, where, as NOx levels have decreased, mean ozone levels have increased (AQEG, 2009). Different ozone trends in urban and rural areas, are leading to a reduction in urban ozone decrement (the amount by which ozone level is lower in urban than the surrounding rural areas). Therefore, ground level ozone is emerging as an urban pollutant in contrast to traditional rural pollutant. This has diverted the focus from rural ozone to traffic-related ozone, which might be more

challenging in certain aspects. In urban areas reducing traffic related air pollutants (e.g., NO_2 and particulates) is already a challenge for the policy makers and increasing ozone level may complicate the situation; high population density in urban areas may put more people at risk; damage to buildings, other materials and urban ecosystem might be greater; poor ventilation in urban areas due to buildings that hinder pollutants dispersion may exaggerate the air pollution problem further; and aggregate of pollutants (in contrast to a single pollutants in rural areas where traffic related pollutions are not an issue due to their low concentrations) may have more serious consequences.

In this PhD project the intention is to analyse spatial-temporal variations of ground level ozone concentration in the UK, focusing on urban areas. Urban ozone, also known as traffic-related ozone (e.g., Makra et al., 2010; Lanka et al., 2006) is affected by road traffic in two ways: firstly road traffic emits NOx, VOCs and carbon monoxide (CO) which are considered the main precursors of ozone because ozone is formed by the photochemical oxidation of these compounds in the presence of solar radiation; and secondly locally emitted NO acts as a sink and consumes ozone molecules (Jenkin, 2004; and Derwent et al., 2010). In addition to traffic characteristics (traffic flow, vehicle speed and fleet composition), this PhD project investigates the impact of a number of potential influences including meteorological variables (wind speed, wind direction, temperature, solar radiation, and relative humidity), traffic-related air pollutants (CO, Nitric Oxide (NO), Nitrogen Dioxide (NO_2), and Particulate Matter with aerodynamic diameter of 2.5 μm or less ($PM_{2.5}$)), and spatial parameters (altitude, latitude & longitude, distance from the coast and rural-urban factors) to analyse spatial-temporal variability of traffic-related ground level ozone.

In this chapter the main aims (section 1.2) and objectives (section 1.3) of the project are described. Furthermore, relevance of this project which justifies the importance of the project is provided (section 1.4).

1.2 Aims of this thesis

The aim in this project is to characterise the spatial and temporal variability of ozone concentration in the new perspective i.e. as an urban rather than a rural pollutant. In urban environment ozone concentration is directly affected by road traffic, a source of ozone precursors (e.g. NOx and VOCs) and a local sink (ozone titration by freshly emitted NOx). The former is a positive whereas the latter is a negative contribution to ozone concentration. However, in the urban environment NOx as a sink plays a more dominant role and is the main cause of ozone urban decrement (Jenkin, 2008). Therefore, local road traffic

theoretically should affect ozone concentration negatively, but the effect of local traffic gets confounded by the regional and global scale phenomena which need to be accounted for, if the local contribution to urban ozone is to be understood. This study investigates the effect of road traffic on ozone concentration in two ways: firstly to analyse hourly road traffic characteristics (traffic volume, vehicle speed and fleet composition) data to describe their association with ozone; secondly to compare ozone concentration at urban and rural sites and analyse the differences.

Furthermore, the project aims to model the effect of meteorological variables on ozone concentration from an urban perspective. It is reported (e.g., Jenkin, 2008; Derwent et al., 2007) that year to year variation in meteorological parameters may mask the observed ozone trend caused by changes in precursor emissions. The relationship between ozone concentration and meteorology, although has been investigated previously (e.g., Duenas et al., 2002; Camalier et al., 2007; Baur et al., 2004), the traditional focus on rural ozone and the associated higher density of ozone monitoring stations in rural areas has limited the relative availability of urban data and tended to bias more general research, such as the relationship between ozone and metrological conditions, towards trends in rural areas. More recently as a result of ozone emerging as a pollutant of concern for the urban environment, ozone monitoring stations have been installed in urban areas in the UK and elsewhere. However, urban environments are high complex and local topography, transport infrastructures and buildings can all significantly distort exposure to air pollution. Therefore our ability to better understanding and ideally manage future ozone trends is likely to be highly dependent on our ability to develop more accurate local scale ozone models with the help of local meteorological parameters.

Most of the existing research describing the association of ozone with traffic related air pollutants, road traffic characteristics or meteorology is based on linear regression, describing the average (mean) relationship between the dependent and independent variables; such models fail to perform when applied to estimate atypically high ozone concentrations. Furthermore, linear regression assumes normal distribution and a linear relationship between the dependent (ozone) and independent variables, which is not met by ozone or other air pollutants data. This project intends to change the focus on mean to other statistical metrics (quantiles), as these provide a greater insight into the whole ozone distribution, rather than just the central tendency (e.g., mean, median or mode). Although average or median is a useful metric and provides important information about the overall ozone level, the tails of distribution, particularly the right tail which corresponds to atypically high ozone concentration is especially important from public health perspective.

The aim of this project is, therefore, to characterise traffic-related ozone concentration with the help of historical ozone data from rural and urban monitoring sites, spatial characteristics (easting and northing, altitude, distance from the coast and site types), road traffic characteristics (traffic flow, vehicle speed and fleet composition), other air pollutants (e.g. NOx, CO, VOCs, $PM_{2.5}$) and meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction), taking into account the whole ozone distribution.

1.3 Objectives

The core aim of this PhD project can be sub-divided into a set of objectives, which define the steps that will be taken to achieve the desired outcome. The objectives of this thesis are as follows:

- To analyse the diurnal, weekly and seasonal cycle of ozone concentration and characterise the variations with the help of meteorological variables, other air pollutants (especially NOx) and road traffic characteristic (chapter 5);
- To analyse ozone frequency distribution to determine whether ozone concentration is normally distributed. This is important to decide whether to apply parametric or non-parametric statistical tests (chapter 5).
- To investigate the relationship between ozone and other air pollutants (NO_2, NO, CO, VOCs, and $PM_{2.5}$) and, ideally, better understand their role in controlling the variations in ozone concentrations in the UK (chapter 6);
- To investigate the effect of local road traffic characteristics (traffic flow, vehicle speed, and fleet composition) on traffic related ozone concentrations and quantify their contribution to ozone concentrations on local levels (chapter 7);
- To quantify the association of ozone and meteorological variables, taking into account the whole ozone distribution(chapter 8);
- To model the spatial variability of ozone in the UK with the help of geographical (spatial) parameters and to investigate as to how ozone concentration is affected by the associated variables (e.g., altitude, distance from the coast etc.) (chapter 9);
- To characterise temporal trends in ozone concentrations in urban and rural areas, analyse their differences, characterise the factors responsible, and discuss their implications for future ozone-related air quality management practices (chapter 10).

1.4 Relevance of this research

Stringent policy is required to reduce pollutant emissions, however high quality scientific evidence as a basis for policy enforcement is now firmly established (Williams, 2004). The public policy concern over the impact of road traffic on local air quality has stimulated a substantial body of research aimed at advancing underlying vehicle and traffic management technologies, promoting healthier transport modes and informing public policy action. As a result of stringent emission policies in the UK, the concentrations of many traffic related air pollutants (e.g., VOCs, NO, SO_2 and particulates) have gradually declined (Carslaw et al., 2011; AQEG, 2005; AQEG, 2004). However, the observed concentrations of some air pollutants (e.g. ozone and NO_2) do not seem to suggest a declining trend as expected (AQEG, 2009, Carslaw et al., 2011). More concerned is the potential that some pollutants (e.g. ozone), which were not previously believed to threaten public health due to their low concentration levels, particularly in urban areas are now demonstrating an increasing trend and are posing a threat to human health and the natural urban ecosystem. Several authors (e.g., Jenkin, 2008; Derwent, 2007; Carslaw, 2005) have reported increasing ozone concentrations in the UK. It is reported by the European Environmental Agency (EEA, 2012) that despite efforts to mitigate ozone pollution, the number of exceedances of EU ground-level ozone concentration standards for protecting human health (Directive 2008/50/EC) remained at serious levels during summer 2011. As in previous years, the long-term objective for the protection of human health (maximum daily eight-hour mean concentration of 120 $\mu g/m^3$) was exceeded in all EU Member States, even though 2011 had unusually low temperatures and increased rainfall during the summer months, conditions that would typically be associated with relatively low ozone levels. EEA (2012) concluded that decreased anthropogenic emissions of some ozone precursors (NOx, CO and VOCs) in the past two decades did not demonstrated significant reductions in the number of exceedances, therefore the ozone pollution problem requires further mitigation efforts.

Traditionally air pollutants like NOx (e.g. Carslaw, 2005; Carslaw and Beevers, 2005) and particles (PM_{10} and $PM_{2.5}$) (AQEG, 2005) have been linked and studied extensively in conjunction with road traffic, in contrast ozone is rarely linked with road traffic because ozone is a secondary air pollutant which is not directly emitted by road traffic and rather is formed in the atmosphere by photochemical reactions of NOx and VOCs. However, recent trends show that mean ozone concentration is increasing in urban areas at greater rates than in rural areas, which is believed to be due to decreasing NOx levels in urban areas. NOx is negatively correlated with ozone and any reduction in its concentration will invariably result in an associated increase in ozone concentration. The local ozone reduction by NOx works in the opposite way to the regional effect of road traffic, which is a source of precursors

(e.g., NOx and VOCs) for ozone formation. In urban areas the local negative effect is dominant over the positive regional effect. This results in relatively low ozone concentrations in urban areas by comparison to nearby rural areas. But this difference (ozone urban decrement) is decreasing and may disappear in the next couple of decades or so (Williams, 2007). This highlights how road traffic plays an important role in controlling ozone variations in urban areas, which require further investigation to be better-understood with the help of advance statistical techniques and high resolution data of ozone and road traffic characteristics.

In addition to characterising the effect of meteorology, road traffic and other air pollutants on ozone concentrations, this project intends to devise a new approach for ozone modelling using geographical or spatial parameters of the monitoring sites, which includes easting and northing (or latitude and longitude), altitude, distance from the coast and site type (or rural-urban factor). Although some individual spatial parameters have been analysed in conjunction with ozone concentrations: for example, Coyle et al. (2002) investigated the effect of altitude on ozone concentration; Entwistle et al. (1997) investigated the effect of proximity to coast on ozone concentration; and Jenkin (2008) described variations in ozone concentration along South-East to North-West transect in the UK. However, these have not been investigated in aggregate to account for their interaction and derive a relationship for modelling ozone spatial variability. This project intends to develop this further to make a model for ozone temporal and spatial prediction, using easting, northing, altitude, distance to the coast, and site type (rural-urban factor) as covariates. The data for most of the parameters are available at the UK AURN website or can be derived from other freely accessible sources; and the model can explain a considerable proportion of variation in ozone concentration (see chapter 9 for more details).

The outcomes of the project will add to the scientific understanding of ozone, improve predictive ozone modelling and will aid policy makers in the development of effective mitigation strategies.

1.5 Thesis layout

The main aim of this PhD project is to characterise the spatial-temporal variability of traffic-related ozone concentrations with the help of historical ozone data, spatial characteristics (easting and northing, altitude, distance from the coast and site types), road traffic characteristics (traffic flow, vehicle speed and fleet composition), traffic related air pollutants (e.g. NOx, CO, VOCs, $PM_{2.5}$) and meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction), taking into account the whole

ozone distribution. In this chapter the main aims and objectives and relevance of this project are described. This PhD project intends to focus on traffic-related ozone which is more challenging than rural ozone in terms of management and potential adverse impacts on human health, building materials and ecosystem. The project aims to provide an insight into the decreasing urban decrement, focusing on the role of traffic related emissions particularly NOx, which is a precursor as well as a scavenger for ozone.

The next chapter (Background) provides an overview of ozone formation, the importance of ozone and its role in the atmospheric chemistry, which will facilitate understanding of the later chapters. A discussion of the current state of knowledge and literature, which are relevant to the work presented in this thesis, is provided in chapter 3 (Literature Review). The literature review include: (a) the impact of spatial characteristics; (b) ozone temporal trends; (c) the effect of meteorology; (d) the effect of road traffic; and (e) modelling of ozone. The methodology of the project, including a description of the models (Quantile Regression Model and Generalised Additive Model), which are employed in this thesis, is provided in chapter 4. The methodology of each chapter is described in a separate section. Furthermore, data sources, various metrics and units to express ozone and other parameters, and general statistics (e.g., correlation analysis and graphical presentations) are described in chapter 4. The next 5 chapters: Frequency Distribution and Temporal Variation of Ozone – Chapter 5; The Relationship of Ozone with Traffic Related Air Pollutants – Chapter 6; The Impact of Road Traffic on Ground Level Ozone – Chapter 7; Ground Level Ozone and Meteorology – Chapter 8; Spatial Analysis of Ozone Variations in the UK – Chapter 9; and Temporal Trends in Ozone Concentration in the UK – Chapter 10 cover the main data analysis and results of this thesis. These chapters characterise ozone temporal and spatial variations and analyse the association of ozone with several independent variables, such as meteorology, traffic characteristics, and traffic related air pollutants. Finally all chapters are summarised in Chapter 11(Summary and Further Works) along with a summary of the main findings of this thesis and suggestions for potential future work.

CHAPTER 2: BACKGROUND

2.1 Introduction

Ozone (O_3) is a secondary air pollutant and is formed by photochemical oxidation of Volatile Organic Compounds (VOCs) and nitrogen oxides (NOx) in the presence of solar radiation (AQEG, 2009). Ozone is a reactive oxidant and is actively involved in many chemical reactions including biochemical reactions, causing various health problems, damage to agricultural crops and other materials (e.g., Bell and Treshow, 2008). Furthermore, ozone plays a vital role in atmospheric chemistry and contributes to the greenhouse effect (IPCC, 2001).

Atmospheric ozone levels are dependent on the amount of ozone precursors (sources), the amount of reactants (sinks) and meteorological conditions. High ozone concentrations are usually observed during periods with sustained high temperatures and sunshine, because such conditions favour photochemical ozone formation. Photochemical reactions can take some time to proceed, therefore regional transport of ozone and its precursors can also exert a strong influence on the UK ozone levels. High temperatures, coupled with the re-circulation of air masses laden with ozone precursors over Europe and the UK are often conducive to ozone pollution episodes (PORG, 1998).

This chapter discusses the mechanism that drive these general trends, the associated ozone sources and sinks (section 2.2), the chemistry (section 2.3), the importance (2.4) and also briefly consider the methods, used to monitor ozone (section 2.5).

2.2 Sources and sinks of tropospheric ozone

Tropospheric or ground level ozone is an important natural component of the lower atmosphere. Ozone is not directly emitted to the atmosphere by combustion processes, rather it is formed photochemically from the sunlight-initiated oxidation of VOCs in the presence of NOx and therefore ozone is considered as a secondary air pollutant (AQEG, 2009). Ozone is naturally found both in the upper (stratosphere) and lower atmosphere (troposphere). In the stratosphere ozone absorbs ultraviolet (UV) radiation and protects us from the harmful effect of the UV radiation. At the top of the troposphere ozone acts as a greenhouse gas and contributes to global warming. At the bottom of the troposphere, where we live and breathe, ozone is a toxic air pollutant and is considered one of the most harmful air pollutants (WHO, 2008). At the ground level, ozone can act to adversely affect human life, agricultural crops, biodiversity and materials (Bell and Treshow, 2008). This is because ozone molecule is an unstable and reactive oxidant and readily deposits onto most surfaces,

including biological tissues e.g. lungs, eyes, or plant membranes (Coyle et al., 2002). The human health impacts of ozone derive from its irritant properties and its induction of an inflammatory response in the lungs, causing health problems and premature deaths (WHO, 2008).

Atmospheric ozone concentration is not only dependent on its precursor emissions (e.g., VOCs and NOx) and other air pollutants (e.g., particles and carbon monoxide) that can affect ozone concentration in different ways, such as particles can provide a surface for ozone dry deposition and carbon monoxide can react with hydroxyl radical (OH) to produce peroxide radicals that consume nitric oxide (NO), but also on meteorological conditions (e.g. solar radiation, temperature, relative humidity, wind speed and wind direction). Furthermore, ozone concentration at a given location in the UK can be influenced by a combination of global (hemispheric), regional and local-scale effects (Jenkin, 2008**).** The European Environment Agency (EEA) describes the total UK ozone levels as the sum of background ozone and the ozone produced locally by photochemistry in the UK; where background ozone is a mix of ozone produced from emissions on other continents and ozone descended from the stratosphere (EEA, 2009). Figure 2.1 presents source attribution of ozone for a rural location in southern England, where approximately two-thirds of the ozone found at this rural site was transported by large-scale intercontinental processes and one-third produced from photochemical formation on the regional scale within Europe (Derwent, 2008). Figure 2.1 shows that only a part of the European ozone levels are controlled by the European precursor emissions; sources in other continents and stratospheric ozone also play a significant role in ground-level ozone concentration. However, in summer regional ozone production by ultraviolet radiation from European precursor emissions contributes dominantly to ozone episodes (EEA, 2009; Jenkin, 2008).

The main sink for ozone in the UK is dry deposition to surfaces (including the human respiratory tracts), and uptake by vegetation; however in urban areas and roadsides location the removal of ozone by chemical reaction with NOx, more specifically with NO in the atmosphere represents a further sink for ozone (PORG, 1998; EEA, 2009). Because of the NOx-scavenging effect ozone concentrations are generally lower in urban areas than in the surrounding rural areas. Consistent with this effect, UK ozone monitoring data collected in urban areas is typical 30% to 50% lower by comparison with that observed at nearby rural monitoring stations (PORG, 1998). The amount by which ozone concentration is lower in urban areas than in surrounding rural areas is referred to as the ‘urban decrement’. Reductions in NOx emissions over the last 10 to 15 years, however have led to a reduction in the urban decrement, so that ozone concentrations in urban areas have generally increased (AQEG, 2009).

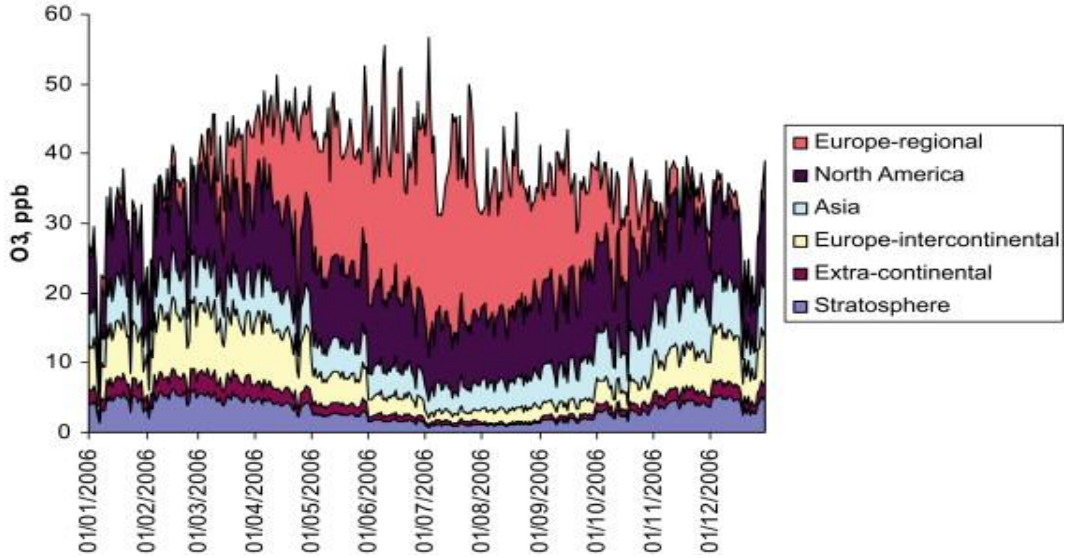


Figure 2.1. Source attribution of the ozone found at a rural location in southern England during 2006. Europe-regional refers to the ozone advected directly; North America to that formed over that continent and over the western North Atlantic and eastern Pacific; Asia to that formed over that continent and over the western Pacific; Europe-intercontinental to that advected around latitude circles and back into Europe; and stratosphere to that descended from the stratosphere by the process known as Strato-Tropospheric Exchange (STE) (Figure source: Derwent, 2008).

2.3 Ozone chemistry

Gas phase processes in urban areas are dominated by NOx (NOx = NO + NO_2), which is mainly produced from traffic exhaust emissions by internal combustion engines. NOx can be formed in any high temperature combustion process that occurs in the presence of nitrogen through the thermal decomposition of molecular oxygen leading to the formation of NO.

$$2N_2 + O_2 \rightarrow 2NO + 2N \quad ... (1)$$

$$N + O_2 \rightarrow NO + O \quad ... (2)$$

NOx emitted from the vehicle exhaust is dominated by NO and is generally 95 % of the total NOx emissions, in contrast to 5% NO_2. There are also trace levels of other oxides of nitrogen present, e.g. nitrous oxide (N_2O). However, the ratio of NO_2/NO is believed to have changed as result of increasing emission of primary NO_2, particularly from the new

generation diesel engines (Carslaw et al., 2011). Carslaw et al. (2011) have estimated an in increase in the emission of primary NO_2 from around 5–7% in 1997 to about 15–16% in 2009. The increase in primary NO_2 in London has been more marked than other UK locations. Based on 23 long-running roadside sites, primary NO_2 in London has increased from around 5% in 1998 to about 21% in 2009 (Carslaw et al., 2011). The principal factor accounting for the increase in the observed primary NO_2 values is considered to be the increased use of oxidation catalysts and particle filters on light duty diesel vehicles (AQEG, 2009). Higher values in London are consistent with a large fraction of the London bus fleet using continuously regenerating particle filters.

Latham et al. (2001) has shown that the actual proportion of primary NO_2 varies according to factor such as vehicle type, operating conditions, fuel type and emission abatement technology and can be much higher than 5%. It is shown that diesel vehicles tend to have high proportion of NO_2 than petrol vehicles, and for the former the average NO_2 proportion of 25 % was obtained (Latham et al., 2001). On roadside locations the NO_2 concentrations are limited by the local concentrations of ozone rather than the emissions of NO from vehicles. During day-light the NOx chemistry shown below plays a dominant role.

$$NO + O_3 \rightarrow NO_2 + O_2 \ldots (4)$$

$$NO_2 + h\nu \rightarrow NO + O\,(^3P) \ldots (5)$$

$$O\,(^3P) + O_2 + M \rightarrow O_3 + M \ldots (6)$$

In the above Equations ‘M’ is an un-reactive molecule such as nitrogen (N_2) or oxygen (O_2) molecule; and O (^{3}P) denotes a ground state or low energy oxygen atom, which reacts with molecular oxygen (O_2) to form ozone (O_3). In the absence of other reactions, Equation 4 to 6 show that the level of oxidants (NO_2 and ozone) remains conserved, with the partitioning between the component forms ozone and NO_2 controlled by the overall levels of NOx, ozone and solar intensity. All three reactions are rapid and equilibrium is reached when the rate of ozone formation equals the rate of ozone removal. This is a Photostationary (or null) state, where no net ozone formation occurs and it dominates oxides of nitrogen chemistry and normally takes place in an un-polluted atmospheric environment.

For net ozone formation the processing of hydrocarbons in the presence of NOx is required. In a polluted air VOCs and CO plays a crucial role in ozone production. Photolysis of ozone by short-wave UV light yields a reactive O (^{1}D) atom, which may lose energy by collision with O_2 and N_2 molecules in air and then react with O_2 to re-form ozone (Equations 7 and 8) or may react with water vapour (H_2O) to generate hydroxyl radicals (OH) (Equations 7a and 8a).

$$(O(^1D) + M \rightarrow O(^3P) + M \ldots (7)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \ldots (8)$$

$$O_3 + hv \rightarrow O(^1D) + O_2 \ldots (7a)$$

$$O(^1D) + H_2O \rightarrow OH + OH \ldots (8a)$$

OH radicals react with RH (e.g., methane - CH_4) or CO and leads to the formation of organic peroxy radicals (RO_2) (Equations 9 and 10) or hydroperoxy radicals (HO_2) and water (H_2O) (Equations 11 an 12).

$$RH + OH \rightarrow H_2O + R \ldots (9)$$

$$R + O_2 + M \rightarrow RO_2 + M \ldots (10)$$

$$CO + OH \rightarrow H + CO_2 \ldots (11)$$

$$H + O_2 + M \rightarrow HO_2 + M \ldots (12)$$

What happens to RO_2 and HO_2 depends whether the atmosphere is clean (low in NOx) or polluted (e.g., a typical urban environment generally high in NOx). In clean air these radicals undergo self and cross reaction forming peroxides (H_2O_2), alcohol (ROOH) and aldehydes (RCHO) and are lost through wet deposition. The result is loss of ozone in Equation (7a). In a polluted atmosphere in the presence of NOx, the RO_2 and HO_2 can react with NO to form NO_2 and an alkyl radical (RO). The alkyl radical quickly reacts with oxygen forming an aldehyde (RCHO) and a hydroxy radical (HO_2). The HO_2 also reacts with NO, forming an additional NO_2 and regenerating the OH.

$$RO_2 + NO \rightarrow RO + NO_2 \ldots (13)$$

$$RO + O_2 \rightarrow RCHO + HO_2 \ldots (14)$$

$$HO_2 + NO \rightarrow OH + NO_2 \ldots (15)$$

These reactions shift the equilibrium between NO and NO_2 towards NO_2 leading to greater rates of net ozone formation. The cycle can be closed by reaction of OH with NO_2 to form nitric acid (HNO_3), which is highly soluble and is lost to the condensed phase.

$$OH + NO_2 + M \rightarrow HNO_3 + M \ldots (16)$$

The full pathway of ozone formation and its reaction with other chemicals is summarised in Figure 2.2.

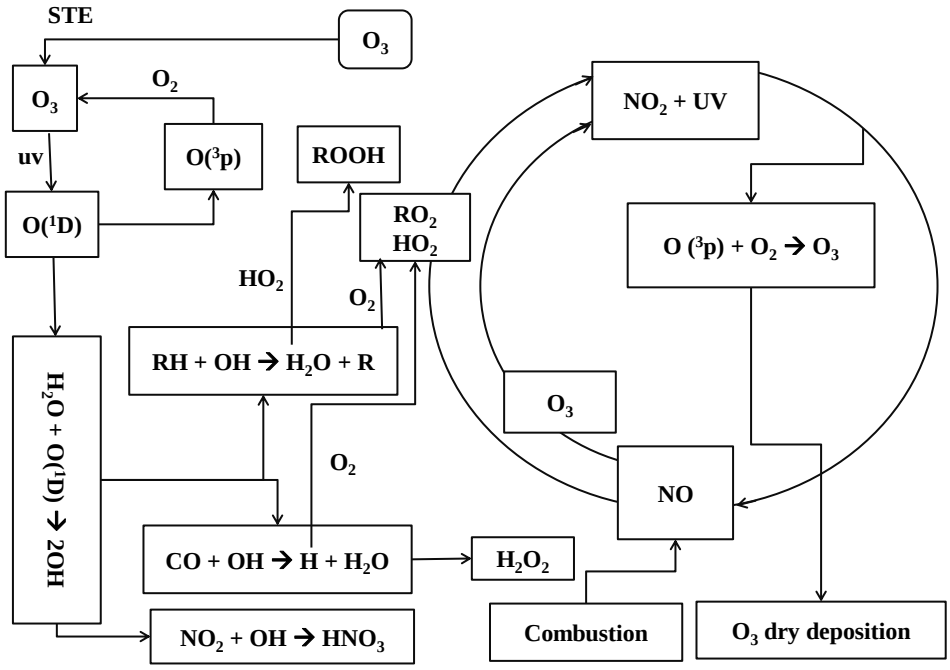


Figure 2.2: Photochemical ozone formation, showing various sinks and sources of ozone. STE – Strato_Tropospheric Exchange, RO_2 – organic peroxy radicals, OH – hydroxyl radicals, HO_2 – hydroperoxy radicals, O_3 – ozone, NO – nitric oxides, NO_2 – nitrogen dioxides, $O(^3p)$ – ground state oxygen atom, $O(^1D)$ - higher energy oxygen atom, R – alkyl radicals (e.g. CH_3), RH – hydrocarbons (e.g. CH_4), H_2O_2 – hydrogen peroxides, ROOH – alcohols, H_2O – water, CO – carbon monoxides, CO_2 – carbon dioxides, HNO_3 – nitric acids, UV – ultraviolet radiation, UV ~ 310 nm is required for ozone photolysis and UV < 435 nm for NO_2 photolysis (Figure Source: Munir et al., 2012 and Cape, 2008).

2.4 Importance of ozone

Ground level ozone is one of the eight priority air pollutants, identified as part of the Air Quality Strategy for England, Scotland, Wales and Northern Ireland (AQS, 2000), by virtue of their adverse impact on human health and the natural environment. Many of the adverse effects of ozone previously discussed (e.g., Bell and Treshow, 2008; Coyle, 2006; EEA, 2009), contribute to its selection as one of the most harmful atmospheric species. Elevated levels of ozone has adverse effects on human health, crop yields and tree growth, changes the composition of natural plant communities, causes changes in biodiversity and damages building and other materials, which are discussed briefly below (sections 2.3.1 – 2.3.5).

2.4.1 Human health impact

The human health impacts of ozone derive from its irritant properties and its induction of an inflammatory response in the lungs, causing health problems and premature deaths (EEA, 2009; AQEG, 2009). The World Health Organisation (WHO, 2008) has reported that elevated ozone pollution causes about 21000 premature deaths and 14000 respiratory hospital admissions annually in 25 European Union countries. Furthermore, ozone affects the health of large populations causing minor restricted activity days, medication use for respiratory problems, and coughs and lower respiratory symptoms. Both short and long term-exposure of humans to high ozone concentrations are reported to cause adverse health effects. Short term exposure to ozone may affect pulmonary function, lung inflammation, lung permeability, respiratory symptoms, increased medication usage, morbidity and mortality; whereas long term exposure is linked with inflammatory responses, lung damage and persistent structural airways and lung tissues changes in early life (WHO, 2008). Several epidemiology studies (e.g. Koken et al., 2003; Kinney, 1999) have reported an association between ozone and hospital admissions or emergency visits for respiratory conditions, mal-lung function, and a variety of other health problems.

Experimental studies have shown that ozone causes direct cellular damage by damaging the antioxidant mechanisms in cells lining the airway walls. Prolong exposure of animals to high doses results in persistence inflammation of the small airways, similar to that induced by cigarette smoking. It can also induce fibrosis in the lung (Walters and Ayres, 2001). Several physiological studies have demonstrated a consistent curvilinear relationship between inhaled ozone and respiratory function (Walters and Ayres, 2001); where increasing inhaled ozone concentration had a greater effect than either increasing duration of exposure or increasing ventilation by exercise. The sensitivity is not confined to those with respiratory disease and rather occurs just as frequently in normal individuals, however, individuals vary in susceptibility to ozone pollution.

In a modelling study Schlink et al. (2006) investigated the effect of ozone on respiratory symptoms and reported that a significant adverse effect of ozone can be detected only when restricting the analysis to days with 8 hours average concentrations above 60 $\mu g/m^3$. Based on a panel study of children in Leipzig, Schlink et al. (2006) identified a nonlinear (quadratic) concentration response relationship between ozone and respiratory symptoms. Below 60 $\mu g/m^3$ the effect was non-significant, suggesting the existence of a threshold concentration for ozone. In a recent study Yang et al. (2012) used three exposure metrics of ozone concentrations (1hour maximum, maximum 8 hour average and 24 hour average) to examine its short-term association with daily mortality in Suzhou, China. Yang et al. (2012) found that the current level of ozone in Suzhou was positively associated with death rates

due to various health problems, particularly cardiovascular diseases. The association between ozone exposure and risk of cardiovascular mortality was stronger than that for all other causes of mortality risk. There are several potential underlying mechanisms for the link between ozone exposure and cardiovascular mortality (Yang et al., 2012). Inflammation of pulmonary tissues can induce a spectrum of mediators and alter cardiac functions or irritant receptor mediated stimulation of parasympathetic pathways. Among various metrics of ozone, maximum 8 hour average and 1 hour maximum concentrations seemed to be more strongly associated with increased mortality rate compared to 24 hour average concentrations. This is probably because maximum 8 hour average and 1 hour maximum concentrations reflect a more biologically relevant exposure (for example, peak vs. average exposure) or because they more strongly correlate with average population exposures compared with 24 hour average concentrations. Temporal metrics that reflect peak pollution levels may be the most biologically relevant if the health effect is triggered by a high, short term dose rather than a steady dose throughout the day (Yang et al., 2012).

The UK Expert Panel on Air Quality Standards (EPAQS) has recommended an eight hour running mean (8 hrm) of 100 μgm^{-3} (50 ppb) as the critical level for ozone effects. The government adopted this as its air quality standard, with the objective that by 31 December 2005 it should not to be exceeded more than 10 times a year.

2.4.2 Impact on agricultural crops

Air pollution has a significant negative effect on vegetation productivity and crop yield, particularly during the latter half of the 20th century the effect has been more pronounced (Bell and Treshow, 2008). Over 90% of vegetation damage caused by air pollution is believed to be the result of tropospheric ozone alone (Felzer et al., 2007). Many organisms have evolved mechanisms to protect themselves against oxidative damage, however ozone concentration now regularly exceeds the ability of these mechanisms to cope and effects can be observed. Ozone is well documented as the air pollutant most damaging to agricultural crops and other plants (Mauzerall and Wang, 2001).

The effects of ozone on vegetation have been studied on a range of levels, e.g. small scale laboratory work using plant cultures, highly regulated greenhouse and growth chamber experiments, and large scale field trials (Felzer et al., 2007). Ozone pollution is known to have a substantial effect on agricultural production in North America, Western Europe and many other countries in the World (Wahid, 2006). Air pollution not only reduces the productivity of crops but also affects their nutritional quality. Experiments have shown reduced starch in wheat (Wahid, 2006), decreased fruit sugar in grapes (Soja et al, 1997) and reduced oil content in rape seed (Ollerenshaw et al, 1999). Bell and Treshow (2008)

reported that reducing ozone concentration by 30 - 40 % an annual benefit of €2000 million and $300 million can be achieved in Europe and USA, respectively. The trend of increasing emission of ozone precursors in parts of Asia, Latin America and Africa suggest that future ozone impacts on crops in these areas could be very serious (Bell and Treshow, 2008).

Absorption of ozone by leaves is a function of both stomatal conductance and ambient ozone concentrations. Ozone exposures induces a range of effects in plants depending upon duration and magnitude of exposure; ranging from cell and tissue death, accelerated senescence, changes in cell wall structure, decrease in photosynthetic and productive capacity (Bell and Treshow, 2008).

Plants are able to protect themselves from permanent injury due to ozone exposure either through thick cuticles, the closure of stomata, or detoxification of ozone near or within sensitive tissue. These protection devices come at a cost of either a reduction in photosynthesis, in the case of stomatal closure, or in carbohydrate used to produce detoxification systems (EPA, 1996). For detoxification to occur, it appears that the plant produces an antioxidant that reacts with ozone, thus protecting the tissue from damage. Ozone that has not been destroyed reacts at the biochemical level to impair the functioning of various cellular processes (EPA, 1996). Tolerance mechanisms based on reduced stomatal conductivity in the presence of ozone would likely reduce growth of tolerant plants. Similarly, tolerance mechanisms based on the productivity of antioxidant compounds allocate plant resources away from growth to the production of the defence compounds. Furthermore, ozone may modify any stage of the disease cycle directly, by affecting the causal organism itself, or indirectly, by effects on the host plant. Conversely, the plant-pest interaction may modify the sensitivity of the host plant to ozone (EPA, 1996).

Three statistically independent groups of crops, based on their sensitivity to ozone were identified by Mills et al. (2007). These are ozone sensitive crops (wheat, water melon, pulses, cotton, turnip, tomato, onion, soybean and lettuce); moderately sensitive crops (sugar beet, potato, oilseed rape, tobacco, rice, maize, grape and broccoli); and ozone resistant (barley and fruits like plum and strawberry). The sensitivity of a crop species may change with the developmental stage. In the case of wheat, sensitivity may increase during the transition from vegetative growth to reproductive growth, as suggested by Lee et al. (1988). High sensitivity to ozone from anthesis until harvest was reported by Amundsen *(*1987), where exposure of spring wheat between anthesis and grain filling to high ozone concentration showed greater effects on the yield, as compared to exposure before anthesis. Similarly, a study on tomato crop showed greater effect on yield when exposed to high ozone concentrations during flowering and initial fruit set, whereas in bean, exposure during pod development was most effective (Younglove et al., 1994). Crop sensitivities to ozone

exposure vary both by crop species and by the type of strain within a species (cultivar), as well as being influenced by various meteorological factors, including temperature, humidity, soil moisture, and radiation (Heck et al., 1984).

According to United Kingdom Photochemical Oxidants Review Groups (PORG, 1993), at 35 ppb ozone concentrations the more sensitive crops such as potatoes, pulses and wheat were affected, whereas at 45 ppb or above, all the major crops showed significant yield reductions. United Nation Economic Commission for Europe (UNECE) has defined critical levels for agricultural crops above which available evidence suggest that adverse effects are likely to occur with an increased exposure to pollutants. Critical levels are described in different ways for different pollutants, including mean concentrations, cumulative exposures and fluxes through plant stomata. The effects vary between receptor and pollutant and include growth changes, yield losses, visible injury and reduced seed production (UNECE, 2004). Critical levels defined in term of cumulative exposure index (e.g., AOT40 ppb hr) are the one most widely used for assessing the impact of ozone on agricultural crops in the UK and Europe (Bell and Treshow, 2008). AOT40 are accumulated ozone concentrations over 40 ppb (80 $\mu g/m^3$) and are estimated to assess the impact of ozone concentration on agricultural crops. The critical level of AOT40 for agricultural crops is 3000 ppb h (Coyle et al., 2002), which is accumulated during daylight hours for the three months (May, June, and July) when clear sky radiation is above 50 W/m^2 (Fuhrer et al., 1997). More details on AOT40 can be found in chapter 9 and the references therein.

2.4.3 Impact on other materials and buildings

Ozone has a damaging effect on certain materials, including polymers, rubbers, surface coatings and textiles. In combination with NOx and sulphur dioxide (SO_2), ozone has been shown to corrode metals and damage some types of stone (PORG, 1998). The mechanism of damage to materials by ozone and the concentration at which the damage occurs is not well defined as yet (Coyle et al., 2002), however a provisional level of 20 ppb as an annual average ozone concentration was set for an acceptable rate of materials deterioration at a UNECE workshop in 1993. This level is currently exceeded in almost all of the UK areas with the exception of some urban areas. Ozone concentration is lowest in urban areas where the density of at-risk materials is highest. Estimates of the current cost of damage to materials caused by ozone are of the order of several £100 million for the UK (PORG, 1998); however the methods used to produce these estimates are very uncertain and can only give an indication that the costs are substantial.

The effect of ozone on materials and in particular on cultural heritage buildings, where the damage is often impossible to recover (Screpanti and De-Marco, 2008) might increase as a

result of increasing ozone concentrations in urban areas (Jenkin, 2008). Ozone exerts a direct corrosive effect on natural rubber, plastic materials, textiles, paint and surface coating (Leith and Cape, 1998). Laboratory studies have shown a synergistic effect of SO_2 and ozone in terms of their corrosive effect on zinc, copper, nickel and calcareous stone materials (Kucera and Fitz, 1995). Material corrosion is affected both by climatic and pollution conditions. A recent study by Screpanti and De-Marco (2008) in Italy showed that the high concentration of ozone in synergistic action with other pollutants (e.g., NOx and SO_2), lead to a corrosion exceeding the tolerable thresholds of 4.8 mm/year (International Cooperative Programme - ICP, 2004) for cultural heritage buildings in the case of both limestone and copper, in 34% and 97% of Italian territory, respectively. They reported that corrosion rates were still substantially high even though SO_2 concentrations have decreased. This effect may be attributed to the increasing ozone concentration in urban areas that plays a more important role than in the past.

2.4.4 Ozone as a greenhouse gas

Greenhouse gases absorb and emit radiation within the thermal infrared range, which has a wavelength longer than that of visible light and is generally considered to be from 0.74 μm to 300 μm. This process is the fundamental cause of the greenhouse effect, a process believed to be resulting in an elevation of the average surface temperature (IPCC, 2001). The primary greenhouse gases in the troposphere are water vapour, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone. Ozone plays an important role in global warming and is a direct as well as an indirect greenhouse gas (IPCC, 2001). As a direct greenhouse gas it absorbs infrared radiation directly and is thought to have caused around one third of all the direct greenhouse gas induced warming seen since the industrial revolution (IPCC, 2001).

In addition, ozone is a reactive oxidant and reacts with several other atmospheric chemicals (e.g. NOx, VOCs and OH). Through chemical impact on OH, ozone modifies the lifetimes of other greenhouse gases, such as CH_4. However, the tropospheric chemical processes determining the indirect greenhouse effects are highly complex and not fully understood (IPCC, 2001). Because of the central role that ozone and OH play in tropospheric chemistry, the chemistry of CH_4, CO, non-methane hydrocarbons (NMHC), and NOx is strongly inter-correlated, making the interpretation of the effects associated with emission changes rather complex.

The greenhouse effect of ozone varies in space and time, particularly with the altitude. Forster and Shine (1997) and IPCC (2001) have provided details on the dependence of the surface temperature response on the height and type of ozone perturbation. They have

suggested that surface temperature is particularly sensitive to ozone concentration at altitude of 8 to 15 km. See IPCC (2001) and references therein for more details. The aim here is to highlight the importance of tropospheric ozone and appreciate that ozone is not only a harmful air pollutant but also an important greenhouse gas.

2.4.5 Ozone effect on atmospheric chemistry

2.4.5.1 Ozone as a source of OH

OH is one of the most important chemical species in the atmosphere, due to its high reactivity with both organic and inorganic compounds. Reaction with OH is the major sink for most atmospheric trace gases (e.g. SO_2, CH_4 and NO_2). Once formed, tropospheric OH reacts with CH_4 or CO within a second. The local abundance of OH is controlled by the local abundances of NOx, CO, VOC, CH_4, H_2O and ozone as well as the intensity of solar UV; and thus it varies greatly with time of day, season, and geographic location.

The principal source of OH in the troposphere is photolysis of ozone by solar radiation with $\lambda \leq 0.32$ μm, which split ozone molecule into molecular oxygen (O_2) and energetically excited oxygen atom O (^1D). The chemical reaction is shown in Equation 7a.

Most of the O (^1D) atoms dissipate their energy as heat to an un-reactive molecule M, such as N_2 and change to ground state low energy atoms O (^3p), which then react with O_2 and form ozone molecules again (see Equations 7 and 8). However, some O (^1D) reacts with water vapour to form OH (see Equation 8a).

Being a powerful oxidant, once formed OH quickly reacts with other trace gases, for instance OH react with CO, NO_2, hydrogen sulphide (H_2S) and SO_2 and form CO_2, nitric acid (HNO_3), SO_2, and sulphuric acid (H_2SO_4), respectively and thus act as sink for these pollutants. The local abundance of OH is controlled by the local abundances of NOx, CO, VOC, CH_4, ozone, and H_2O as well as the intensity of solar UV; and thus it varies greatly with time of day, season, and geographic location.

In addition to ozone being a source of OH, these radicals (OH and HO_2) together with NOx are key catalysts in the production of tropospheric ozone.

2.4.5.2 Ozone and other chemical

Ozone reacts with several atmospheric chemicals and hence plays a vital role in atmospheric reactivity. The most important of these reactions are the conversion of hydrogen sulphide

(H_2S) to SO_2; and the conversion of NO to NO_2. SO_2 is consecutively oxidized slowly to form sulphur trioxide (SO_3) and sulphuric acid (H_2SO_4).

$$H_2S + O_3 \rightarrow SO_2 + H_2O \quad ... (17)$$

$$SO_2 + O_3 \rightarrow SO_3 + H_2O \quad ... (18)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad ... (19)$$

The above reactions proceed to completion when there are excessive quantities of ozone present, however, when ozone concentration are equal to or below those of hydrogen sulphide, then only the reaction shown in Equation 17 takes place.

Ozone also reacts with halogens, for example, bromine (Br) and chlorine (Cl) to form their oxides, as shown below:

$$Br + O_3 \rightarrow BrO + O_2 \quad ... (20)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad ... (21)$$

Equation 20 and 21 play important role in the stratosphere chemistry, where they destroy ozone and are responsible for the well known phenomenon of the stratospheric ozone hole. The catalytical Cl in Equation 21 is produced from the oxidation of industrially manufactured chlorofluorocarbons (CFC), which were used as refrigerants, propellants in aerosol cans, inflating agents in foam materials, solvents and cleansing agents. These inert materials are entirely anthropogenic in nature and have residence times up to several hundred years in the troposphere and eventually find their way into the stratosphere where they absorb UV radiation (0.19 to 0.22 μm) and get decomposed generating a Cl atom, which depletes stratospheric ozone (Equation 21). It is worth mentioning that naturally occurring stratospheric ozone protects humankind against skin cancer caused by strong ultraviolet radiation from the sun. For details on mechanism of stratospheric ozone depletion, its chemistry, and its health and environmental consequences see Wallace and Hobbs (2006) and Harrison (2001).

2.5 Measurement of ozone

The most commonly used instruments for measuring ground level ozone concentrations are UV photometric ozone analysers (Figure, 2.3), where ambient air is drawn through a cell in which the absorption of UV radiation is measured at the 254 nm emission line of a mercury lamp. The strong absorption by ozone at this wavelength produces a detectable absorption measurement when ozone is present in the cell. The absorption cell alternately samples

ambient air coming directly from the atmosphere and ambient air diverted through a manganese dioxide scrubber that converts ozone catalytically to oxygen but leaves all other trace gases intact and the relative humidity almost constant. The UV irradiance is therefore measured in the presence and absence of ozone in the ambient air. The measured irradiance in the presence of ozone is related to the measured irradiance in the absence of ozone by the Beer-Lambert law shown below:

$$I = I_0 \exp(-\alpha CL) \quad \ldots (22)$$

I = light intensity after absorption by ozone

I = light intensity at zero ozone concentration

α = specific ozone molar absorption coefficient

L = path-length (cm) of the cell, and

C = ozone concentration (molecules cm^{-3})

By comparing the two irradiance signals it is possible to determine the concentration of ozone in the cell, provided that the length of the cell and the absorption cross section for ozone are known. Ozone measurements are reported as parts per billion volume or partial pressure. The detection limit for ozone is 0.05 ppb.

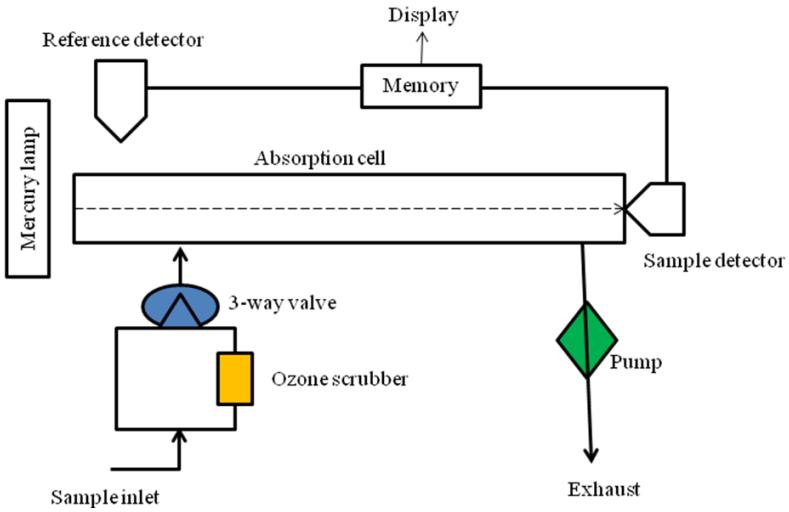


Figure 2.3. Schematic diagram of a UV photometric ozone analyser (Figure source: modified from Harrison, 2001).

2.6 Summary

Tropospheric ozone is formed photochemically from the sunlight-initiated oxidation of VOCs in the presence of NOx and therefore is considered as a secondary air pollutant. Ozone concentration varies considerably in time and space in relation to meteorological variables, the level of its precursors and local topographical parameters. Ozone concentrations are generally higher in sunny rural areas downwind from the large urban agglomerations and lower in urban areas due to gas phase titration of ozone by locally produced NOx.

In the stratosphere, ozone absorbs high energy UV radiation and acts as a protective shield for biodiversity on the earth surface, whereas in the tropospheric ozone is one of the more harmful air pollutants and adversely affects human health, agricultural crops, buildings and other materials. Ozone also plays a vital role in atmospheric chemistry by producing OH radicals and reacting with several other gases. Furthermore, ozone is third most important greenhouse gas. The UV absorption of ozone at 254 nm is used for its determination at level down to 0.05 ppb. Ozone concentration in the UK and elsewhere is most often monitored by UV photometric analyser, which can take reading at intervals of less than one minute.

In this chapter some background materials regarding the formation, chemistry, and importance of ozone were presented. Next chapter critically reviews what already has been published on ground level ozone, particularly on topics relevant to this project. Critical review aims to determine what has already been established, what are the strengths and weaknesses of published literature and to identify the knowledge gap where more work is required that is the intended subject of this PhD.

CHAPTER 3: LITERATURE REVIEW

3.1 Introduction

Ground level ozone concentration is mainly influenced by three main phenomena (Cape, 2008): (a) photochemical ozone formation; (b) Strato – Tropospheric Exchange (STE); and (c) ozone loss to its sinks (e.g., titration by NOx and dry deposition). Photochemical ozone formation is driven by the concentrations of precursors, mainly NOx and VOCs, and influenced by meteorological factors, such as temperature, solar radiation and atmospheric mixing rates. In urban areas, road traffic is one of the main sources of both NOx and VOCs, however, other important sources include power stations and biomass burning for NOx and industrial (mainly chemical plant) and biogenic emissions for VOCs.

Ozone is also transported downwards from the stratosphere by STE, a process that is coupled to global weather patterns and sea surface temperatures, and therefore linked to long-term changes in climate (Olsen et al., 2007). It is reported that in addition to sea surface temperatures, climatic circulation patterns also affect the rate of STE exchange (Olsen et al., 2007; Collins et al., 2003). The third contributory factor to tropospheric ozone concentrations is the removal of ozone at the ground level by reaction in or on the surfaces of plants and soil, a process known as dry deposition. In addition to uptake by plants leaves, bare soil and external leaf surfaces also act as efficient sinks for ozone. The overall loss at the ground level approximately balances the transfer into the troposphere from the stratosphere (Cape, 2008). Furthermore, ozone concentration in urban areas and at roadside locations is reduced by gas phase titration by NOx, which result in zone concentration in urban areas being significantly lower than the surrounding rural areas (Jenkin, 2008; Munir et al., 2012). The amount by which ozone concentrations in urban area are lower than that in the surrounding rural areas is known as urban decrement.

These processes are dependent on meteorological factors (e.g., temperature, solar radiation, relative humidity, wind speed and wind direction), spatial characteristics (e.g., easting and northing, altitude, distance from the coast and site types), road traffic characteristics (traffic flow, vehicle speed and fleet composition), and traffic related air pollutants (e.g., nitrogen oxide (NOx), carbon monoxide (CO), volatile organic compounds (VOCs), particulate matter of size 2.5 μm or less ($PM_{2.5}$)). Therefore, in this PhD project these parameters are used to characterise spatiotemporal variability of ground level ozone in the UK.

In this chapter an account has been taken of what has already been published by other authors on tropospheric ozone. The purpose is to review what knowledge and ideas have

been already established on ground level ozone and what are their strengths and weaknesses. This can be an indication of what is known, what is not known and what is controversial in the present literature, and hence can be helpful in understanding the research gap in ground level ozone.

The following sections consider ozone in terms of the following influences: the impact of spatial parameters (section 3.2); temporal trends (section 3.3); meteorology (3.4); and road traffic (section 3.5); while the later section (3.6) considers how these are addressed within current ozone modelling practices.

3.2 The impact of spatial characteristics

Ozone concentration varies considerably throughout the UK. Spatial variations of ozone can be linked with several phenomena, including ozone titration by freshly emitted nitric oxides (NO), dry deposition (to ground surface, plants and other materials), vertical and horizontal movement, and photochemical ozone formation (e.g., PORG, 1998; Coyle et al., 2002). The contribution of an individual process may vary with certain spatial characteristics: for instance, ozone titration by NOx is higher in urban areas (AQEG, 2009; Jenkin, 2008); dry deposition is lower to water surfaces (Entwistle et al., 1997); photochemical ozone formation rate is higher in sunny areas of the country (Jenkin, 2008); and higher altitudes exhibit higher average ozone concentrations (Chevalier et al., 2007).

Coyle et al. (2002) used the methodology described by PORG (1998) and developed empirical methods to quantify the spatial pattern in surface ozone concentration, incorporating the influences of altitude and local NOx sources. Coyle et al. (2002) used altitude as a surrogate to wind speed. The procedure was originally developed for rural sites and may over-estimate the ozone concentration levels in urban areas because it does not account for the urban decrement (the amount by which urban ozone concentration is lower than the rural ozone concentration) which is caused by the titration of ozone by NOx. To account for urban influence or urban decrement an urban correction was added to the mapping procedure suggested by Stedman et al. (1997), which is estimated as below:

$$UI = (\text{mapped value} - \text{measured value}) / \text{mapped value}$$

Where UI stands for Urban Influence, which should be zero for a rural monitoring site and between 0 and 1 for an urban site depending on the magnitude of NO emissions in that area. However, this approach has limited application in regions where ozone measurements are not already available. According to Coyle et al. (2002) annual average ozone concentrations are positively correlated with altitude, which was used as surrogate for wind vector. As a

result, annual mean ozone concentrations increase towards the north and decrease towards east across the UK. However, this approach fails to model higher episodic ozone concentrations, which are more dependent on summer time photochemical ozone formation and hence are more related to the precursors of ozone and solar radiation, rather than just the altitude of the monitoring sites.

Atmospheric turbulence is considerably enhanced in mountainous and hilly areas which affect pollutants circulation (Chevalier et al., 2007). Ozone concentration near the ground surface is reduced by dry deposition and NOx titration, therefore background ozone level increases with height. Chevalier et al. (2007) reported that ozone concentration was positively correlated with altitude above sea level and varied from 25 ppb to 53 ppb over the range 100 m - 3500 m. Chevalier et al. (2007) also reported that the ozone gradient was very steep up to 1000 m (around 30 ppb per km) and gentler but still meaningful above (around 3 ppb per kilometre). Possible reasons for increasing ozone with altitude include: greater dry deposition and NOx titration of ozone near ground surfaces; greater atmospheric turbulence in mountainous and hilly areas, increasing dispersion rates and reducing the effective mixing time for reactive species; and reduced night-time ozone depletion in higher mountain regions. However, ozone is a complex air pollutant and is affected by several factors, which include meteorological parameters, emissions of precursors, various sinks including scavengers (e.g., NO) and local geographical characteristics. Therefore, only altitude or height of the monitoring site cannot characterise ozone and the approach used by Chevalier et al. (2007) have limited use.

Jenkin (2008) described variations in ozone concentration in the UK along southeast to northwest transect. Jenkin (2008) used the mean number of hours when ozone concentration was equal to or greater than180 $\mu g/m^3$ based on the average of the data over the period 1990–2006 for 13 rural sites. The data were presented in relation to a north-westerly coordinate, starting from Lullington Heath in the southeast. The data showed a general decreasing trend with distance northwest but also displayed a degree of scatter. The scatter was linked with the altitude of the site, greater altitude showing a tendency towards a greater number of hour's exceedances. However, as mentioned above, other parameters, like easting and northing coordinates, distance from the coast and sites type (rural-urban factor), may provide further insight into the ozone spatial variability, which were not considered in this study. Furthermore, Jenkin (2008) did not use any advanced statistical models to characterise ozone spatial variation and his study is mainly based on exploratory data analysis and linear regression, which may not be suitable for ozone data analysis as suggested by Baur et al. (2004).

Entwistle et al. (1997) investigated the effect of proximity to sea coast on ozone concentration and reported that ozone deposition was less to water surface than to ground surface or plants leaves. Therefore coastal sites showed higher ozone concentration during on-shore wind than the inland monitoring sites. During off-shore wind the difference was reduced (Entwistle et al., 1997). This study highlights the difference in ozone concentration at coastal and non-coastal monitoring sites; however the study has not accounted for the confounding factors, like rural – urban factors, altitude, and local changes in atmospheric conditions, which might affect the outcome of the study. Furthermore, it would have been useful if dry deposition rates of ozone to different surfaces (e.g., water, plant leaves, ground materials etc.) were quantified and compared to provide a more quantitative and robust analysis.

The above authors provide some useful directions on how ozone concentration is affected by the spatial parameters. This study intends to investigate the influence of the relationship between the above variables and ozone concentrations using an extending dataset which includes a number of monitoring sites and data series not available to these previous studies. Furthermore, building on the above information, some more spatial variables are included (e.g., easting and northing coordinates, rural-urban factor), which provide further insight into the ozone spatial variability. Jenkin (2008) used a south – westerly gradient, which is extended here using a latitude longitude gradient to provide better spatial definition. Furthermore, urban/rural factors are extension on the Steadman urban correction. Finally, using these spatial parameters a statistical model has been developed that can be applied for studying ozone spatial behaviour. Understanding ozone spatial trends (maps) are essential for defining the areas (communities) at most risk and estimating the amount of damage caused by ozone pollution. The model developed in this study can help pin point the areas at greater risks. NOx concentration, which is closely related to ozone concentration can substitute rural-urban factor in the model. The inclusion of NOx improves the model performance and can help predict variation in ozone concentration caused by changes in NOx concentration in the future.

3.3 Ozone temporal trends

Trend is a relationship between time and pollutant concentration and trend analysis is one of the most important and common tasks in the study of air pollution. Trends are assessed to provide a general idea as to how the concentrations of air pollutants have changed over time; or to establish statistically whether a pollutant have significantly increased or decreased i.e., whether the trend is positive or negative and whether significant or not.

Ozone trends have been extensively investigated over the last decade or so and the factors believed to be responsible for ozone trends are discussed by several authors, such as Cape (2008), Jenkin (2008), Carslaw (2005), Derwent et al. (2007), and Derwent et al. (2010). Ozone trends at both rural and urban locations in the UK are influenced by trends in global, regional and local-scale effects (Jenkin, 2008). Average positive (increasing) trends have been reported by many authors (Carslaw, 2005; Derwent et al., 2007; Jenkin, 2008; and AQEG, 2009). The gradual increase in average ozone concentration might have been caused by the hemispheric baseline ozone concentration resulting from global scale effects, which influences the baseline levels of ozone brought into the UK from the Atlantic Ocean (Derwent et al., 2007 and Jenkin, 2008).

Jenkin (2008) reported a significant decreasing (negative) trend in the annual maximum ozone concentration and contributed it to reductions in the emissions of anthropogenic VOC and NOx in the EU since the early 1990s. Derwent et al. (2010) and Cape (2008) have given the same reason for peak ozone reduction in the UK. Furthermore, Jenkin (2008) reported that the negative trends in the maximum ozone concentration at the urban sites are consistently slower than at the rural sites and contributed this to the progressive reduction in NOx emissions that has a local increasing impact on ozone concentrations through reducing ozone scavenging. This effect operates in the opposite sense to the decreasing impact of VOC and NOx emission reductions on regional-scale ozone formation. The former has a positive whereas the latter has a negative impact on ozone concentrations, i.e. reducing NOx at local levels causes ozone levels to increase due to less scavenging effect, whereas at regional level reducing NOx levels would causes ozone concentration to decrease due to less precursors available for ozone formation.

The above are some of the important studies that have analysed long term ozone trends and mostly reported positive trends in mean ozone concentrations. These studies have certain limitations, for instance, Derwent et al. (2007) and Carslaw (2005) analysed background temporal trends using ozone data only from one monitoring station (Mace Head). Several authors (e.g., Jenkin, 2008) have reported that ozone trends demonstrate significant spatial variability due to geographical characteristics (e.g., altitude and proximity to coast). Jenkin (2008) has shown that ozone positive trends at urban sites were not only significant but greater than the rural trends, which were attributed to NOx reduction in urban areas which has an increasing effect on ozone due to less scavenging effect. Some sort of comparison with other monitoring site or urban – rural comparison would have improved the study further. Secondly, these studies are based only on mean concentration, which could be biased by outliers or high / low ozone concentrations. Robust metrics (e.g., median or various quantiles) present more realistic results as they are un-affected by extreme values.

Jenkin (2008) analysed ozone trends at several rural and urban monitoring stations and compared the trends to assess how ozone trends varied at urban and rural sites. Furthermore, Jenkin (2008) quantified trends at several selected percentiles, including mean, median, minimum and maximum trends. However, Jenkin (2008) applied linear regression to quantify the trends, which is the main weakness of the study. Furthermore, ozone concentrations are not distributed normally and the temporal trends are non-linear, therefore nonparametric approaches for trends analysis would have been a better option. In addition, trends are analysed on annual basis and no consideration is given to the seasonal variation of trends, for example, temporal trends may vary during different seasons, such as spring, summer, autumn, and winter. Quantifying trends in various seasons or even different month of the year could provide further insight into ozone temporal trends.

European Environmental Agency (EEA, 2012) has reported that the number of exceedances of EU ground level ozone concentration standards for protecting human health (Directive 2008/50/EC) remained at serious levels during the summer of 2011; therefore the ozone pollution problem requires further mitigation efforts. Derwent et al. (2010) have discussed the reasons for why episodic ozone levels have not declined enough to meet World Health Organisation (WHO, 2006) air quality guidelines for protecting human health and reported that whilst NOx and VOC precursor emissions have declined by about 50–60%, episodic ozone levels have only declined by 30%. This is an indication of the importance of nonlinearities inherent in the relationship of ozone with NOx and VOC. The underlying reason, according to Derwent et al. (2010) for not meeting the WHO air quality guideline is that the policy-makers have not set a high enough ambition level for the agreed reductions in European NOx and VOC emissions. In their estimation VOC and NOx emission reductions needed to be reduced by about 70%, in contrast to 50 – 60 % by 2010 for the WHO air quality guidelines to have been achieved in the UK and Europe.

The above review highlights several important points: firstly, average ozone concentration demonstrates positive trend over the last couple of decades or so; peak ozone concentration has reduced over time but the reduction is not enough to meet air quality guidelines; and further efforts are required to cut air pollutants emission to reduce ozone concentration in both rural and urban areas. Detailed analysis of the existing literature reveals that most of the research has been conducted on ozone trends in rural areas (e.g., Derwent et al., 2007; Carslaw, 2005). Jenkin (2008) reported that average positive trend was greater and maximum negative trend was lower at urban than rural sites, suggesting urban ozone concentration is increasing at faster rate than the rural ozone concentration. AQEG (2009) has also reported that ozone level in urban areas is increasing at faster rate than in rural areas, most probably caused by reduction in NOx emission from road traffic in urban areas.

Locally emitted NOx is an ozone scavenger and reduces ozone concentration by gas phase titration and keep ozone levels lower in urban areas (urban decrement), therefore, NOx is mostly negatively correlated with ozone and any reduction in NOx concentration may result in ozone concentration to increase (Jenkin, 2004). But recent trends are upsetting the tradition pattern of high ozone concentration in rural areas than in urban areas. If this trend continues, ozone concentration in urban areas may equate that in rural areas and the urban decrement may disappear (Williams, 2007). As mentioned before (Chapter 2), the density of ozone vulnerable materials and human population is greater in urban areas, which might pose greater potential risk to human health and damage to building and other materials in the future.

This PhD project focuses on ozone trends in urban areas using a non-parametric approach. A comparison between rural and urban trend is made to analyse the decreasing urban decrement. Carslaw et al. (2011) have shown that atmospheric NOx trends during the last 6 years or so (2004 to 2009) have stabilised due to reduction in NOx emissions. Therefore to see the effect of NOx stabilisation on ozone trends, in addition to long term trend analysis, the trends during most recent years (2004 to 2011) are analysed, which have not been reported before and may reflect a truer sense of the new trends in ozone concentration. This study analyses average trends as well as trends at various selected quantiles of the ozone distribution, including first quartile, median, third quartile, and maximum of hourly ozone concentration. The quantile approach is not affected by outliers in air quality data and better suits ozone data analysis, which shows a heavy right tail distribution (e.g., Munir et al., 2011 and the references therein).

3.4 The effect of meteorology

Ground level ozone concentration at a particular location is mainly dependent on local meteorology and atmospheric chemistry. Meteorological factors such as temperature, solar radiations, relative humidity, and wind speed can influence the transport, dispersion and chemical reactions of air pollutants. Substantial variations in meteorological conditions can exert a large impact on ozone concentration and often mask long term trends in ozone concentration that could otherwise be more readily traced to changes in precursor emissions such as NO_x and VOCs (Duenas et al., 2002; Gardner and Dorling, 1999). Summer and spring time high ozone episodes are caused by the high level of solar radiation and temperatures in the UK and elsewhere (AQEG, 2009).

Duenas et al. (2002) studied the impact of temperature, pressure, relative humidity, wind direction, wind speed, and rainfall and found that temperature, wind speed and relative

humidity were the most important meteorological factors influencing the variation in ozone level. Several studies (e.g. Andersson et al., 2006; Baur et al., 2004; Cardenas et al., 1998) have investigated the effect of various meteorological variables on ozone concentration. The meteorological factors affect horizontal and vertical transport of pollutants, ozone chemistry (e.g., aqueous phase chemistry, photochemical ozone formation), dry and wet deposition, and precursor emissions from anthropogenic (e.g., NOx and VOCs) and natural sources (e.g., isoprene) (Andersson et al., 2006). Modelling studies (e.g., Derwent et al., 2007) show that winds blown from large cities like Birmingham and London or continental Europe carry polluted air masses, high in VOCs and NOx, which act as precursors for photochemical ozone production when atmospheric conditions are favourable (e.g., hot sunny conditions).

Most of the above studies (e.g., Duenas et al., 2002; Pont and Fanton, 2000) share a number of common limitations. Firstly, the meteorological variables and air quality data are not collected at the same locations, as most of the air quality monitoring sites in the UK and elsewhere do not have facilities for collecting meteorological data. Secondly, their outcomes are based on qualitative analysis or very basic statistical tests. Simple linear regression and multiple linear regressions are commonplace in the ozone research literature (e.g. Soja and Soja, 1999; Pont and Fanton, 2000; Tidblad et al., 2002; Pai et al., 2009). Linear regressions explicitly assume normality of the error term and linearity of the relationship between response variable (in this case ozone) and the covariates. However, ozone data are not normally distributed and have non-linear association with predictors and hence the results could be erroneous (Baur et al. 2004). Therefore, several researchers (e.g., Baur et al. 2004; Gardner and Dorling, 1999; Reimann et al., 2008) have reported that linear regression models may not be suitable for ozone data analysis. Furthermore, most of these studies, except Baur et al. (2004), have analysed mean effects of the meteorological variables on ozone. As said in other chapters, mean could be biased by few very large or small data points and hence could affect the applicability of the study. Air quality models applying robust approaches (nonparametric, and based on median or various quantiles), might be more suitable for ozone and meteorological data analysis. The effect of meteorology on ozone concentration varies in different seasons, which is mostly overlooked in these studies.

This project uses meteorology and ozone data collected at the same monitoring site (Kirkstall roadside monitoring site in Leeds), which provides a better representation of the local environment for chemical (e.g. ozone chemistry) and physical processes (e.g. ozone vertical and horizontal dispersions). It is also an established fact that ozone behaviour and interaction with other factors vary spatially, therefore the investigations carried out at one place and the model developed as a result may not be applicable at another location. This study provides a local model for studying ozone behaviour and its interaction with

meteorology in Leeds, UK. The model (quantile regression model) developed in this study can be applied to non-normal ozone distribution and can handle the non-linearities in the association of ozone and meteorology (Baur et al., 2004).

3.5 The effect of road traffic

Road-traffic is considered to be one of the major sources of ozone precursors and contributes about 40, 41 and 11 % of the total emission of NOx, CO, and non-methane hydrocarbons (NMHC), respectively in the UK (NAEI, 2011). The amount of road traffic-emitted air pollutants is substantially higher in large urban areas. At the local level freshly emitted NO by road-traffic reacts with ozone molecules and produces NO_2. Hence road-traffic provides a local sink for ground level ozone resulting in ozone concentration in urban areas being lower than the surrounding rural areas. This phenomenon of lower ozone concentration in urban areas is referred to as the urban ozone decrement (AQEG, 2009).

Numerous researchers have investigated the relationship between road traffic and traffic related air pollutants, for instance NOx and $PM_{2.5}$ (Carslaw, 2005; Carslaw and Beevers, 2005; AQEG, 2004; AQEG, 2005); however very few considered road traffic in conjunction with ozone concentration, most probably because ozone is not emitted directly by road traffic, and is rather formed in the atmosphere. Berastegi et al. (2001), Pont and Fontan (2000) and Bronnimann and Neu (1996) investigated the effect of road traffic on ground level ozone concentration. Using linear regression and time series analysis Berastegi et al. (2001) found that 81% to 99.6% of total variance of long term ozone changes could be associated with road traffic. Linking up to 99.6 % ozone variation with only road traffic emission seems unrealistic as this means only 0.4 % variation is controlled by other emission sources, meteorological variables, and geographical parameters (for example see Derwent, 2008 and PORG, 1998). Furthermore, Berastegi et al. (2001) have employed linear regression model, which violate the basic assumptions of normality and linearity as ozone data is non-normal and its association with meteorology is non-linear. Secondly, Berastegi et al. (2001) have ignored the effect of background ozone, which must be addressed before quantifying the effect of local traffic; otherwise the result could be distorted. Pont and Fontan (2000) studied the variations of weekend and weekdays ozone in 5 large French cities and concluded that a 40% reduction in road traffic would not have a significant effect on ozone concentrations. These authors have, however not used any traffic flow, speed and fleet composition data and used CO to estimate traffic level. Although CO can be used as a relatively generic marker for traffic flow, modern monitoring practices mean that we can now look more directly at the relationship between different traffic characteristics (e.g. speed, flow and composition) and air quality.

Bronnimann and Neu (1996) studied variations in ozone concentration during weekdays and weekend and found that different ozone patterns exist during favourable (presence of solar radiation that causes photochemical ozone formation) and unfavourable (cloudy and cold) meteorological conditions. The research used 8 years of both urban and rural ozone data, as well as both traffic counts and meteorological data and found that generally mean ozone concentration was l0-15% lower on Sunday than on Thursday or Friday. Quantifying road traffic flow variations during different days and then comparing that with percent ozone difference would probably have resulted in better quantification of the association between ozone and road traffic flow. Secondly, a comparison between urban and rural sites or comparison between sites with different traffic flow would have provided further insight into the association between ozone and road traffic, rather than just comparing different days. Gao et el. (2004) investigated the ozone weekend effect in Southern California in 1997 and concluded that ozone levels were higher during weekends due to less NOx scavenging effect. However, the ozone concentration used in this study was predicted from the emission data of its precursors (e.g., NOx and VOCs) rather than by direct measurement. The approach, although understandable in the absence of local ozone measurements, would obviously introduce high levels of uncertainties because this type of ozone modelling introduces additional uncertainties associated with both the emission inventory data on precursors and atmospheric reaction rates for ozone formation.

The intention in this study is to quantify urban decrements in the UK, which is caused by freshly emitted NOx. Urban decrements are analysed not only for mean values but also at various quantiles of ozone distribution, particularly at both tails of ozone distribution to characterise the difference at extreme ozone concentration. This study also intends to analyse synchronised measured ozone concentration, traffic flow, vehicle speed and fleet composition data collected at the same site to quantify the impact of local road traffic on urban decrements in Leeds, which has not been done before and hence will probably better characterise the mechanism that associate vehicle activity and ozone. Most of the existing studies on the topic investigate how ozone concentration varies over weekend and weekdays without using any traffic flow, speed and fleet composition data. However, those studies that did use monitoring data, have neglected the effect of background ozone concentration. Ozone concentration at a particular location is the sum of local (urban decrement) and regional (background) component (for details see Clapp and Jenkin, 2001, and Jenkin, 2004). The regional component needs to be accounted for before addressing the local urban decrement. In this chapter the background effect on ozone concentration has been addressed to remove the regional effect before applying the model to investigate the effect of local traffic.

3.6 Modelling of ozone

Various models have been used to predict ozone concentrations, establish long or short term ozone trends, understand underlying mechanisms in the formation and destruction of ozone, and study the health and environmental impacts of ozone (Baur et al., 2004; Gardner and Dorling, 2000).

3.6.1 Modelling techniques

Statistical models for predicting ozone concentrations are numerous and may be divided into four main categories: regression-based models, extreme value approaches, neural networks, and space-time models (Baur et al., 2004).

Multiple linear regressions are the most widely used methodologies for modelling the dependence of ozone on several independent variables (predictors). Soja and Soja (1999), Tidblad et al. (2002), Paschalidou et al. (2008) and Pont and Fanton (2000) all applied multiple regressions for ozone modelling. Linear regressions explicitly assume normality of the data distribution and linearity of the association between dependent and independent variables, which are not met by ozone and meteorological variables. Therefore some authors (Baur et al. 2004; Gardner and Dorling, 1999) have suggested that linear regression models are not suitable for analysing ozone data.

A comparison of a univariate model based on a polynomial trend combined with first order autoregression, a univariate autoregressive integrated moving average (ARIMA) model and a bivariate temperature and persistence-based regression model for ozone prediction was made by Robeson and Steyn (1990) and concluded that a decomposition of a time series into trend, cycle, and stochastic components was not suitable for forecasting ozone concentrations; probably because ozone concentrations are linked with many other factors (meteorological, traffic and other air pollutants), which are not considered by time series analysis. The same views were expressed by Schlink and Volta (2000). The main weakness of the Robeson and Steyn (1990) study is that it only compares time series and linear regression. Probably by then (1990) most of the latest advanced statistical and machine learning approaches (e.g., Boosted Regression Trees and Quantile regression Models) were not available or perhaps not applied to air quality related issues. Now much more wider choice of parametric and non-parametric models are available to the air quality scientists, which have resulted in much better understanding of the association between ozone and various controlling factors. These two approaches (time series and linear regression) are no more recommended for modelling ozone concentrations as these approaches are based on some assumptions which are not met by air quality data.

A critical review of several statistical techniques (regression, extreme value, and space-time methods) for the meteorological adjustment of ozone was performed by Thompson et al. (2001). They concluded that a number of approaches make useful contributions to the field of air quality, but that no one method is most appropriate for all purposes and all meteorological scenarios. Hence, the choice of methodology will depend on the purpose of the analysis and the meteorological complexity of ozone formation in a given region. Schlink et al. (2003) performed a model inter-comparison exercise in which 15 different statistical techniques for ozone forecasting were applied to ten data sets representing different meteorological and emission conditions throughout Europe. Their results favoured neural networks and generalized additive models (GAMs) on the basis of their performance and ability to handle nonlinearities. Furthermore, GAMs have good learning and adaptability and can be easily transferred to work other data and threshold values. Davis and Speckman (1999) successfully predicted daily 8 hour average ozone concentration at Houston, Texas using a GAM where previous regression models had struggled due to the complex meteorological processes. Aldrin and Haff (2005) also applied GAM to model air pollutants concentrations in Oslo for quantifying the importance of meteorological and traffic-related parameters on the concentrations of particulate matter (PM_{10} and $PM_{2.5}$), NOx and NO_2. More recently, Carslaw et al. (2007) developed a GAM model for assessing trends in traffic related emissions (NOx, NO_2, CO, benzene and 1,3-butadiene) at Marylebone Road, London; and Westmoreland et al. (2007) applied GAM in a busy street canyon in Gillygate, York, comparing the outcomes of GAM with a dispersion model (ADMS-Urban). The predictions made with the GAM showed excellent agreement with measured concentrations of NOx and NO_2 and out-performed ADMS-Urban. GAM not only performed better in reproducing both the magnitude of NOx and NO_2 concentrations but also demonstrated the wind speed and wind direction dependence of pollutant sources. However, the predictions made with ADMS-Urban underestimated the measured NOx by 11% and NO_2 by 21% and there are clear differences in the bivariate polar plots.

Regarding Westmoreland et al. (2007) study, despite the fact that GAM showed better performance in predicting NOx and NO_2, there are several important differences between ADMS-Urban and the GAM technique which should be noted. First, GAM model is developed to predict a single pollutant at a specific location; to cover the whole city or to predict several air pollutants; several different models would be required. In contrast, ADMS-Urban can more easily in one run predict a variety of pollutant concentrations (NOx, NO_2, PM_{10}, SO_2 and O_3) in a range of different locations and could predict concentrations for the whole city (e.g., York) in the form of contour maps. Second, the GAMs created for this study are restricted to sites where traffic counts are available and this should be noted that traffic counts availability is limited at many sites.

A weakness or potential limitation of the Westmoreland et al. (2007) work is that residual autocorrelation was not accounted for in the GAMs and as a consequence, the prediction uncertainties for these models may be optimistic (Wood, 2006). However, previous work using Generalized Additive Mixed Models, which can account for the correlation structure of the data, showed that accounting for the autocorrelation only had a minor effect on the prediction uncertainties (Carslaw et al., 2007). Furthermore, model training and testing datasets used in this models and hence the predictions of the models were based on independent datasets.

Gardner and Dorling (2000) have investigated the use of multilayer perceptron neural network and regression tree models for ozone data analysis. They favoured regression tree models as these were found to be more readily interpretable by comparison with neural networks. Baur et al. (2004) and Sousa et al. (2008) suggested a quantile regression model (QRM) for ozone study; as this method could be used for both parametric and nonparametric regression methods and is capable of handling the non-linearities in the association of ozone and covariates (e.g., meteorology and traffic data). Both Baur et al. (2004) and Sousa et al. (2008) have assessed the model performance only by calculating coefficients of determination (R^2) and compared it with the global R^1 of the QRM model. More recently, Carslaw (2011) and Derwent et al. (2010) have commented against the use of R^2 values for model performance and suggested using a combination of metrics, such as Root Mean Square Error (RMSE), Mean Bias (MB), Normalised Mean Bias (NMB), Mean Gross Error (MGE), Normalised Mean Gross Error (NMGE) and Factor of 2 (FAC2) to obtain more robust measure of model performance.

On the basis of the fact that QRM and GAM can be applied to non-normal ozone distribution and can handle the potential non-linearities in the association of ozone and its predictors, and out-performed most of the other available statistical techniques (as mentioned above), this study intends to apply these two approaches for ozone modelling and extends the use of metrics for model performance as suggested above.

3.6.2 Selection of predictive variables

For accurate ozone modelling among other factors (e.g. quality of data, selection of suitable technique etc.) selection of appropriate predictive variables play a vital role. Models that have fewer predictor variables are easier to be interpreted; whereas models with many independent variables (complex models) not only become difficult to be interpreted and analysed but also are more likely to contain inter-correlated variables that may interferes in their interpretation. Too many predictors can result in over-fitting of a model. In contrast, if an important variable that potentially can have significant contribution in the variation

explained by the model is ignored, it could significantly affect not only the goodness of fit of the model but also the explanation of the underlying structure hidden in the model (Reimann et al., 2008). Fewer predictor variables can result in under-fitting of the model. It means the criterion of model building is parsimony, that is, the model should have fewer independent variables that permit an adequate interpretation of the responses.

For ozone modelling researchers have used various meteorological variables, traffic characteristics, air pollutant concentration and spatial parameters as independent variables, depending on the requirement of the study and the availability of data. Some of the most commonly used independent variables for ozone modelling are: NOx (e.g., Tidblad et al., 2002; Paschalidou et al., 2008), solar radiation (e.g., Paschalidou et al., 2008; Baur et al., 2004), temperature (e.g., Paschalidou et al., 2008; Camalier et al., 2007; Chaloulakou et al., 2003), relative humidity (Duenas et al., 2002; Paschalidou et al., 2008; Camalier et al., 2007), wind speed (Camalier et al., 2007; Duenas et al., 2002; Paschalidou et al., 2008), and wind direction (Derwent et al., 2007; Paschalidou et al., 2008; Chaloulakou et al., 2003).

Furthermore, mean sea level pressure, boundary layer height, previous day ozone concentration (persistence), CO, rainfall and cloudiness have also been used in different studies (e.g. Duenas et al., 2002; Paschalidou et al. 2008). Road traffic volume (Berastegi et al., 2001; Gao et el., 2004; Bronnimann and Neu, 1996), vehicle speed and composition of fleet have also been explored in connection with ozone concentration (Gao et el., 2004). In spatial parameters altitude of the site (Coyle et al., 2002), north-westerly distance from a reference point (Jenkin, 2008), and proximity to the coast (Entwistle et al., 1997) have been used to explain spatial variability in ozone concentration.

The above variables have been extensively investigated in relation to ozone and a general agreement among authors exist on the nature of their effect, however, their relationship change considerably both in space and time. Furthermore, some recent investigations reveal that the association of ozone with meteorological and other variables is not that simple and may vary with changing ozone concentrations or changing meteorology. For instance, Baur et al. (2004) shows that the effect of morning wind speed on ozone concentration was not significant, whereas the effect of afternoon wind speed was not only significant but also variable, changing from a negative association at low ozone concentration quantiles to positive at higher quantiles. Moreover, the strength of the relationship between ozone and its predictors also vary in different regions and different levels of the variables. This is the reason why has ozone proved to be so complicated in its characteristics and behaviour, which make ozone modelling a challenging task for the scientific community.

One important aspect of the relationship between ozone and its predictors that is often

ignored by majority of the authors is that correction parameters (e.g. fit performance and associated fit parameters) change by hours of the day, day of the week, and months or season of the year. For example, ozone concentrations change significantly during different days of the week. Higher ozone concentrations are generally reported at weekends while lower concentrations are more often observed on weekdays (e.g., Pont and Fontan, 2000; Gao et el., 2004). This ozone weekend effect is attributed to variation in road traffic flow during weekend and weekdays. It would be advisable, therefore, to investigate this effect with the help of traffic characteristics or traffic related air pollutants. In contrast, meteorological variable do not demonstrate these types of weekly variations. On the other hand, seasonal cycles of ozone (higher ozone concentration in spring and summer and lower during winter and autumn) are more related with meteorological parameters (e.g., temperature and solar radiation). Traffic related emissions of precursors or traffic flow do not exhibit this sort of seasonal cycle. Therefore, it is vital to take these factors into account before deciding on the type of predictors used in the model.

In this project the effects of meteorology, other air pollutants, and traffic characteristics on ozone concentrations have been investigated, focusing on how the relationship changes at different regimes of the ozone concentration, as proposed by Baur et al. (2004). Furthermore, benefitting from and extending on Jenkin (2008) and Coyle et al. (2002), the spatial variability of ozone is investigated with the help of spatial parameters (altitude, easting and northing coordinates, distance from the coast, and site type or rural-urban factor). These parameters have never been used together in an aggregate form and have the potential to explain considerable variations in ozone concentration.

Process based global and regional models are widely used tools to study transport and transformation of air pollutants and to assist environmental assessment and policy making. Below a brief description of chemical transport models is provided regarding the basic process and their inputs data.

3.6.3 Chemical Transport Models and Box Models

Chemical Transport Models (CTMs) are an important quantitative tool that links emissions of primary air pollutants and precursors of secondary air pollutants quantitatively to ambient concentrations (Chipperfield, 2006). CTMs consist of mathematical representations of the relevant physical and chemical atmospheric processes, which are solved using numerical algorithms to obtain pollutant concentrations as a function of space and time for a given set of pollutant emissions and meteorological conditions (e.g., Russell and Dennis, 2000). CTMs are also referred to as air quality simulation models, emission-based models, source-

based models, source-oriented models, source models, process based models and comprehensive models (NARSTO, 2004).

The CTMs consist of a system of coupled modules (or models) (NARSTO, 2004), which include:

- A Geographical Information System (GIS) (and other pre-process or codes) for manipulating and inputting data to the various other models of the system;
- An emission model for estimating gridded biogenic and anthropogenic emissions as a function of time, based on emission factors and activity;
- A meteorological model that simulates atmospheric physical processes and estimates gridded fields of variables such as winds, clouds, temperature, and humidity for the time span of the modelled period;
- An air-quality model, composed of a chemical mechanism, surface deposition and transport model and a numerical solver, which predicts the concentrations of atmospheric constituents on the basis of inputs from the emission and meteorological models;
- A post-processor and graphical analysis package for displaying and analysing the model results; and
- Often a user interface that allows the user to conveniently and efficiently interact and manipulate model inputs, codes, and analysis routines.

There are two subcategories of CTMs based on the reference frame employed (NARSTO, 2004): (a) Eulerian or grid-based models; (b) Lagrangian or trajectory models. Eulerian models use a reference frame that is fixed in space. The simplest form of an Eulerian model is the 1-dimensional box model. A one-box model for an atmospheric species X is shown in Figure 1. It describes the abundance of X inside a box representing a selected atmospheric domain (e.g., an urban area, or the whole UK). Transport is treated as a flow of X into the box (F-in) and out of the box (F-out). The production and loss rates of X inside the box may include contributions from emissions (E), chemical production (P), chemical loss (L), and deposition (D). The terms F-in, E, and P are sources of X in the box; the terms F-out, L, and D are sinks of X in the box. The mass of X in the box is often called an inventory and the box itself is often called a reservoir. The one-box model does not resolve the spatial distribution of the concentration of X inside the box. It is frequently assumed that the box is well-mixed in order to facilitate computation of sources and sinks. However, most Eulerian CTMs are three dimensional (3-D) grid-based models. Chemical and physical transformations are treated in situ within each grid cell, and transport and diffusion processes move chemical species between grid cells.

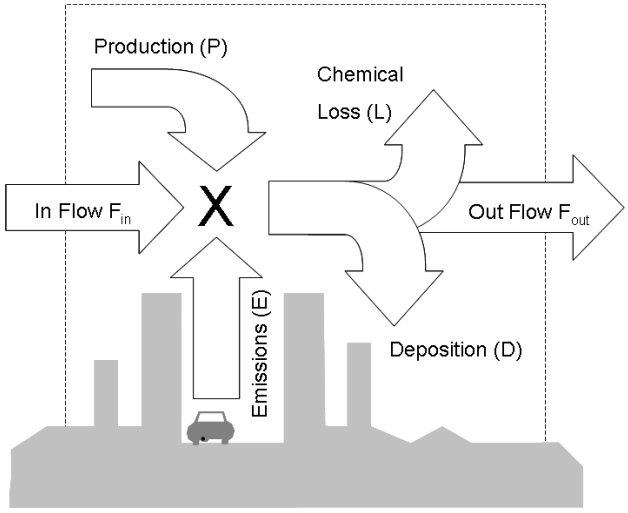


Figure 3.1. A box model for an atmospheric species 'X' (Figure, modification of Jacob, 2004).

Lagrangian trajectory models, on the other hand, use a reference frame that follows the movements of individual air parcels from sources to receptors. Transformations take place within the parcels and the transport processes that are not resolved by the mean advective transport (e.g., vertical turbulent diffusion) may move chemical species between parcels or increase the size of parcels. According to Jacob (2004) a major difference of trajectory model from the box model treatment is that the transport terms F-in and F-out are zero because the frame of reference is now the travelling puff (a volume of fluid with dimensions sufficiently small that all points within it are transported by the flow with the same velocity, but sufficiently large to contain a statistically representative ensemble of molecules). Getting rid of the transport terms is a major advantage of the puff model, but may be offset by difficulty in determining the trajectory of the puff (Jacob, 2004). In addition, the assumption that all points within the puff are transported with the same velocity is often not very good. Wind shear in the atmosphere gradually stretches the puff to the point where it becomes no longer identifiable. Lagrangian models are usually simpler in their formulation and less demanding in their computational requirements than Eulerian models. However, they are also limited by their simplicity in that they generally do not treat several atmospheric physical processes realistically, including differential advection due to vertical wind shear, vertical transport, and horizontal diffusion. Therefore, the CTMs used for policy and regulatory purposes are likely to be 3-D Eulerian grid models due to the need for realistic representations of all relevant processes. However, Lagrangian CTMs may still be useful for screening assessments, where their lower computational requirements are an asset, and for studies where realistic treatments of chemicals processes are required but

simpler representations of transport and diffusion processes are acceptable (NARSTO Synthesis Team, 2000).

3.6.3.1 Several ozone related CTMs

(a) TOMCAT / SLIMCAT

TOMCAT/SLIMCAT is a three-dimensional (3D) off-line chemical transport model (CTM). TOMCAT stands for Toulouse Off-line Model of Chemistry and Transport and SLIMCAT stands for Single Layer Isentropic Model of Chemistry and Transport. The model uses winds and temperatures from meteorological analyses (e.g. from the UK Met Office) to specify the atmospheric transport and temperatures and calculates the abundances of chemical species in the troposphere and stratosphere (Chipperfield, 2006). The model has the option of detailed chemical scheme(s) for the stratosphere and troposphere. The model can be used to simulate the past and current atmosphere, help interpret observations, and to diagnose the extent of problems such as stratospheric ozone depletion or tropospheric pollution. The first version of TOMCAT was written by Martyn Chipperfield Meteo-France in Toulouse in 1992 with the help of Pascal Simon. At this stage the model was used for stratospheric chemistry studies. From 1993 the use and development of the model followed Chipperfield to the Department of Chemistry at the University of Cambridge. Around 1995 MPC wrote SLIMCAT. This was a stratosphere-only version of TOMCAT formulated on isentropic levels. At this time TOMCAT became a 'tropospheric' model and various people in Cambridge helped to add treatments of e.g., convection, boundary layer mixing, and tropospheric chemistry. Chipperfield moved to the University of Leeds in 1999 where the model development continues. Recently, SLIMCAT has been extended downwards to include the troposphere. As the two former models were so similar, it made maintenance/development easier to merge TOMCAT and SLIMCAT into a single library with a choice of vertical coordinate (and other things), so that one model covers all of the applications. Depending on the coordinate use, the model is still referred to as TOMCAT or SLIMCAT.

Typical resolutions of TOMCAT / SLIMCAT models are 5 x 5 degrees for multiannual runs to up to 1 x 1 degree; Forced by meteorological analyses, usually ECMWF and sometimes UKMO; Options of detailed stratospheric or tropospheric chemistry schemes; Options of detailed aerosol microphysics; Chemical data assimilation scheme; and Embedded trajectory code. For more details see Chipperfield, 2006; Chipperfield, 1999; Arnold et al., 2005; and Chipperfield et al., 2002.

(b) MOZART Models

The MOZART (Model for Ozone and Related chemical Tracers) is a three-dimensional chemical-transport model. The MOZART model was developed in the framework of the NCAR (National Center for Atmospheric Research) Community Climate Model (CCM) and aimed at studying the distribution and budget of tropospheric ozone and its precursors. The model, developed with a horizontal resolution of 2.8° in longitude and latitude, includes 25 levels in the vertical between the Earth's surface and an upper boundary located at approximately 35 km altitude. In its present configuration the model calculates the global distribution of 56 chemical constituents with a time step of 20 min, and accounts for surface emission and deposition, large-scale advective transport, subscale convective and boundary layer exchanges, chemical and photochemical transformations, as well as wet scavenging. Transport is simulated “off line” from CCM with dynamical variables provided every 3 hours from pre-established history tapes (Emmons et al., 2010). MOZART Model requires meteorological fields from either climate models or assimilations of meteorological observations and is built on the framework of the Model of Atmospheric Transport and Chemistry (Rasch et al., 1997). Convective mass fluxes are diagnosed by the model, using the shallow and mid-level convective transport formulation of Hack (1994) and deep convection scheme of Zhang and MacFarlane (1995). Vertical diffusion within the boundary layer is based on the parameterization of Holstlag and Boville (1993). Wet deposition is taken from the formulation of Brasseur et al. (1998). Advective transport incorporates the flux from semi-Lagrangian transport algorithm of Lin and Rood (1996). Various versions of MOZART model are available: MOZART, MOZART2, MOZART3, and MOZART4. These physical processes have not been updated from MOZART-2. MOZART-3 is an extension of MOZART-2 with detailed stratospheric chemistry (Kinnison et al., 2007). MOZART-4 is a global chemical transport model for the troposphere and includes a number of updates over the previous tropospheric version MOZART-2 (Horowitz et al., 2003).

(c) Oslo CTM Model

The Oslo CTM3 is an off-line global chemical transport model (CTM), developed at the Department of Geosciences at the University of Oslo (UiO) and later at Center for International Climate and Environmental Research – Oslo (CICERO). The model has comprehensive chemistry for the troposphere and an optional comprehensive chemistry scheme for the stratosphere (Eleftheratos et al., 2013). It is driven by meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF) and Integrated Forecast System (IFS) model. The Oslo CTM2 is a global off-line chemical transport model. In the IFS forecasts, a spectral resolution of approximately 0.5×0.5° grid resolution, longitude/latitude, with 60 vertical layers is applied. The horizontal resolution of the Oslo CTM2 can be varied between 5.6°×5.6°, longitude/latitude, 2.8°×2.8°, 1.9°×1.9°, and 1°×1°,

into which the IFS spectral fields are truncated (Eleftheratos et al., 2013). The IFS data, available as gridded data, are averaged into the model grid. The Oslo CTM2 has been applied in model/model comparisons and tested against observations (e.g., Gauss et al. 2003; Isaksen et al. 2005; Andersen et al. 2006).

(d) CLaMS (Chemical Lagrangian Model of the Stratosphere)

CLaMS is a modular chemistry transport model (CTM) system developed at Forschungs-zentrum Julich, Germany. CLaMS was first described by McKenna et al. (2000) and was expanded into three dimensions by Konopka et al. (2004). CLaMS has been employed in recent European field campaigns (e.g., THESEO, EUPLEX, TROCCINOX and SCOUT - O_3) with a focus on simulating ozone depletion and water vapour transport. CLaMS is composed of four modules and several preprocessors. The four modules are: a trajectory module; a box chemistry module; a Lagrangian mixing module; and a Lagrangian sedimentation scheme. CLaMS operates on a Lagrangian model grid: an air parcel is described by three space coordinates and a time coordinate. The time evolution path that an air parcels traces in space is called a trajectory.

The following meteorological data sets have been used for CLaMS model: European Centre for Medium-Range Weather Forecasts (ECMWF); United Kingdom Met Office (UKMO); and European Centre Hamburg Atmospheric Model (ECHAM4). To initialize the chemical fields in CLaMS, data from a large variety of instruments have been used, including satellite data, air craft and balloons data, and from two-dimensional chemical models, and chemistry-climate models.

There are numerous other CTMs which are developed around the world, such as The Chimere chemistry-transport model (lmd, 2009), EMEP MSC-W chemical transport model (Simpson et al., 2012), the chemical transport model REM-CALGRID (Stern et al., 2009), CSIRO chemical-transport modelling system (Cope et al., 2009), GEOS–Chem Model (Yantosca et al., 2012), just to mention a few.

3.6.3.2 Comparisons of CTM and statistical models

The CTM approach is distinctly different to a statistical approach because it is driven by theory rather than measured data. CTMs are developed based on the understanding of how pollutants are emitted, dispersed and interacted. Also, the methods use inputs like emission rates, dispersion coefficients, reaction rates, etc, which can be determined or even estimated using laboratory based studies rather than in-situ monitoring. So, CTMs can be developed for species that are currently not monitored. This makes them a good research tool for investigating the global impact of recent identified pollutants or to assess the importance of

a particular reaction pathway (NARSTO, 2004). However, they sometimes need careful handling, for example calibration using monitoring data. By comparison, statistical models are empirical using real measurements. This limits them to species which are already being monitored in sufficient detail. A summary of the important differences between statistical and CTMs are listed below:

- CTMs consist of mathematical representations of the relevant physical and chemical atmospheric processes, and therefore can help understand or improve the understanding of a chemical and physical process involved in the formation, transformation, or destruction of a pollutant. On the other hand, statistical models are based on the statistical relationship of various covariates with the modelled (dependent) variable and are not based on any chemical or physical process.
- CTM can model several air pollutants (e.g., ozone, NO_2 and SO_2) at the same time, whereas statistical models can only be run for one pollutant (e.g., ozone) at a time (Westmoreland et al., 2007). For example, TOMCAT can more easily in one run predict a variety of pollutant concentrations (NOx, NO_2, PM_{10}, SO_2 and O_3) in a range of different locations and could predict concentrations for the whole city or country (e.g., London or UK) in the form of contour maps.
- CTM requires much more data as compared to statistical models and the types of data are very specific. Inputs to CTMs include the emission rates of primary air pollutants and precursors of secondary air pollutants, meteorology (three-dimensional fields of winds, turbulence, temperature, pressure, boundary layer height, relative humidity, clouds and solar radiation), and boundary conditions (baseline or background conditions in the case of source-specific models). By contrast statistical models can be developed with whatever is available.
- Statistical models quantify the relationship between independent (predictor or explanatory) variables and dependent (response) variable and generally take much shorter times to run than CTM models.

3.7 Summary

This chapter reviews the existing literatures on ozone concentration, its association with other variables (e.g., spatial parameters, meteorological variables, etc.) and the modelling techniques used for ozone data analysis. The purpose is to review what knowledge and ideas have been already established on ground level ozone and what are their strengths and weaknesses. At the end of each section, a short paragraph has been added stating how this project adds to the present body of knowledge on ground level ozone.

The main points that have been reviewed are: the impact of spatial parameters on ozone concentration; temporal trends of ozone; the effect of meteorology on ozone concentration; the effect of road traffic characteristics on ozone concentration; and various modelling techniques used for ozone data analysis. It is concluded that various geographical parameters, road traffic and meteorological variables play a vital role in controlling ozone concentration. Although a reasonable amount of research has been conducted in these areas, there is still significant scope to refine modelling approaches, particularly on improving the quality of data (e.g. using synchronised data collected at the same site), choice of model (e.g., use of non-parametric model that can handle nonlinearities in the association of ozone and its predictors), and selection of predictive variables (e.g., selecting minimum number of variables that can provide adequate model performance). It is observed that in the past main focus of the research has been on rural ozone, most probably because ozone levels have been relative low in urban areas, however, future work is required to better characterise ozone trends, particularly in urban areas where ozone levels are increasing much more rapidly. In conjunction with urban ozone, the relationship of ozone and road traffic characteristics need to be explored further with the help of monitored traffic and ozone data (in the past surrogates have been used either for ozone or traffic characteristics) and applying appropriate statistical techniques at the local level in the UK. Process based models (e.g., Chemical Transport Models) are currently used to study many ozone - related research questions, one of the research questions that evolved as part of this study was ‘could statistical modelling approaches actually provide a more practical means to many of the questions that we currently use CTMs to address?’. Therefore in this project statistical modelling approach has been adopted to analyse the spatial – temporal variability of traffic related ozone and its association with different parameters (e.g., meteorological and geographical parameters, traffic characteristics, and other air pollutants).

The previous chapters (Introduction, Background, and Literature Review) provide the context for this project by describing the established body of research associated with ground level ozone. Following on from this, the next chapter (Methodology) describes how

this project was carried out. This includes description of the data, sources of the data, general statistics and the main model used in the project.

CHAPTER 4: METHODOLOGY

4.1 Introduction

Literature review revealed that a wide range of modelling techniques, including time series, regressions, space-time analysis, extreme values approaches and neural network have been applied to model ground level ozone concentrations (e.g., Thompson et al., 2001; Schlink et al., 2003; Baur et al., 2004). Among these a number of approaches make useful contributions to the field of air quality, however no one method is most appropriate for all purposes and all meteorological scenarios (Thompson et al., 2001). Hence, the choice of methodology depends on the purpose of the analysis, nature and type of data, and the complexity of ozone formation and interaction with other variables in a given region. Quantile Regression Models (QRMs) are favoured by Baur et al. (2004) and Sousa et al. (2008), whereas Generalised Additive Models (GAMs) are favoured by Schlink et al. (2003), Aldrin and Haff (2005), Carslaw et al. (2007) and Westmoreland et al. (2007) for ozone and air quality modelling, on the basis of the fact that QRMs and GAMs can be applied to non-normal ozone distribution and can handle the potential non-linearities in the association of ozone and its predictors. Furthermore they outperform most of the other available statistical techniques. Therefore, this PhD project intends to use these two models to investigate the association of ozone with several independent variables (as discussed in section 4.2.3 to 4.2.5).

This chapter describes the methodology of this PhD project, which includes descriptions of the statistical models applied (QRM and GAM), types of data (ozone concentrations, spatial parameters, meteorological variables, traffic characteristics and other air pollutants concentrations), and monitoring sites (the UK Automatic Urban and Rural Network (AURN) and Kirkstall roadside monitoring site, part of the air quality monitoring facilities at the Institute for Transport Studies, University of Leeds). In additions, several other statistical tests, including Correlation Analysis, Smooth Trend Function, Theil-Sen Functions, Multiple Regressions, Kolmogorov-Smirnov and the Shapiro-Wilk test have been applied, which are described in this chapter. Graphical presentations include histograms, density plots, box plots, scatter plots, time variation plots, polar plots, pollution rose plots, and time plots are also briefly described.

Several statistical metrics, such as Root Mean Square Error (RMSE), Normalised Mean Gross Error (NMGE), Mean Gross Error (MGE), Coefficient of determination (R^2), Mean

Bias (MB), Normalised Mean Bias (NMB) and Factor of 2 (FAC2) have been described (see section 4.7 for more details), which are used to assess the performance of the models.

The methodology for each chapter is described in a separate section first, followed by a more detailed description of the main models (QRM and GAM), data source, description of some important concepts (e.g., AOT40, SOMO35, defined in section 4.8), methods of measurements etc. Justification for the selection of each test or model is provided. Firstly, a brief background to the project is provided to re-emphasise the importance of the project and then the materials and methods are described.

4.2 Project outline and methodology

Most of the research on ground level ozone in the past has been carried out in rural areas, due to the fact that ozone concentration in urban areas was lower than in rural areas (PORG, 1997) and was posing relatively low risk to human health and natural environment in urban areas. The difference in ozone concentration in urban and rural areas is caused by gas phase titration of ozone by NOx, mainly emitted by road traffic. NOx is negatively correlated with ozone and any reduction in NOx concentration results in ozone concentration to increase (Jenkin, 2004). Since 1990 UK emissions of NOx have fallen by 60 %, primarily as a consequence of tighter European vehicle emission standards in road transport (NAEI, 2011). This has caused ozone concentration to increase, particularly in urban areas (Jenkin, 2008). A recent report by Air Quality Expert Group (AQEG, 2009) has also reported that ozone in urban areas is increasing at faster rate than in rural areas. If this trend (faster rate of ozone increase in urban areas) continues, urban ozone concentration may equate the rural ozone concentration in the next couple of decades or so (Williams, 2007). This has diverted the focus on ozone from rural to urban areas, which might be more challenging in certain aspects. In urban areas increasing ozone level might pose new challenges for the policy makers. Ozone spatiotemporal behaviour, impact on human health, urban ecosystem and building materials, interaction with meteorological variables, and association with other traffic related air pollutants might be different to that in rural areas. Therefore the effects of these factors on ozone concentration need to be investigated.

Review of literature (chapter 3) shows that the effect of road traffic on ozone concentration has not been fully investigated, particularly in the UK. Furthermore, it is felt that the use of spatial parameters in ozone modelling needs further investigation. The effects of meteorology and other air pollutants on ozone concentration in an urban environment perspective with the help of high resolution data and appropriate modelling technique need to be explored. This PhD project intends to characterise ozone concentration with the help

of historical ozone data, spatial characteristics (easting and northing, altitude, distance from the coast and site types), road traffic characteristics (traffic flow, vehicle speed and fleet composition), other air pollutants (e.g. NOx, CO, VOCs, $PM_{2.5}$) and meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction), focusing on the whole distribution of ozone concentration. The project is based on the statistical analysis of measured data of ozone and other variables, obtained from the UK AURN and the host institute, the Institute for Transport Studies, University of Leeds.

In the following subsections (4.2.1 to 4.2.6) methodology used in each chapter has been considered separately.

4.2.1 Frequency distribution of ozone (Chapter 5)

Before applying a classic (parametric) statistical test it might be important to check data distributions and if the data are non-normally distributed, robust and non-parametric methods should be applied which do not assume normality of the data and linearity in the association of dependent and independent variables. Chapter 5 investigates ozone distribution to determine whether ozone is normally distributed or not. Different seasons and monitoring sites have been considered and variations in ozone concentrations are explained in terms of its correlation with meteorology and NOx concentration.

This study (Chapter 5) is based on the statistical analysis of ozone data measured at several air quality monitoring sites in the UK. The sites include 2 roadsides (Kirkstall roadside monitoring site in Leeds and Marylebone roadside monitoring site in London), 2 urban centres (Nottingham and Leeds centre) and 1 each rural (Harwell) and remote (Strath Vaich) air quality monitoring sites. All the sites, except Kirkstall roadside monitoring site are part of the UK AURN (see section 4.3.1 for more details). The Kirkstall site is part of facilities available at the Institute for Transport Studies, University of Leeds for the monitoring of air pollution, traffic and meteorological variables (see section 4.3.2 for more details). At all these sites ozone is measured by ultraviolet absorption analyser, which is the standard method for measurement of ozone in the Europe and UK.

Data distributions can be studied using simple graphical methods, statistics tests or both. The graphical methods used in this study include histograms, density plots and box plots. Histogram is one of the most frequently used diagrams to depict data distribution (Reimann et al., 2008) and is constructed in the form of side by side bars. One glance at the histogram shows whether a distribution is symmetric (both left and right have the same distribution) or skewed (stretched out to one side). Furthermore, it is readily apparent whether the data are unimodal or multimodal and the tails can be easily judged. However, density estimates -

density traces are better suited for comparing data distribution than histograms because they can easily be plotted on top of one another in different line styles or colours (as shown in section 5.5). In addition to graphical presentation, a variety of statistical tests are also available for testing normality (e.g. Kolmogorov-Smirnov and the Shapiro-Wilk tests). In general the Shapiro-Wilk test is statistically preferable to other tests (Reimann et al., 2008), because it is powerful, very simple to compute using linear coefficient tables and that the test is quite sensitive against a wide range of alternatives (e.g., asymmetry, long-tailedness and to some degree to short-tailedness) even when applied to small data sets (details on Kolmogorov-Smirnov and Shapiro-Wilk test can be found in Reimann et al. (2008) or other statistics reference books).

Time variations in daily, weekly, and seasonal cycles of ground level ozone have also been analysed in Chapter 5 using hourly ozone data from four AURN monitoring sites (Leeds Centre, Harwell, Strath Vaich, and Marylebone) and Kirkstall road monitoring site in Leeds. Firstly ozone data from four monitoring sites (Leeds Centre, Harwell, Strath Vaich, and Marylebone) were used to compare the diurnal, weekly and seasonal variations in ozone concentrations and then cluster analysis (k mean) was used to analyse the diurnal cycles of ozone at Kirkstall monitoring site. K-means clustering is a method of cluster analysis that divides n observations into k clusters (sub-group). Each observation in the cluster belongs to the cluster with the nearest mean. The algorithm used is called k-means algorithm which is an iterative refinement technique. K initial means are randomly selected from a given dataset. The better option is to select them as far away from each other as possible. In the next step, each observation is associated with the nearest mean to create k clusters. For each k cluster new k centroids (barycentres) are calculated. The centroid of each of the *k* clusters becomes the new means. Creating k clusters and calculating new mean for them is repeated until no more changes occur (convergence has reached). The algorithm aims at minimising a squared error function (the sum of squared distances to the cluster centres).There is no general theoretical solution to find the optimal number of clusters for a given dataset. A simple approach is to have multiple runs with different k classes and choose the best one. It is important to note that increasing k, results in smaller error function but also increases risk of overfitting.

4.2.2 Ozone and other air pollutants (Chapter 6)

Ground level ozone is formed photochemically from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of NOx in the atmosphere and is therefore considered as a secondary air pollutant (see Chapter 2 for more details). Ozone concentrations are not only dependent on meteorological and spatial variables but also on other air pollutants. Ozone is involved in chemical reactions with various chemical species

in the atmosphere including NOx, hydrocarbons (HC), carbon monoxides (CO) and hydroxyl radical (OH). NOx, HC and CO are considered the main precursors of ozone and lead to the formation of ozone, when conditions are favourable (hot sunny condition). In contrast, NOx is also considered a local sink for ozone, as it is involved in gas phase titration of ozone.

Chapter 6 describes the association of ozone with other air pollutants. The study is based on mean hourly data of ozone ($\mu g/m^3$), HC ($\mu g/m^3$), NO ($\mu g/m^3$), NO_2 ($\mu g/m^3$), $PM_{2.5}$ ($\mu g/m^3$) and CO (mg/m^3). The data were obtained from Kirkstall and Marylebone monitoring sites (for detail see section 4.3). Quantile regression model (described in section 4.5) was used for data analysis. Furthermore, graphical presentations (e.g., time variation plots and scatter plots) were used to depict the association of ozone with other air pollutants.

4.2.3 Ozone and road traffic (Chapter 7)

Road traffic in urban areas is a major source of ozone precursors (e.g., NOx and HC), which contribute positively to ozone formation. In contrast, locally produced NOx serves as a sink and depletes ozone in urban areas, particularly at roadside locations.

The effect of road traffic on traffic-related ozone concentration has been investigated in 2 ways. Firstly, the effect of road traffic on ozone concentration has been investigated in terms of the differences in ozone concentration at urban and rural monitoring sites with the help of quantile regression model, analysing ozone data from 80 monitoring sites (shown in Figure 4.1). Ozone concentration (ppb) hourly data are obtained from the UK AURN and are converted to yearly mean or other metrics as required. The ‘type’ of monitoring sites (urban or rural) is a qualitative or categorical variable and therefore needs to be handled differently from numerical variables. The sites are mainly divided into 2 types (rural and urban) in this study. Dummy variables are assigned to urban and rural site type. Dummy - *proxy* variable is a numerical value that stands in for qualitative data in a regression model and can take values of 0 or 1, where 0 indicates absence and 1 indicates presence of urban factor, therefore 1 is assigned to urban and 0 to rural sites. Rural sites with a value of 0 will cause the coefficient of the variable to disappear and urban with a value 1 will cause the coefficient to act as a supplemental intercept in the quantile regression model. The coefficient can be interpreted as the difference in ozone concentration between urban and rural monitoring sites, keeping all other factors the same (for more details see chapter 7).

As a case study, in the second part the study analyses hourly average ozone concentration (ppb), traffic flow (number of vehicles/hour), and vehicle speed (km/h) collected at the Kirkstall roadside monitoring site in Leeds UK, from January 2008 to May 2009. Hourly mean ozone concentration, traffic flow and speed data are collected at Kirkstall roadside

monitoring site (described in section 4.3.2). Along with some general statistics (e.g., Spearman correlation and graphical presentation), Quantile regression model was applied for data analysis, which has been described in section 4.5.

4.2.4 Ozone and meteorology (Chapter 8)

Meteorology plays a vital role in photochemical ozone formation (e.g. temperature and solar radiation) and ozone removal or dilution (e.g. wind). The year to year variation in ozone concentration due to meteorological effects may mask the variation caused by the amount of precursors emission (Gardner and Dorling, 1999).

The effects of meteorological variables (wind speed, wind direction, temperature, solar radiation, and relative humidity) on ozone concentration have been investigated in Chapter 8, using hourly mean data of these variables for a period of nearly two years (November 2007 to October 2009), collected at Kirkstall roadside monitoring site in Leeds (for detail see section 4.3). Along with some general statistics (e.g., Spearman correlation and graphical presentation including time variation plots and scatter plots), Quantile regression model was applied for data analysis, which has been described in section 4.5.

4.2.5 Ozone spatial variability (Chapter 9)

Understanding ozone spatial trends (maps) are essential for defining the areas (communities) at most risk and estimating the amount of damage caused by ozone pollution (Coyle et al., 2002).

Chapter 9 describes the spatial variability of ozone concentration in the UK. In total data from 80 monitoring sites are used. The sites environment can be categorised into seven types: Rural Background (RB), Rural Background Agriculture (RBA), Rural Background Nature (RBN), Suburban (SU), Urban Background (UB), Urban Industrial (UI) and Urban Traffic (UT) (UK-AIR, 2012: http://uk-air.defra.gov.uk/networks/site-types). These can be broadly grouped into three main categories (types) i.e. urban (54), suburban (5) and rural (23) sites, as shown in Figure 4.1. The sites along with some important characteristics have been listed in table 4.1. For more details on the monitoring sites see section 4.3.1. The spatial variables used in this study are easting and northing Coordinates (m), altitude (m), distance from coast (km), and site type (rural-urban factor). NOx is included in the model as an alternative to site type. NOx is closely related to ozone and improves the performance of the model. In addition NOx is useful for assessing the variation in ozone concentration caused by NOx reduction in urban areas as a result of stringent emission policies.

Using British National grid reference, an easting is the distance (expressed in meters) along the horizontal axis and a northing is the distance along the vertical axis of the false origin (the UK southwest corner of the SV square). Easting & northing and altitude of the monitoring sites are given on the UK AURN website. Distance from the coast for each monitoring site was estimated using Google Earth version 6.1.0.5001 (Google Earth, 2011). NOx concentrations are not monitored at several ozone monitoring sites, in which case spatially lagged (nearest situated sites with similar or nearly similar environmental type) NOx concentrations were used. The sites where NOx data are not available are: Auchencorth Moss (Bush Estate), Bottesford (Market Harborough), Great Dun Fell (Eskdalemuir), Lerwick (Fort William), Lough Navar (Derry), Mace Head (Derry), Sibton (St Osyth), Strath Vaich (Fort William) and Weybourne (St Osyth). The names in the parentheses are the spatially lagged NOx monitoring sites. The altitude for Blackpool Marton, Norwich Lakenfield and Port Talbot Margam are not given at the AURN website, therefore their altitudes were estimated using the R package 'loa' (Ropkins et al., 2012).

The study uses generalized additive model (GAM), in contrast to other chapters where quantile regression model (QRM) is applied (described in section 4.5). Due to the nature of the data (number of data points, 80 sites) GAM is more suitable for this study (see section 4.6 for more details on GAM).

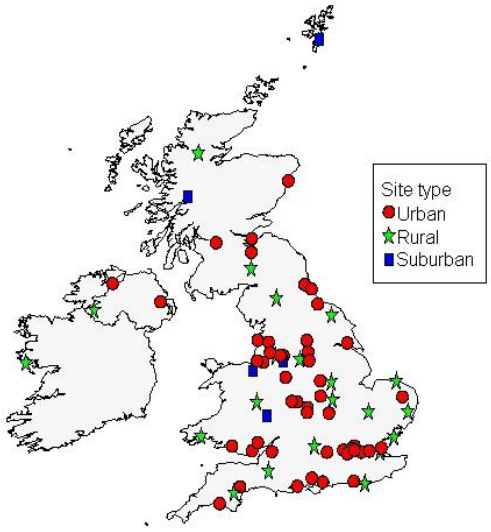


Figure 4.1. Ozone monitoring sites, coded by site type (urban 54, rural 23, and suburban 5). The map was generated using the R Package loa (Ropkins et al., 2012) and NACIS (North American Cartographic Information Society) Natural Earth maps sourced from: http://www.naturalearthdata.com (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

4.2.6 Ozone temporal trends (Chapter 10)

Temporal trend is a relationship between time and pollutant concentrations and is one of the most important and common tasks in the study of air pollution. Trends are calculated to have a general idea as to how the concentrations of air pollutants might have changed over time; or to establish statistically whether a pollutant have significantly increased or decreased i.e. whether the trend is positive or negative and whether significant or not.

In Chapter 10 temporal trends in ground level ozone concentrations are investigated using hourly data from 15 rural and 5 urban monitoring sites, during 1993 to 2011. The sites were chosen on the basis of data availability over the 19 years period. The sites are shown in Figure 4.2. Ozone trends during the last 8 years (2004 to 2011) have also been investigated for the same monitoring sites to investigate how ozone trend has changed most recently. Trends were estimated for minimum (quantile 0), first quartile (quantile 0.25), median (quantile 0.5), mean, third quartile (quantile 0.75) and maximum (quantile 1) of hourly ozone concentration. To estimate annual or seasonal trend two functions (TheilSen and smoothTrend) of the openair-package (Carslaw and Ropkins, 2012) were applied in the R programming language (R Development Core Team, 2012). The codes were adopted as required (e.g. to estimate median, maximum or any other selected quantile trend).

As described in details in Munir et al. (2011) that ozone concentration is non-normally distributed and therefore non-parametric statistical tests needs to be applied for ozone data analysis. Many authors (e.g., Derwent et al., 2007) applied Mann–Kendall test for investigating ozone trends, which is a non-parametric test (described by Salmi et al., 2002). It is reported that the slope and associated p value of Mann-Kendall test lead to very similar results to the TheilSen estimates (Carslaw and Ropkins, 2012). The TheilSen approach provides consistency between the p value and the uncertainty intervals in the slope and therefore has been preferred over the Mann-Kendall test. Furthermore, TheilSen test tends to yield accurate confidence intervals even with non-normal data and non-constant error variance (homoscedasticity) and is resistant to outliers, as it is based on the median of the slopes. TheilSen test calculate slopes between all pairs of points and the median of the slopes is selected as TheilSen estimate, which is taken as the trend of the pollutant for the given period.

To account for the meteorological effect (to deseasonalise the trend) seasonal-trend decomposition using Loess (STL) was applied. The locally weighted regression smoothing technique (Loess) was developed by Cleveland et al. (1990) and has been widely used in data analysis and as a tool for seasonal-trend decomposition. The nonparametric nature of

STL makes it suitable for dealing with nonlinear trends. The technique is also able to deal with missing data (for more details on STL see Cleveland et al., 1990; Carslaw, 2005).

Smoot-trend function has also been applied to fit a smooth non-linear line to the trend, along with 95 % confidence intervals. The smooth line is essentially determined by using generalised additive model (GAM). To estimate trend GAM actually models the relationship between ozone concentration and time, i.e, ozone = f (time) + ε, where f is the smooth term, time is the monthly or annual time period and ε is the error term. The amount of smoothness in the trend is optimised in a way that it is neither too smooth (therefore missing important features) nor too variable (perhaps fitting noise rather than real effects). Readers are referred to Wood (2006) for details on GAM and to Carslaw et al. (2007) and Carslaw and Ropkins (2012) on its applicability to air quality data analysis or estimating trends in air pollutant concentrations.

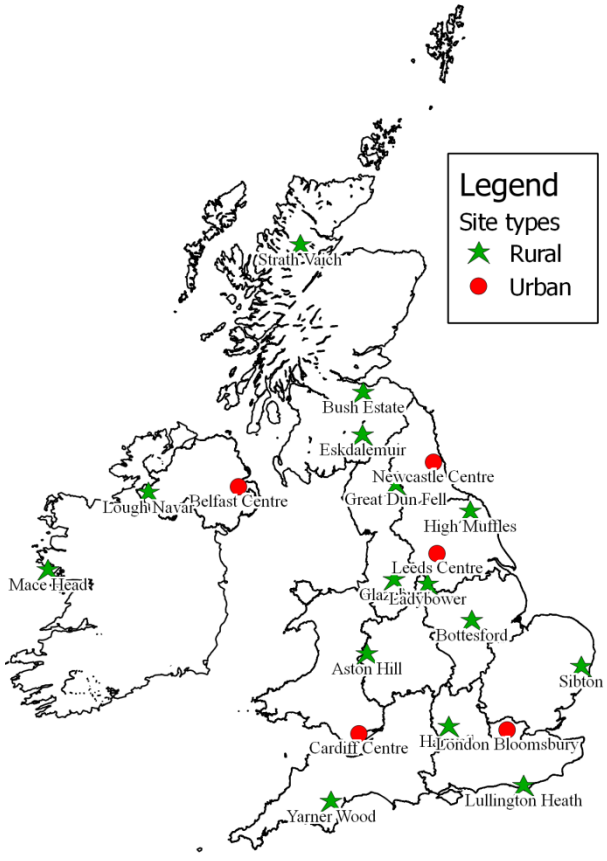


Figure 4.2. Showing 15 rural and 5 urban sites which are part of the UK AURN and are used for estimating ozone trends (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

4.3 Data sources

The data used in this project come from two sources: The UK AURN and the Kirkstall roadside monitoring site, described below.

4.3.1 The UK AURN sites

The UK AURN (UK-AIR, 2012), set up by the UK Department for Environment, Food and Rural Affairs (DEFRA) provides in-depth information on air pollution in the UK, which includes information about the network, data archive, information about air pollution, and latest air pollution levels. The AURN is the most important and comprehensive automatic national monitoring network in the country, which is made up of 127 sites, across the UK (UK-AIR, 2012). Several air pollutants are monitored across the country, including ozone, NOx, CO, HC, particles and SO_2. Ozone has been monitored in the UK for nearly 40 years and the numbers of monitoring sites have been increasing with time. At present there are 54 urban, and 28 rural (including 5 suburban) ozone monitoring sites. The sites environment can be categorised into seven types: Rural Background (RB), Rural Background Agriculture (RBA), Rural Background Nature (RBN), Suburban (SU), Urban Background (UB), Urban Industrial (UI) and Urban Traffic (UT) (UK-AIR, 2012: http://ukair.defra.gov.uk/networks/site-types). These can be broadly grouped into three main categories (types) i.e. urban (54), suburban (5) and rural (23) sites, as shown in Figure 4.1. Each monitoring site has been assigned a unique number which help locate the site on the UK map (Figure 4.3), according to table 4.1. For more details regarding the monitoring sites see the UK-AIR website (UK-AIR, 2012).

Table 4.1 gives details of the 82 ozone monitoring sites in the UK. Type of sites defines the environment where the site is located; the abbreviations R, B, U, T, N, A, I and S stand for Rural, Background, Urban, Traffic, Natural, Agricultural, Industrial and Sub. Two of the monitoring sites (Canterbury and Birmingham Acocks Green) started monitoring ozone in 2011, therefore 5 years mean ozone concentration is given as NA (not available). Sibton (1973), Harwell (1976) and Bottesford (1977) are the sites that have been monitoring ozone for over 30 years.

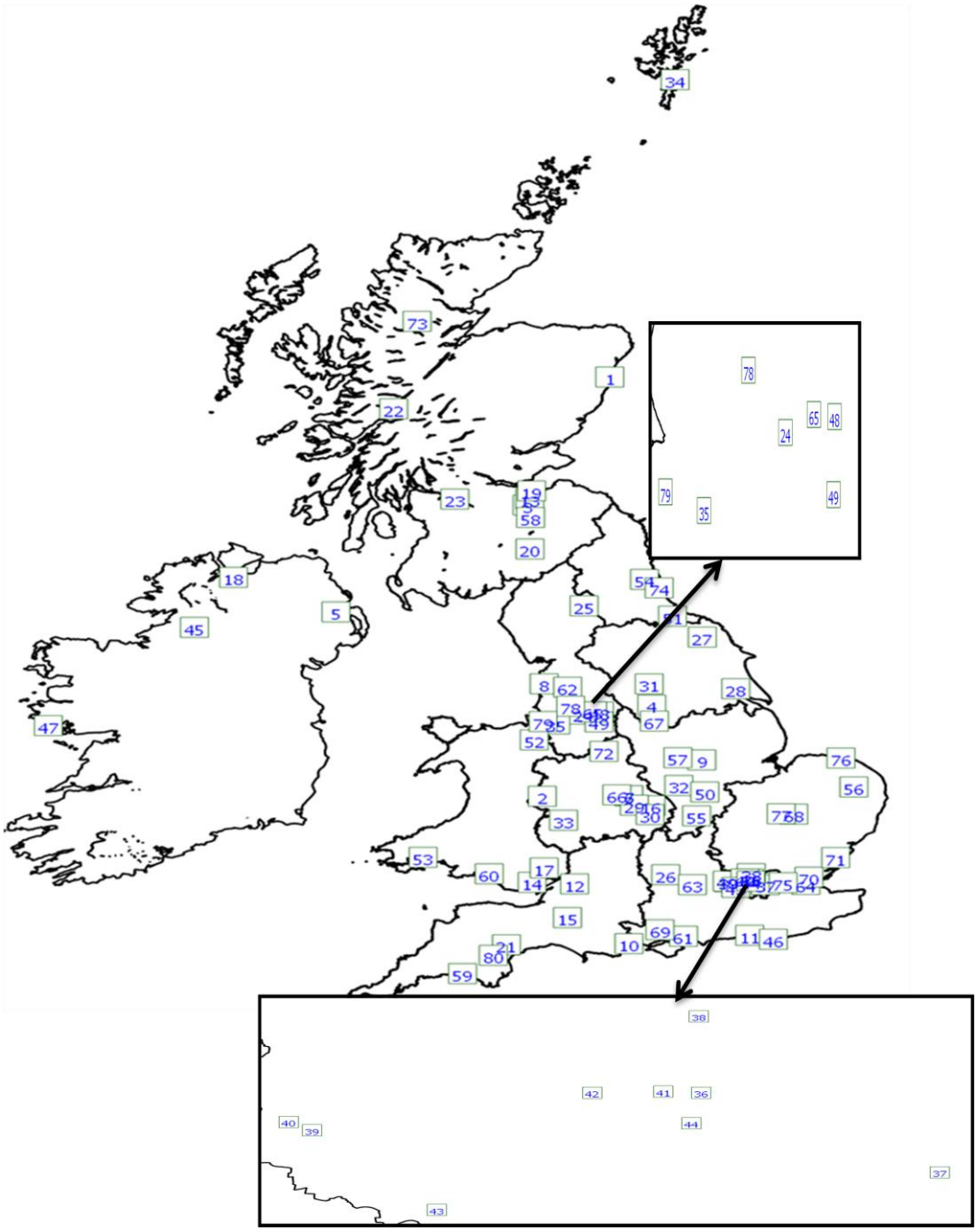


Figure 4.3. showing 80 ozone monitoring sites on the UK map, indicated by a unique number according to table 4.1 (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

Table 4.1. The UK AURN ozone monitoring sites (information obtained November 2011). See Appendices for some more information regarding the monitoring sites.

NO	Name	Easting	Northing	NO	Name	Easting	Northing
1	Aberdeen	394395	807384	41	*L. Marylebone	528124	182021
2	Aston Hill	329901	290056	42	L. N. Kensington	524048	181757
3	Auc. Moss	322167	656123	43	L. Teddington	515544	170422
4	Barnsley Gawber	432524	407479	44	L. Westminster	529777	178963
5	Belfast Centre	146343	529814	45	Lough Navar	17635	520943
6	Bir. Tyburn	411595	290443	46	Lullington Heath	553827	101623
7	Bir. T. Roadside	411576	290495	47	Mace Head	-125891	410255
8	B.P. Marton	333770	434759	48	Man. Piccadilly	384312	398338
9	Bottesford	479770	337646	49	Man. South	383911	385824
10	Bournemouth	412323	93350	50	M. Harborough	483339	295889
11	Br. Preston Park	530523	106232	51	Middlesbrough	450470	519619
12	Bris. St Paul's	359494	173930	52	Mold	323553	363412
13	Bush Estate	324630	663886	53	Narberth	214445	212667
14	Cardiff Centre	318419	176531	54	Newcastle Centre	425025	564916
15	Char. Mackrell	352198	128774	55	Northampton	476112	264515
16	C. Mem. Park	432786	277487	56	Nor. Lakenfields	623634	306948
17	Cwmbran	330438	195486	57	Nottingham Centre	457440	340049
18	Derry	59378	580399	58	Peebles	324816	641084
19	Ed. St Leonards	326265	673131	59	Plymouth Centre	247753	54621
20	Eskdalemuir	323552	603018	60	Port T. Margam	277410	188724
21	Exeter	291933	92845	61	Portsmouth	465695	103673

	Roadside						
22	Fort William	210853	774411	62	Preston	355251	430131
23	Glasgow Centre	258944	665022	63	Read. Ne. Town	473468	173213
24	Glazebury	368756	396030	64	Rochester Stoke	583155	176320
25	Great Dun Fell	371035	532223	65	Salford Eccles	377925	398730
26	Harwell	446859	186022	66	S. W. Bromwich	400399	291419
27	High Muffles	477567	493918	67	Sheffield Centre	435135	386893
28	Hull Freetown	509480	429323	68	Sibton	636272	271907
29	Ladybower	416585	389646	69	Southamp. Centre	442580	112255
30	Leamington Spa	431943	265737	70	Southend-on-Sea	585820	186218
31	Leeds Centre	429966	434260	71	St Osyth	610428	213216
32	Leicester Centre	458776	304088	72	S.O.T. Centre	388352	347897
33	Leominster	349776	258430	73	Strath Vaich	234789	875013
34	Lerwick	445347	1139676	74	S.L. Silksworth	438149	554476
35	Liverpool Speke	343889	383604	75	Thurrock	561067	177899
36	L. Bloomsbury	530117	182045	76	Weybourne	609831	343799
37	L. Eltham	543984	174671	77	Wicken Fen	556313	269184
38	L. Haringey	529898	189134	78	Wigan Centre	357817	406024
39	L. Harlington	508294	177806	79	Wirral Tranmere	332056	386712
40	L. Hillingdon	506940	178616	80	Yarner Wood	278615	78956

*In the table L. means London, N. mean North, Auc. mean Auchencorth, Man. means Manchester, B.P. mean Black pool, Bir. means Birmingham, T. means Tyburn, M. means Market, Br. mean Brighton, Char. means Charlton, Nor. means Norwich, C. Mem. means Coventry Memorial, Ed. St. means Edinburgh Saint, Port T. means Port Talbogh, Red. Ne.

means Reading New, S.W. means Sandwell West, Southamp. means Southampton, S.O.T. means Stoke-on-Trent, S.L. means Sunderland.

4.3.2 The Kirkstall monitoring site

The Kirkstall air quality monitoring site is part of the facilities available at the Institute for Transport Studies, University of Leeds. The site is located on Kirkstall Road (A65), which runs from northwest to southeast through the city of Leeds. There is a petrol pump just across the road only 50 meter from the site and a used car garage about 20 m from the site. The monitoring site is on the northeast side of the Kirkstall road between Woodside View and Woodside Terrace in an open place [53°48'31.38"N and 1°35'21.40"W] (Figure 4.4). In addition to having several particle monitoring instruments, the site also monitors CO, NO_X, ozone and HCs using commercial gaseous analysers (described in section 4.8). Furthermore, the site monitors wind speed, wind direction, temperature, humidity and solar radiation.

Road traffic characteristics were measured using Traffic Detector Loops. The Loops were placed in the upper layers of the road surface at both directions i.e. the southeast carriageway (towards city centre) and the northwest carriageway (out of Leeds city centre). The vehicles are classified into 6 categories according to European 6 bin scheme: (1) motorcycles, (2) cars (cars or light-vans), (3) trailers (cars with trailers), (4) vans (rigid heavy van or mini-buses), (5) artics (articulated heavy vehicles), and (6) buses (buses and coaches).

Figure 4.4. Kirkstall roadside air quality monitoring site, Leeds (Figure source: Background map obtained from Google earth).

4.4 General statistics

Correlation analysis is applied to estimate the degree of co-variance between any pair of variables. The Pearson and Spearman Rank are the two most widely used methods for estimating correlation analysis. Spearman Rank correlation is a non-parametric or distribution free approach and does not require data to be normally distributed. As the ozone and NOx data analysed in this study do not follow a normal distribution, therefore this study will be mostly using Spearman Rank correlation for quantifying the association between ozone and the independent variables. The Spearman Rank correlation is far less influenced by the outliers and thus probably provides more realistic estimates of the points in the main body of the data. Where used, R^2 is the square of Pearson correlation coefficient, calculated by the modStats function of the openair package in R. Kolmogorov-Smirnov and the Shapiro-Wilk test are used to determine the normality of zone and other variables data. Moreover, graphical presentations (scatter plots, histograms, time variation plots, polar plots and pollution rose plots, etc.) have been used to present the outputs of the analysis.

R programming language (R Development Core Team, 2012) with several specialist packages is used to do most of the statistical analysis. Package 'mgcv', version 1.7 – 12 (Wood, 2011) is used for running the generalized additive model; and 'quantreg', version 4.76 (Koenker, 2011) is used to run quantile regression model. 'Openair', version 2.13.2 (Carslaw and Ropkins, 2012) is used for running modStats, editing and formatting data, and making graphs (e.g., scatter plots, time variation plots, time plots and many more). The R package 'loa', version 0.2.3 (Ropkins et al., 2012) was used for drawing the UK maps and calculating the altitude of some monitoring sites, where data were not available on the UK AURN website. Google Earth version 6.1.0.5001 (Google Earth, 2011) and Quantile GIS version 1.7.3 **(**QGIS Development Team, 2011) have also been used in the project for getting spatial data and mapping procedure. In addition, in-house code was written for adjusting the existing codes to the requirement of the project, particularly for estimating the local and global goodness of fit for quantile regression model, for modifying the outputs of the ,mgcv, and estimating temporal trends for selected quantiles.

4.5 Quantile regression model

It has been reported by several researchers that ground level ozone concentration is statistically non-normally distributed (Duenas et al., 2002; Munir et al., 2011) and that the association between ozone and its predictors is nonlinear (Baur et al., 2004; Gardner and Dorling, 2000). This means that the contributions of the explanatory variables (e.g., traffic characteristics) to ozone concentration vary significantly at different ozone concentrations.

Classic statistical techniques that explicitly assume normality of the data and linearity of the relationship between dependent and independent variables, if applied to ozone data analysis, may results in erroneous outcomes (Reimann et al., 2008). This suggests that statistical models should have the capability to address the above issues when applying to analyse ozone data. Quantile regression model (QRM) allows the covariates to have different contribution at different quantiles of the ozone distribution and is robust (insensitive) to departures from normality and to skewed tails. Readers are referred to Koenker (2005) and Hao & Naiman (2007) for the details of QRM; and to Baur et al., (2004), Sousa et al., 2008, and Munir et al., (2012) for the applicability of QRM to ground level ozone concentrations. Baur et al., (2004) and Sousa et al., 2008 modelled the impact of meteorology on ozone concentration, whereas Munir et al., (2012) modelled the effect of other air pollutants on ozone concentrations.

Modelling a dependent variable (y) against a set of independent variables, ordinary least square (OLS) regression specifies the conditional mean function, whereas QRM specifies the conditional quantile function. OLS and QRM are shown in Equation (4.1) and (4.2), respectively (Hao and Naiman, 2007).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_n X_n + \varepsilon_i \quad \ldots \quad (4.1)$$

$$Y^{(p)} = \beta_0^{(p)} + \beta_1^{(p)} X_1 + \beta_2^{(p)} X_2 + \ldots + \beta_n^{(p)} X_n + \varepsilon_i^{(p)} \quad \ldots \quad (4.2)$$

In Equation (4.1) and (4.2) β_0 represents the intercept, $\beta_1$to β_n the slopes (gradients) of the covariates and ε_i the error term. The p shows the pth quantile and its value lies between 0 and 1. Equation (4.1) gives one coefficient for each variable, on the other hand Equation (4.2) can have numerous quantiles and will require a separate Equation for each quantile and therefore will produce numerous coefficients for each variable. This study adopts 10 quantiles and therefore 10 Equations will generate the same number of quantile regression coefficients ($\beta_1^{0.1}$, $\beta_1^{0.2}, \ldots, \beta_1^{0.9}$ $\beta_1^{0.99}$) for each covariate. The equidistant quantiles make them easier to interpret, however they do not have to be at equal intervals (Hao and Naiman, 2007).

4.5.1 Estimating model performance for QRM

In linear regression, the performance of the model is measured by the coefficient of determination (R^2); whereas in QRM local goodness of fit can be represented by R^1 (τ), which measures the local performance of model for a given quantile. The value of R^1 (τ), like R^2, lies between 0 and 1 (Koenker and Machada, 1999). OLS uses least square criterion whereas QRM is based on minimising a sum of weighted distances (Hao and Naiman, 2007). Different weights used depend on whether observed dependent variable (ozone

concentration) is greater or smaller than the predicted variable. R^1 (τ) and R^2 are calculated differently and have different natures, as the former is a local whereas the latter is a global measure of performance and therefore are not directly comparable.

Koenker and Machado (1999) suggest measuring R^1 (τ) by comparing the sum of weighted distance for the model of interest with the sum in which only the intercept is used. If observed dependent variable (e.g., ozone concentration) is denoted by o, its predicted or modelled value by f, quantiles by τ, their respective values by q, and predicted variable using only intercept in the model by μ (it is normally equal to the mean of variable), then R^1 (τ) can be calculated as follows (adopted from Hao and Naiman, 2007).

$$R^1(\tau) = 1 - \frac{\sum_{o \geq f} \tau |o-f| + \sum_{o<f} (1-\tau)|o-f|}{\sum_{o \geq \mu} \tau |o-q| + \sum_{o<\mu} (1-\tau)|o-q|} \quad \ldots (4.3)$$

A global goodness of fit (denoted by R^1) can be estimated for QRM to make it comparable with OLS model. To estimate R^1 for QRM, this study adopts the amalgamated quantile regression model (AQRM) technique suggested by Baur et al. (2004). The first step in estimation of R^1 is to run QRM and determine quantile regression coefficients for all the quantiles used in the model. QRM will normally give numerous predictions according to the number of quantiles used in the model. To turn that into one global prediction, the dataset is divided into the same number of subsets as the number of quantiles and then the model for that respective quantile is used to predict dependent variable. The predicted value for these quantiles is then re-integrated in such a way that it corresponds to the observed value in the exact order. Finally global goodness of fit is estimated using the following Equation.

$$R^1 = 1 - \frac{\sum_i (o-f)^2}{\sum_i (o-\mu)^2} \quad \ldots (4.4)$$

The package 'quantreg' does not provide local or global goodness of fit estimation; therefore dedicated R codes were written for this study (the codes are given in Appendix 4). Several other statistical metrics were estimated for the model, which are described in section 4.7.

4.6 Generalised additive model

Generalised additive models (GAMs) are statistical models developed by Hastie and Tibshirani (1990) for blending properties of generalized linear models with additive models. GAMs assume that the mean of the dependent variable depends on additive predictors through a nonlinear link function. GAMs permit the response probability distribution to be

any member of the exponential family (e.g. normal, exponential, gamma, Poisson and many other) (Wood, 2006). Therefore, GAMs relax the normality requirement of the data and can handle the non-linearity in the association of dependent and independent variables (Wood, 2006), which are explicitly assumed by the linear regression models (as stated in section 4.5).

Schlink et al. (2003) performed a model inter-comparison exercise in which 15 different statistical techniques for ozone forecasting were applied to ten data sets representing different meteorological and emission conditions throughout Europe. Their results favoured neural networks and GAM methods on the base of their performance and ability to handle nonlinearities in the association of ozone with its predictors. Davis and Speckman (1999) successfully predicted daily 8 hour average ozone concentration at Houston, Texas using a GAM where previous regression models had struggled due to the complex meteorological processes. Aldrin and Haff (2005) also applied GAM to model air pollutants concentrations in Oslo for quantifying the effects of meteorological and traffic-related parameters on the concentrations of particulate matter (PM_{10} and $PM_{2.5}$), NOx and NO_2. More recently, Carslaw et al. (2007) developed a GAM model for assessing trends in traffic related emissions (NOx, NO_2, CO, benzene and 1,3-butadiene) at Marylebone Road, London; and Westmoreland et al. (2007) applied GAM in a busy street canyon in Gillygate, York, comparing the outcomes of GAM with a dispersion model (ADMS-Urban). The predictions made with the GAM showed excellent agreement with measured concentrations of NOx and NO_2 and out-performed ADMS-Urban.

4.6.1 Model development

Firstly a GAM model was developed to study only the effect of site type (urban or rural) on ozone concentration (the results are shown in section 9.3.4). As site type (RB, RBA, RBN, SUB, UB, UI, and UT) is a qualitative or categorical parameter, therefore it needs to be handled differently. GAM model can handle a categorical variable as shown below. The model developed is shown as follows:

$$\text{Ozone} = f(\text{as.numeric}(\text{site-type})) + \varepsilon \quad \ldots\ldots\ldots (4.5)$$

To develop a GAM model for the analysis of annual mean ozone concentration, the spatial variables easting & northing (m), altitude (m), distance form coast (km) and NOx ($\mu g/m^3$) have been used as independent variables and annual mean ozone concentrations ($\mu g/m^3$) as dependent variable. The effect of easting and northing has been modelled as an interactive term. Various models were investigated out of which one was selected on the basis of their performances, which is given below:

ozone = f (easting, northing) + f (altitude) + f (distance from coast) + f (NOx) + ε . (4.6)

In Equation (4.5 and 4.6) the 'f' term is the smooth function of the covariates and ε is the residual, which is assumed to be normally distributed. Each smoother is controlled by a single smoothing parameter, chosen automatically by the generalized cross validation (GCV) method. The inclusion of a term in the model can be assessed by considering the effect on the GVC score of excluding the term: a lower GVC score if the term is removed indicates that omitting the term would be beneficial (Wood and Augustin, 2002). For more details regarding the smooth function and GAMs readers are referred to Wood (2011) and Wood (2006). The easting and northing can be substituted with latitude and longitude without having any significant effect on the performance of the models. When easting and northing were entered in the model as additive terms i.e. f (easting) + f (northing), the goodness of fit (R^2 – value) slightly decreased. Furthermore, when NOx was split to its components (NO_2 and NO) the model performance did not improve. Several metrics were calculated to assess the performance of the model, which are described in section 4.7.

4.7 Statistical metrics

Several metrics are available for assessing the performance of a model; however no single statistic encompasses all aspects of interest. For this reason it is advised to consider several metrics for assessing the performance of a model (Carslaw, 2011). However, there is a need for some form of simplification and rationalisation by adopting a limited number of metrics to encourage a large degree of harmonisation between the evaluation approaches adopted by the researchers (Derwent et al., 2010). The metrics adopted in this project are: Root Mean Square Error (RMSE), Normalised Mean Gross Error (NMGE), Coefficient of determination (R^2), Normalised Mean Bias (NMB) and Factor of 2 (FAC2). The definition and formulas for these metrics are given below, where P is the predicted or modelled value and O is the observed value of the dependent variable.

(1) The RMSE is a commonly used metric that provides a good overall measure of how close modelled values are to predicted values.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_1^n (\mathrm{Pi} - \mathrm{Oi})^2}{\mathrm{N}}}$$

(2) The MB is an indication of the mean over or under estimate of prediction.

$$\mathrm{MB} = \frac{1}{\mathrm{N}} \sum_1^n \mathrm{Pi} - \mathrm{Oi}$$

(3) To estimate NMB the value of MB is divided by the observed concentration to get normalised value.

$$\mathrm{NMB} = \frac{\sum_1^n \mathrm{Pi} - \mathrm{Oi}}{\sum_1^n \mathrm{Oi}}$$

Based on many years modelling experience over a wide range of pollutants of policy relevance, scientist have recommended that air quality models are considered acceptable if NMB values lie within the range between -0.2 and +0.2 and faulty if not (Derwent et al., 2010).

(4) MGE is the absolute value of MB as it does not take account of the negative or positive sign. The units of MB and MGE are the same as the observations and so are readily understood.

$$\mathrm{MGE} = \frac{1}{\mathrm{N}} \sum_1^n |\mathrm{Pi} - \mathrm{Oi}|$$

(5) NMGE is the same as NMB, but it ignores whether a prediction is an over or under estimate (absolute value).

$$\mathrm{NMB} = \frac{\sum_1^n |\mathrm{Pi} - \mathrm{Oi}|}{\sum_1^n \mathrm{Oi}}$$

(6) The correlation coefficient is a measure of the strength of the linear relationship between two variables. Most often correlation coefficient is squared to calculate coefficient of determination (R^2), which is the ratio of the explained variation to the total variation and is a measure that allows us to determine how certain one can be in making predictions from a certain model.

$$\mathrm{R}^2 = 1 - \frac{\sum_1^n (\mathrm{Oi} - \mathrm{Pi})^2}{\sum_1^n (\mathrm{Oi} - \mu\mathrm{i})^2}$$

Where μ is the mean of the observed value and is equal to the predicted value of the model when only intercept is used as independent variable.

(7) FAC2 is the fraction of modelled values within a factor of two of the observed values. In other words FAC2 is a count of the fraction of points within 0.5 and 2 times the observed values. FAC2 is defined as the fraction of model predictions that satisfy:

$$0.5 \leq \frac{Pi}{Oi} \leq 2.0$$

An air quality model is considered acceptable if more than half of the model predictions lie within a factor of 2 of the observations and faulty if not (Derwent et al., 2010). The above definitions and estimations are based on Carslaw (2011) and Derwent et al. (2010).

4.8 Other statistics (metrics or standards)

In addition to hourly average, 24 hour average or annual average, other metrics (standards or critical values) were also considered for expressing ozone concentrations, such as AOT40 and SOMO35. Firstly these metrics are briefly described and the method of their calculation is explained. More details can be found in the references cited.

4.8.1 AOT40

AOT40 are accumulated ozone concentrations over 40 ppb (80 µg/m^3) and are estimated to assess the impact of ozone concentration on agricultural crops. The critical level of AOT40 for agricultural crops is 3000 ppb h (Coyle et al., 2002), which is accumulated during daylight hours for the three months (May, June, and July) when clear sky radiation is above 50 W/m^2 (Fuhrer, et al., 1997). Air quality strategy for England, Scotland and Wales (AQS, 2007) recommends the calculation of AOT40 over 12 hours (08:00 to 20:00) of the day; and when AOT40 values reach the critical level (3000 ppb h), it is considered that ozone concentration has exceeded the threshold level and is likely to cause damage to agricultural crops. To remove the effect of annual variations in ozone concentration, assessments of the critical level are based on the average AOT40, taken over the most recent 5 years (2007 to 2011) as suggested by Coyle et al., 2002. For further details on AOT40 see UNECE, 2004; and Coyle et al., 2002.

Ozone concentration data were obtained from UK-Air (2012) for all ozone monitoring sites considered in this study for the most recent five years (2007 – 2011). Firstly AOT40 were calculated for each year and then averaged over the 5 years. Special codes were developed in R for calculating AOT40, which are described below.

Firstly ozone data for the three months (May, June and July) and 12 hours each day (08:00 to 20:00 hr) were selected for each year and then AOT40 were calculated using the following code:

AOT40 = sum (ifelse (ozone - 40) < 0, 0, ozone - 40)

The above function makes sure to subtract 40 ppb (80 µg/m^3) from each hour and sum up the positive values only, converting all negative values to zero. AOT40 are sensitive to missing values, therefore a correction to full time coverage has been applied:

$$AOT40_{estimate} = AOT40_{measured} (N_{period} / N_{valid})$$

Where N_{valid} is the number of valid hourly values and N_{period} is the total number of hours in the period.

4.8.2 SOMO35

SOMO35 stands for the Sum of Ozone Means Over 35 ppb. For quantification of the health impacts the World Health Organisation recommends the use of the SOMO35 indicator. It is defined as the yearly sum of the daily maximum of 8-hour running average over 35 ppb. For each day the maximum of the running 8-hours average for ozone is selected and the values over 35 ppb are summed over the whole year.

Firstly 8 hour running mean for ozone concentrations were calculated using 'rollingMean' function of 'openair package', and then maximum value for each day was selected using the time average function as shown below.

Max = timeAverage (data, avg.time="day", statistic="max")

For calculating SOMO35 special code was developed in R which is as given below:

SOMO35 = sum (ifelse (rollingOzone - 35) < 0, 0, rollingOzone - 35)

The above function makes sure to subtract 35 ppb (70 µg/m^3) from each 8 hour running mean ozone and sum up the positive values only, converting all negative values to zero. The corresponding unit of SOMO35 is ppb·days or µg/m^3·days. SOMO35 is sensitive to missing values and a correction to full time coverage has been applied:

$$SOMO35_{estimate} = (SOMO35_{measured} \cdot N_{period}) / N_{valid}$$

Where N_{valid} is the number of valid daily values and N_{period} is the number of days per year. SOMO35 are average over 5 years to account for annual variations.

4.8.3 Annual Mean

Annual mean ozone concentration (µg/m^3) is obtained by averaging the hourly concentration over the whole year. It is a useful metric for estimating long term trends in ozone concentrations and is therefore more dependent on NO concentrations, rather than on photochemical ozone formation (Stedman and Kent, 2008).

Several other metrics are used for expressing ozone concentration and ozone spatial or temporal trends vary according to the metric used. Generally peak ozone values, for instance maximum ozone concentrations over a threshold value such as 100 or 120 µg/m^3, maximum

annual daily or annual ozone concentrations are more dependent on photochemical ozone formations and summer time ozone episodes, rather than on NOx concentrations (for details on annual average of the daily maximum of the running 8-h mean with a 70 µg/m^3 cut-off; annual average of the daily maximum of the running 8-h mean with a 100 µg/m^3 cut-off; or number of days with daily maximum of running 8-h mean exceeding 120 µg/m^3 see Stedman and Kent, 2008).

4.9 Data standardisation / normalisation

In this PhD project in several places the air pollutants or other variables data are standardised. Standardisation is done either for graphical presentations or for regression models.

Normalisation for graphical presentation: In graphical presentation the aim was to rescale the variables and make comparison between different variables more convenient. For example, if average vehicle speed (km/hr) and total flow of vehicles (number of vehicles / hour) were to present in a time variation plot, it would be rather difficult to show them on the same plot because average speed would range from about 30 to 70 (km/hr), whereas flow would be in several hundred or even in thousands (vehicles/hour) on some busy roads. Therefore the variables would be better normalised. In all plots where normalised data are used, this project follows the normalisation approach suggested by Carslaw and Ropkins (2012) in the openair package. They suggest that each observation of the variable is divided by the mean of the variable to normalise outputs for graphical presentation.

Standardisation for modelling: Interpretation of regression coefficients is sensitive to the scale of the inputs. One method often used to place input variables on a common scale is to standardise the input variables. A common approach in applied regression is to 'standardise' each input variable by subtracting its mean and dividing by its standard deviation. Subtracting the mean typically improves the interpretation of main effects in the presence of interactions, and dividing by the standard deviation puts all predictors on a common scale. Each coefficient in the standardised model is the expected difference in the outcome, comparing units that differ by one standard deviation in an input variable with all other inputs fixed at their average values (Gelman, 2007).

Statisticians have different opinions regarding data standardisation and its impact on regression coefficients. For example, Bring (1994) notes the incompatibility of scaling the inputs based on their marginal distributions and then interpreting regression coefficients conditionally. King (1986) points out that comparison of rescaled coefficients across data sets are problematic because changing the range of a predictor will change its rescaled

coefficients even if the regression model itself is unchanged. Greenland et al. (1986) discuss challenges in causal interpretations of standardised regression coefficients.

Standardisation of data can be used to facilitate comparability of the relative importance of predictor variables feasible. The advantage of such a process is that, when an explanatory variable has a totally different physical dimension and magnitude from the response variable, scaling through division by standard deviation may help in terms of numerical stability, and enables one to compare effects across multiple explanatory variables. However, in cases where the metrics have meaning to the person interpreting the regression equation and the variables are almost at the same scale, unstandardised coefficients are often more informative. Furthermore, when interaction is considered in a model, scaling could be very problematic even for statistical testing because of a complication involving a stochastic scaling adjustment in calculating the standard error of the interaction effect. Therefore, in this PhD project both approaches are adopted according to the nature of the data and the metrics used for expressing variables.

In Chapter 7, where the effect of road traffic volume, vehicle speed and fleet composition on ozone concentration is investigated, the inputs variables are standardised because the dependent and independent variables are totally at different scales. However, in other chapters, for example where the effect of traffic related air pollutants on ozone is investigated, non-standardised values are used because these are almost on the same scales and in many place the interaction terms are included in the model.

4.10 Data and modelling assumptions

4.10.1 Data assumptions

Air pollutants, meteorological and traffic characteristics data were obtained from two main sources: The host institute (ITS University of Leeds) and AURN website. High precision instruments were used to measure these parameters following the well established standard procedure of data collection, instrument installation, calibration and data verification. For more details regarding air pollutants monitoring and data verification see the UK AURN website (UK-AIR, 2012). The candidate personally was not involved in selection of monitoring sites, instrument installation, calibration, and data verification process, therefore several assumption were made regarding the data quality. These include: (a) the data collected are representative of atmospheric concentrations at the monitoring site. This assumption means that the monitoring sites are accurately specified and various monitoring sites (e.g., rural or urban) represent the environment type correctly; (b) the instrument used to measure various parameters were working properly according to the supplier

specification; (c) the monitoring instruments were properly calibrated; (d) other data QA & QC measures were properly in place (e.g., data verification).

In some places in this PhD project, spatially offset data are used. The monitoring sites have the same or nearly the same properties and therefore it is assumed that the data would not be significantly differently. Especially rural and remote monitoring sites data can represent a wide area of the surrounding area. Due to meteorological and topographical variability, there are always minor differences between different monitoring sites, however these differences are assumed to be insignificant. Wherever such spatially offset data has been employed within this project: (a) this has been fully documented; and (b) an attempt has been make to quantify the likely significance of any associated uncertainty.

4.10.2 Modelling assumptions

Many statistical procedures are based on classical parametric tests, which in turn are based on certain assumptions. If parametric tests are applied and the data do not fulfil the assumptions, then the results are likely to be inaccurate. Therefore, it is very important to check the assumptions before deciding which statistical test is appropriate. The assumptions of parametric tests are:

Normally distributed data: Parametric tests require the data to be normally distributed. Normality of the data can be checked either graphically (e.g., using histogram, density plot etc.) or statistically (e.g., using Kolmogorov–Smirnov test or Shapiro–Wilk test). These tests check to see whether the distribution as a whole deviates from a comparable normal distribution. The scores in the sample are compared to a normally distributed set of scores with the same mean and standard deviation. If the test is non-significant ($p > .05$) it tells us that the distribution of the sample is not significantly different from a normal distribution (i.e. it is probably normal). If, however, the test is significant ($p < .05$) then the distribution in question is significantly different from a normal distribution (i.e. it is non-normal). See Chapter 5 for more details. If data are not normally distributed the model results in non-normally distributed errors. Normally distributed error means that the residuals in the model are random with a mean of 0. This assumption simply means that the mean of the residuals should be zero and the residuals are even distributed about zero for fitted data.

Homogeneity of variance: This assumption means that the variances should be the same throughout the data. In data where the association of several parameters are measured, this assumption means that equal amount of variation in one variable (independent variable) causes the same amount of variation in the other variable (dependent variable). This is also referred to as linearity or homoscedasticity.

Variable types: All predictor (independent) variables must be quantitative or categorical (with two categories), and the response (dependent) variable must be quantitative and continuous. This assumption is met my by the ozone and other parameters data.

Non-zero variance: The predictors should have some variation in value (i.e. they do not have variances of 0). The variance is non-zero in the data used in this project; hence this assumption is met as well.

No perfect multicollinearity: There should be no perfect linear relationship between two or more of the predictors. So, the predictor variables should not correlate too highly (Correlation Coefficient should be < 0.80). Several air pollutants (e.g., NO and NO_2) and meteorological parameters (e.g., temperature and solar radiation) have multicollinearity, however, it is not too high (R < 0.8). Therefore it should not affect the model outcome significantly (for example see Field, 2009).

It is worth mentioning that as shown in later chapters, ozone and other air pollutants data are not normally distributed and that the association of ozone is non-linear with other parameters. Therefore ozone data violates the first two assumptions of the parametric statistical model. Therefore, this study aims to employ non-parametric statistics that can be applied to both normal and non-normal distribution and can address the non-linearities between ozone and other variables.

4.11 Methods of measurement

The UK AURN uses Ultraviolet Analyser and Chemiluminescent Analyser for ozone and NOx measurements, respectively. CO concentrations are measured using Infrared Analyser; whereas $PM_{2.5}$ concentrations are monitored by Tapered Element Oscillating Microbalance (TEOM), Beta Attenuation Monitor (BAM), Gravimetric Monitor, or Filter Dynamics Measurement System (FDMS), which provides a continuous direct mass measurement of particulate matter (UK-AIR, 2012). These techniques represent the current state-of-the-art for automated monitoring networks and, with the exception of the automatic PM_{10} and $PM_{2.5}$ analysers, are the reference methods of measurement defined in the relevant EU Directives. The automated systems for particles are subject to correction for routine monitoring. The standard EU reference method for particulate measurement refers to three devices which might be used: (a) Low Volume System: the LVS-PM10 Sampler; (b) High Volume System: the HVS PM10 Sampler; and (c) Super-high Volume System: the WRAC-PM10 sampler (Wide Range Aerosol Classifier) (EC WGPM, 2002).

The air quality monitoring instruments used at Institute for Transport Studies are supplied by Enviro-technology and they use the following methods for measuring air pollutants:

- CO – Infrared analyser (API M300E);
- NOx – Chemiluminescent analyser (API M200A) ;
- Ozone – Ultraviolet (UV) analyser (API M400E) ;
- HC – Photo ionisation gas chromatograph (syntech spectras GC955-603).

Furthermore, temperature sensor, relative humidity sensor, solar radiation sensor, anemometer are used for meteorological observation. The traffic data used in this PhD project were provided by the Institute for Transport Studies (ITS), University of Leeds. Traffic characteristics were measured at Kirkstall road using Traffic Detectors Loops. The traffic loops were installed by Golden River Limited, as part of a contract to the LANTERN Consortium of the University of Leeds within the SRIF2 Instrumented Junction Project. The consortium included partners in the Institute for Transport Studies, and Departments of Engineering, Chemistry and Computing. The loops were placed in the upper layers of the road surface at both directions i.e. the southeast carriageway towards city centre and the northwest carriageway out of Leeds city centre. The candidate was not involved personally in the monitoring process and received 15 minutes data from ITS, which were further analysed as required.

4.11.1 Units of measurements and quality of data

Air pollutants are mostly expressed as concentration in microgram per cubic meter ($\mu g/m^3$) or milligram per cubic meter (mg/m^3) at the UK AURN website; whereas at the Institute for Transport Studies mixing ratios i.e. part per billion (ppb) or parts per million (ppm) are used for expressing the amount of various gaseous air pollutants and $\mu g/m^3$ for $PM_{2.5}$. However, to make it simple and easy to follow, mostly the word concentration is adopted (e.g., ozone concentration in ppb, rather than ozone missing ratio in ppb). In each chapter it is made clear whether the concentration is in ppb, ppm, $\mu g/m^3$or mg/m^3. Only CO is measured in ppm or mg/m^3, the rest of the pollutants are measured in ppb and $\mu g/m^3$. Wind speed is expressed in meter per second (m/s), wind direction in degree angle from the north, relative humidity in percent (%), temperature in degree Celsius (^oC) and solar radiation in watt per meter square (w/m^2). Furthermore, easting and northing Coordinates and altitudes are expressed in meters (m), and distance to the coast in kilometer (km).

At Institute for Transport Studies, University of Leeds to ensure the quality of data is maintained, automatic nightly calibrations of gaseous analysers, and fortnightly manual zero and span calibrations using calibration gases CO, NO, NO_2 and Benzene are performed routinely. After collection the data go through verification, a process to clean-up the initial data. The data from the UK AURN go through a proper data verification and ratification process before marked as ratified data. AEA carries out the quality assurance and control

(QA/QC) activities for the UK AURN on behalf of Defra, Scottish Government, Welsh Government and DoE in Northern Ireland (UK-AIR, 2012). For details regarding the QA/QC procedures and other details (e.g., instrument requirement, operation condition etc.) see the recent report by Environmental Agency (EA, 2010).

4.12 Summary

In this chapter the methods and materials used in this PhD project are described. Data come mainly from two sources: the UK AURN and the host institute. Traffic characteristics, other air pollutants (CO, NOx, $PM_{2.5}$, and HC), meteorology and ozone data used in this study are mainly collected at the Kirkstall roadside monitoring site; whereas ozone data used in estimating temporal and spatial trends and spatial parameters data are obtained from the UK AURN. In addition to general statistics (e.g., correlation analysis, graphical presentation of the data), two main models are used in this study: QRM and GAM. These models can be applied to non-normal ozone distribution and can handle the non-linearities in the association of ozone and the independent variables. The models and several statistical metrics (RMSE, MB, NMB, GME, NGME, R^2 and FAC2) for assessing the model performance are described briefly. Furthermore, brief descriptions of measurement techniques of various variables, units and data quality have been provided.

In this chapter the data, sources of data and the methodology used in this PhD project are described. In the next chapter (Chapter 5: data distribution) the distributions of the data are investigated in a view to determine whether ozone and other variables data used in this project follow a normal distribution or not, to justify the applicability of the models used in the project.

CHAPTER 5: FREQUENCY DISTRIBUTION AND TEMPORAL VARIATION OF OZONE

5.1 Introduction

Ground-level ozone has been studied extensively throughout the World using classic parametric statistics, most commonly conventional linear regression, for instance Soja and Soja (1999), Pont and Fanton (2000), Tidblad et al. (2002), and Pai et al. (2009) all used linear regression for ozone data analysis. Linear regressions explicitly assume normality of the error term and linearity of the relationship between response variable (in this case ozone) and the covariates (independent variables, explanatory variables or predictors); therefore several researchers (e.g., Baur et al. 2004; Gardner and Dorling, 1999) have suggested that linear regression models may not be suitable for ozone data analysis, as ozone data are not normally distributed (Duenas et al., 2002; Munir et al., 2011) and have non-linear association with its predictors (Baur et al., 2004; Gardner and Dorling, 1999). Very few researchers have considered ozone distributions and even those that do tend to apply parametric techniques.

Ozone concentration is affected by local topographical and meteorological conditions, and therefore demonstrates significant temporal and spatial variations (See chapter 8 and 9 for more details). It is, therefore, important to determine ozone frequency distribution at various locations and during different months of the year, before drawing any conclusions.

This chapter assesses the frequency distribution of ground-level ozone concentration (ppb) at six locations in the UK (Kirkstall roadside Leeds, Marylebone roadside London, Nottingham centre, Leeds centre, Harwell and Strath Vaich). Ozone distribution is also investigated during different months of the year. The distribution of ozone is investigated applying Kolmogorov-Smirnov and Shapiro-Wilk tests and graphical presentations (mainly histograms and density plots). Furthermore, the distributions of some important air pollutants (nitrogen oxides (NOx ppb), carbon monoxide (CO ppm), particulate matter of size < 2.5 µm ($PM_{2.5}$ µg/m^3)), meteorological variables (wind speed - m/s, wind direction - degrees from the north, temperature - ^oC, relative humidity - % and solar radiation - watt/m^2) and road traffic characteristics (traffic flow vehicles/hour, speed m/s) are also investigated.

Temporal variations of ground level ozone concentration (ppb) are analysed using time variation plots and cluster analysis, in a view to have a clear understanding of the variations

of ozone concentration during different hours of the day, days of the week and months of the year.

5.2 Methodology

The study is based on the statistical analysis of hourly mean ozone concentration (ppb) data measured at several air quality monitoring sites in the UK. The sites include 2 roadsides (Kirkstall roadside Leeds and Marylebone roadside London), 2 urban centres (Nottingham and Leeds centre) and 1 each rural (Harwell) and remote (Strath Vaich) air quality monitoring sites. All the sites, except Kirkstall are part of the UK Automatic Urban and Rural Network (AURN). The Kirkstall site is part of facilities available at Institute for Transport Studies (ITS) University of Leeds for the monitoring of air pollution, traffic and meteorological variables (for more detail on monitoring sites see chapter 4). Other air pollutants, meteorological variables and traffic characteristics data were also monitored at the Kirkstall monitoring site.

Data distributions can be studied using simple graphical methods, statistics tests or both. The graphical methods used in this study include histograms and density plots. Histogram is one of the most frequently used diagrams to depict data distribution (Reimann et al., 2008) and is constructed in the form of side by side bars. One glance at the histogram shows whether a distribution is symmetric or skewed (stretched out to one side). Furthermore, it is readily apparent whether the data are unimodal or multimodal and the tails can be easily judged. Density plots - *density traces* are better suited for comparing data distribution than histograms because they can easily be plotted on top of one another in different line styles or colours (as shown in section 5.5). In addition to graphical presentation, a variety of statistics tests are applied for testing normality (e.g. Kolmogorov-Smirnov and the Shapiro-Wilk test).

Time variations of ground level ozone have been analysed using hourly ozone data from four AURN monitoring sites (Leeds Centre, Harwell, Strath Vaich, and Marylebone) and Kirkstall road monitoring site in Leeds. Firstly ozone data from four monitoring sites (Leeds Centre, Harwell, Strath Vaich, and Marylebone) were used to compare the diurnal, weekly and seasonal variations in ozone concentrations and then cluster analysis (k mean) was used to analyse the diurnal cycles of ozone at Kirkstall monitoring site. K-means clustering is a method of cluster analysis that divides n observations into k clusters. Each observation in the cluster belongs to the cluster with the nearest mean. The algorithm used is called k-means algorithm which is an iterative refinement technique. K initial means are randomly selected from a given dataset. The better option is to select them as far away from each other as possible. In the next step, each observation is associated with the nearest mean to create k

clusters. For each k cluster new k centroids (barycentres) are calculated. The centroid of each of the *k* clusters becomes the new means. Creating k clusters and calculating new mean for them is repeated until no more changes occur (convergence has reached). The algorithm aims at minimising a squared error function (the sum of squared distances to the cluster centres).There is no general theoretical solution to find the optimal number of clusters for a given dataset. A simple approach is to have multiple runs with different k classes and choose the best one. It is important to note that increasing k, results in smaller error function but also increases risk of overfitting.

5.3 Results and discussions

5.3.1 Ozone data distribution

Firstly hourly ozone concentration (ppb) data from the Kirkstall site are analysed in details and then compared with data from other AURN sites. The Kirkstall data analysed are for about a 2 years periods (November 2007 to October 2009). Figure 5.1 shows a histogram of hourly ozone concentration collected at Kirkstall site and shows that ozone data are not normally distributed (p-value for Shapiro-Wilk test is less than 0.01). The histogram is negatively skewed (right skewed) with a long right tail. The histogram shows very high frequency (nearly 2500) at ozone levels 0 to 5 ppb (first column). The frequency at ozone concentration 40 ppb or over is relatively low. The first bar of the histogram needs investigations to prove that it comes from genuine measurements and is not due to an error or artefact.

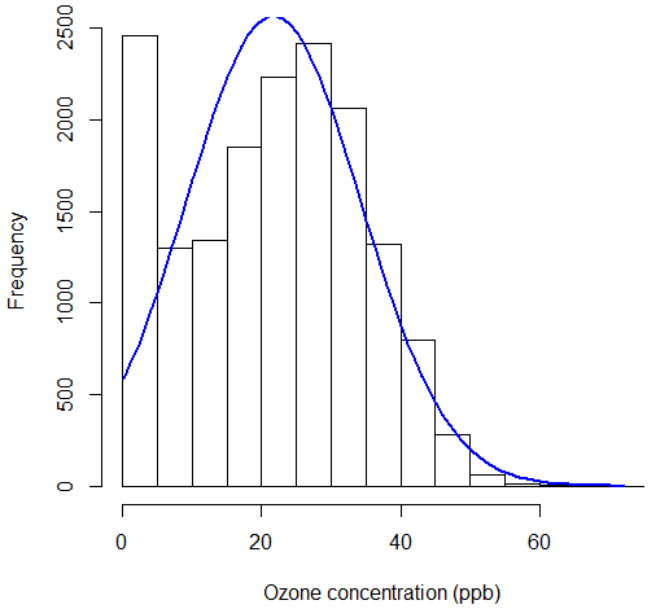


Figure 5.1. Histogram of hourly mean ozone concentration (ppb) from Kirkstall site November 2007 to October 2009 indicates that the data are not normally distributed (p-value < 0.010 from SW test).

5.3.2 Ozone Distribution when ozone < 5ppb

This section explains whether the first bar of the histogram (in Figure 5.1) is a result of genuine ozone measurements or not. Ozone (ppb) hourly average data from Kirkstall site have 16194 data points (excluding missing values). Out of the total 2462 data points have ozone concentrations less than 5ppb and 20 data points have ozone concentrations even less than 1 ppb. Firstly, the lower detection limit of the monitor (photometric ozone analyser, model 400E) is checked, which is < 0.6 ppb and hence it is low enough to give an accurate ozone measurements for any concentration higher than 0.6 ppb. Secondly to check whether these data points are distributed over all 12 months or condensed only in 1 or 2 months. Thirdly to find out if these 2462 data points lie where ozone concentrations are expected to be low (e.g. winter months, night hours) or not. If these data points mostly lie in winter months (day or night) or in summer night time then we can say that they are genuine, otherwise they will be considered due to an artefact and discarded.

Figure 5.2 (bottom right) shows that the 2462 data points when ozone < 5 ppb is distributed in all 12 months regardless of winter or summer season. However the majority of these hours come from winter months (November to February). Data from summer months (not shown here) indicate that ozone concentration less than 5 ppb mostly occurs during night

time hours. Figure 5.2 (bottom left) shows high frequency over night hours (including early morning and evening) and low during day time (especially 10:00 to 16:00). Furthermore, Figure 5.2 (top right) shows similar frequencies for most days except Sunday.

Ozone levels in the UK are normally higher during the summer and lower during the winter (e.g., AQEG, 2009), a trend demonstrated for the Kirkstall data set later in this chapter. Likewise ozone levels are generally observed to be lower at night and higher in the daytime. The reason for low levels of ozone during the winter and at night is most probably the lack (or reduced level) of solar radiation and lower temperatures which are responsible for reduce photochemical ozone production rates. In addition, dry deposition of ozone during the night can further reduce ozone levels. ozone levels are also linked to traffic activity by the NOx scavenging effect, which are generally low on Sunday, therefore Figure 5.2 (top right) shows low frequency of low ozone on Sunday as compared to other days.

The above explanations clearly indicate that the 2462 data points are genuine measurements. This will become clearer in later sections, where the distributions of ozone data from different monitoring stations at which different instruments are used are compared.

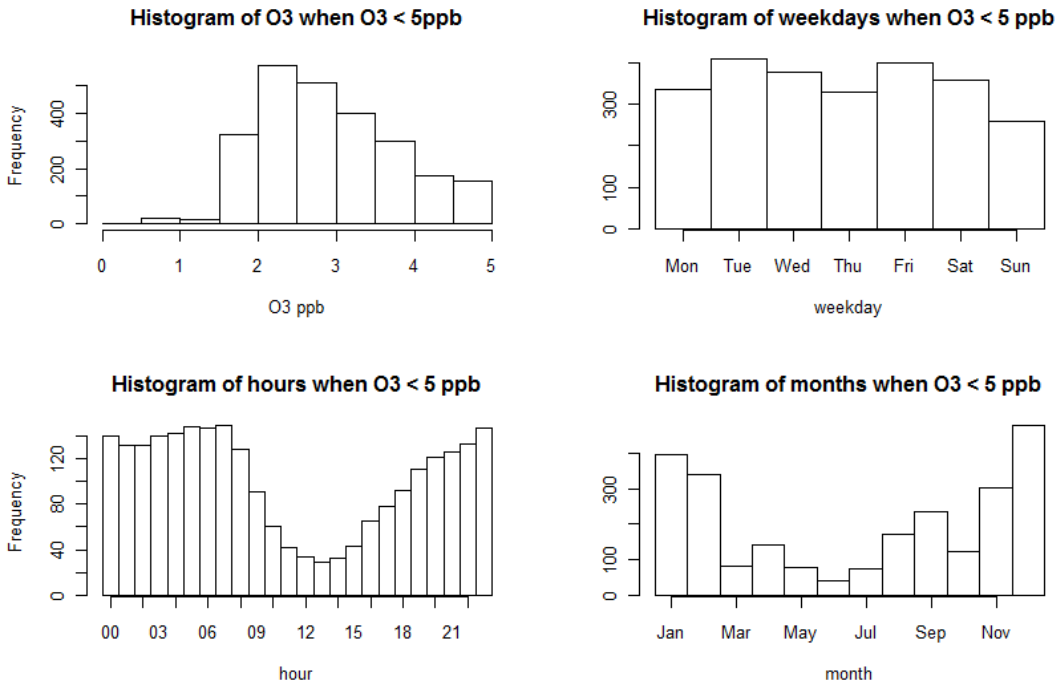


Figure 5.2. Histograms showing the frequency of months, hours and weekday when ozone < 5 ppb during the period November 2007 to October 2009 at Kirkstall monitoring site in Leeds.

5.3.3 Ozone distribution during different months

Histograms of ozone concentrations for each month January to December 2008 are shown in Figure 5.3, showing how ozone distributions vary in different months. Shapiro-Wilk test of normality gives p-values less than 0.01 for each month of the year 2008, which reveals that hourly ozone data do not follow a normal distribution in any month of the year at Kirkstall site.

There are 2 main categories of histograms in Figure 5.3. In the first group (January, February, September, October, November, and December) the highest frequency of ozone is found when the concentration of ozone is 0 to 5 ppb, whereas in the second group (March to Aug) the highest frequency can be observed when ozone concentration are approximately 30 ppb. The first group normally observes unfavourable atmospheric conditions (low temperature and cloudy condition) for ozone formation, which result in low ozone concentration; whereas the second group experiences favourable atmospheric conditions (hot sunny condition) causing ozone concentration to increase. Although the ozone distribution during the relative hotter months seems closer to normal distribution, statistically it still appears to be non-normal (p values < 0.05).

Box plots (Figure 5.4) depict ozone concentration in different months from November 2007 to October 2009 and show that ozone concentrations are high in March, April, May and June and low in January, February and December. May has the highest median, maximum, 25^{th} percentile and 75^{th} percentile ozone concentrations.

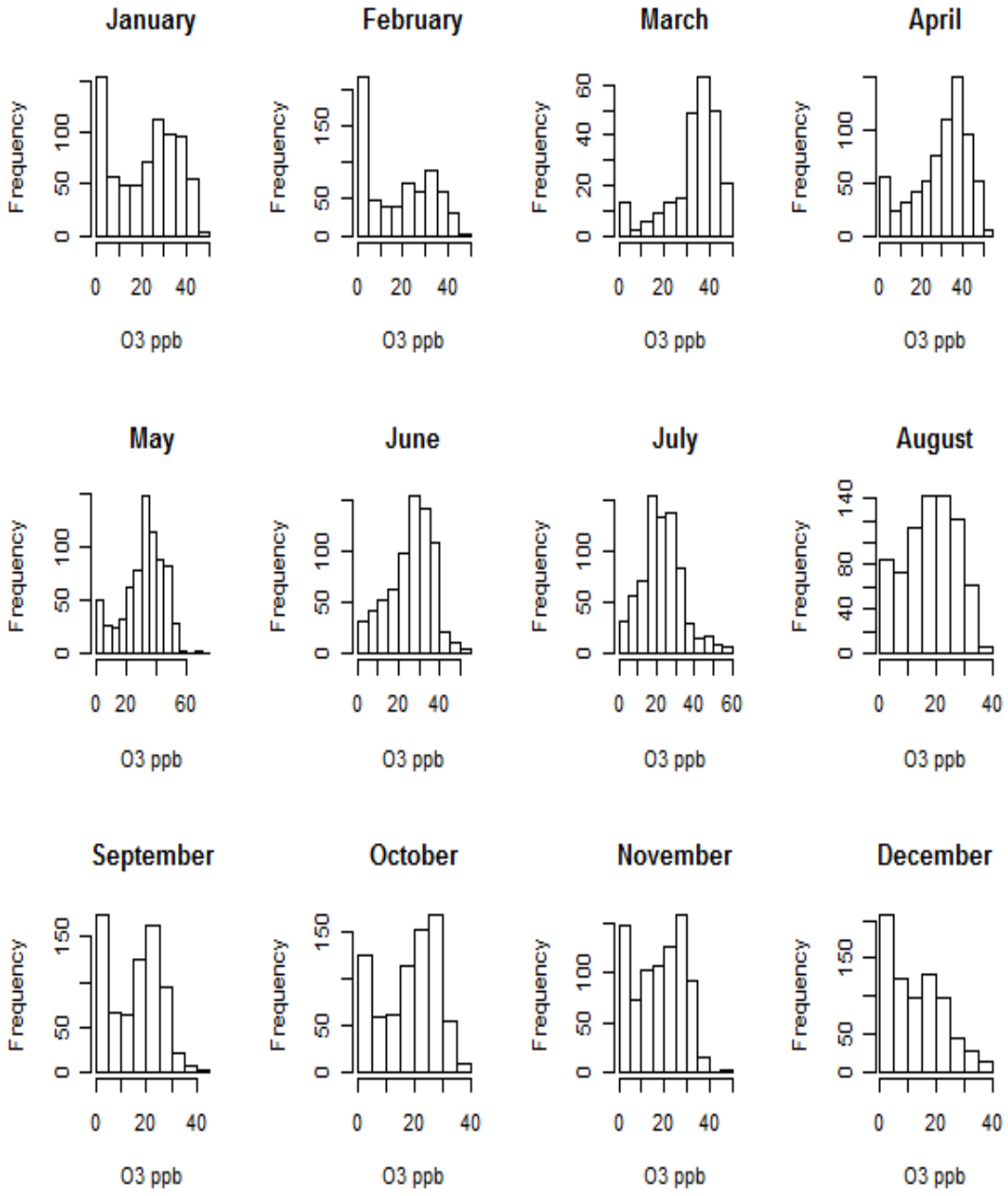


Figure 5.3. The distribution of hourly mean ozone concentration during different months during 2008 from Kirkstall roadside monitoring site.

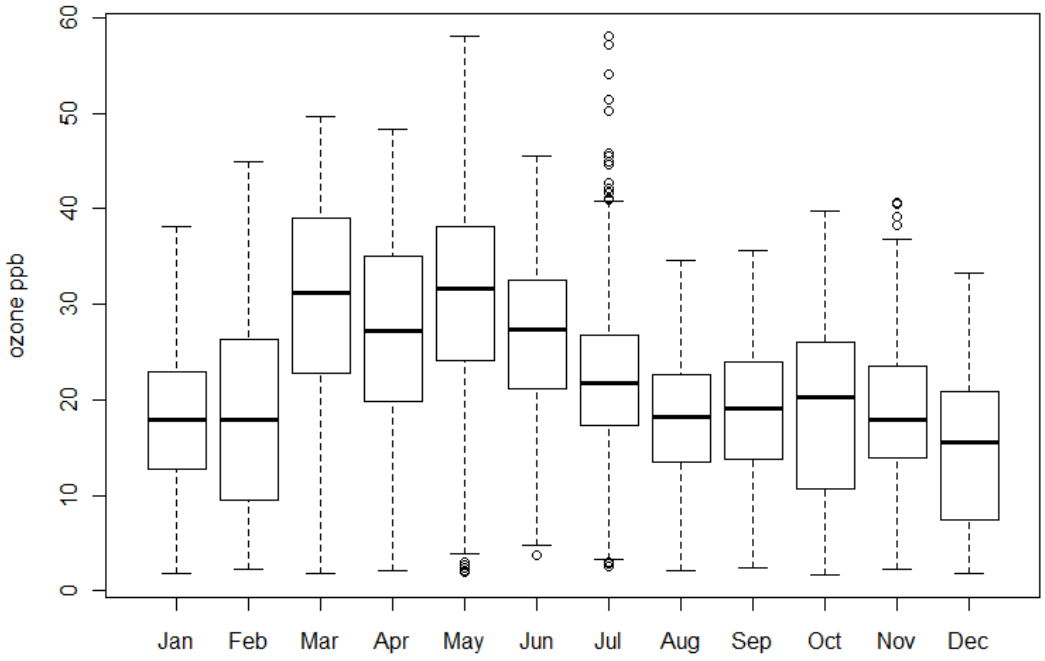


Figure 5.4. Box plot of ozone concentration (ppb) hourly mean data from Kirkstall site for each month November 2007 to October 2009.

5.3.4 Ozone distribution at different sites

Ozone distributions vary spatially from place to place in the UK depending on the type of the monitoring site, i.e. whether the monitoring site is situated in a rural, urban, suburban or at a roadside location (for detailed on different environment types of monitoring sites see chapter 4, section 4.3). Roadside and urban centre monitoring sites are generally characterised by high levels of fresh NOx that react with ozone and keep ozone levels low at these sites. In contrast, rural monitoring sites have generally low levels of NOx and high levels of ozone (AQEG, 2009).

Figure 5.5 shows ozone distributions at 6 different monitoring sites. Ozone distributions at roadside monitoring sites (Marylebone and Kirkstall) show high frequencies at low ozone concentrations i.e. the first column of the histogram is taller than the rest of the columns, which shows that low ozone concentrations occur more frequently than higher ozone concentrations. Particularly at the Marylebone site the frequency of higher ozone concentrations is very low; the reason probably is that Marylebone is situated in London near a very busy road where road traffic exhausts produce a huge amount of fresh NOx (UK-AIR, 2012). Although the Kirkstall site is a roadside monitoring site, the traffic level

on this road in Leeds is not as high as at Marylebone and hence the difference in ozone concentrations at the two sites is understandable. In contrast, the Harwell and Strath Vaich monitoring sites have totally different ozone distributions; the histograms almost look like a bell shaped symmetric diagram, however statistically it is non-normal, as p-values < 0.05. The higher frequencies of ozone at rural and remote sites occur at about 30 ppb. The reason is probably that these sites are far away from busy roads and receive very low fresh NOx inputs. The other two sites Leeds and Nottingham centre (urban centre sites) are intermediate between rural and roadside monitoring sites. These sites although are urban, receive reasonable high levels of fresh NOx which could reduce ozone concentrations but still the frequency of high ozone concentrations are higher than the roadside monitoring sites.

After the comparison of different monitoring sites and studying ozone distributions during different months, it can be concluded that ozone data in the UK do not follow a normal distribution and hence non-parametric statistics should be used for its analysis. The findings of this study are in agreement with previous studies (Duenas et al., 2002 and Baur et al., 2004). Duenas et al. (2002) investigated the distribution of monthly ozone concentration in Spain applying a Kolmogrov-Smirnov test and concluded that normality did not exist at 95% confidence interval. Baur et al. (2004) used graphical presentation (histograms) to see if the distribution resembled a bell shaped curve at various monitoring sites in Greece and concluded that the frequency distributions curves were non-normal and were right skewed.

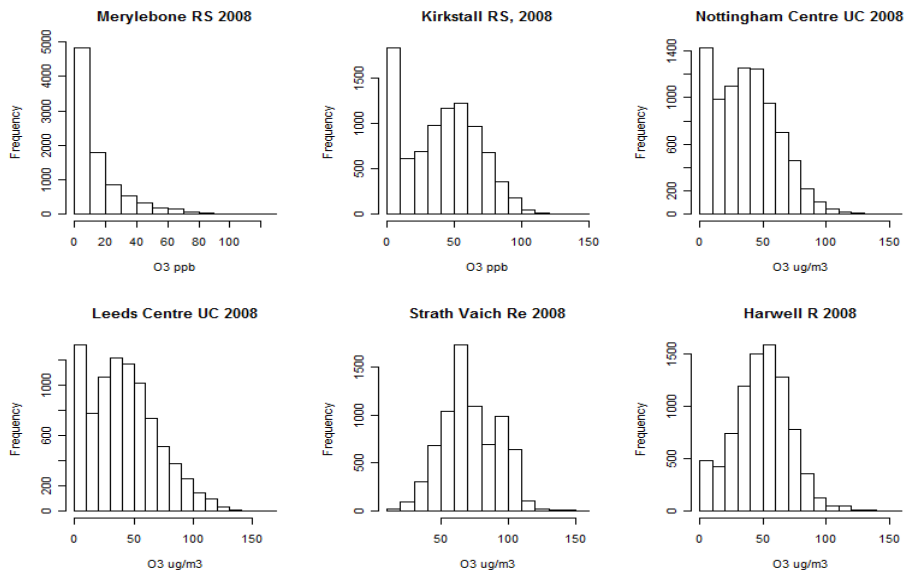


Figure 5.5. Ozone (ppb) hourly data distribution at different monitoring sites in the UK, where RS, UC, Re and R define the type of monitoring site and stand for roadside, urban centre, remote and rural monitoring site, respectively.

5.4 Distribution of air pollutants and meteorological variables

Histograms of some important air pollutants (NOx, CO, $PM_{2.5}$) and meteorological variables (relative humidity, solar radiation, temperature, wind speed and wind direction) are shown in Figure 5.6, which clearly show non-normal distribution of these variables. The frequency distributions for relative humidity and wind direction are negative or left skewed, whereas for all other variables the distributions are positive or right skewed. The results of statistical tests, Kolmogorov-Smirnov (KS) and Shapiro-Wilk (SW) test are shown in Table 5.1. The p-values for these tests for all tested variables are less than 0.01, indicating that the distributions are non-normal.

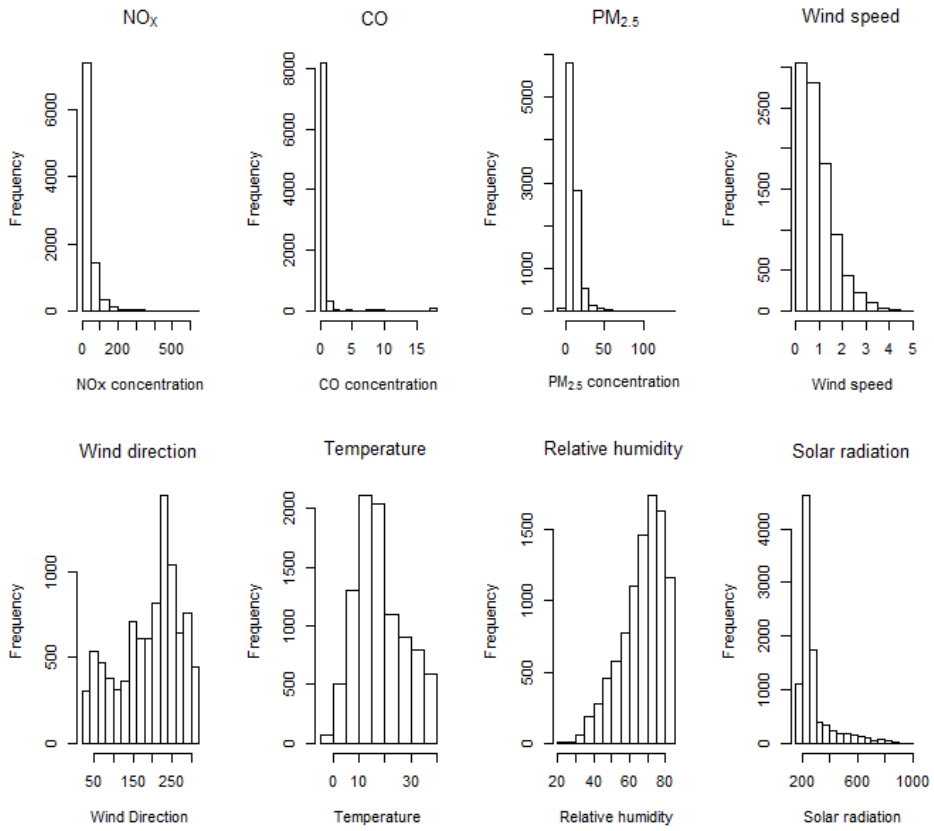


Figure 5.6. Histograms of hourly mean data of NOx (ppb), CO (ppm), $PM_{2.5}$ ($\mu g/m^3$), wind speed (m/s), wind direction (degrees from the north), temperature (^oC), relative humidity (%) and solar radiation ($watt/m^2$) at Kirkstall monitoring site during October 2007 to November 2009.

Table 5.1. The mean, St. Deviation and p-value for Kolmogorov-Smirnov (KS) and Shapiro-Wilk (SW) test using hourly mean data from Kirkstall monitoring site, November 2007 to October 2009.

Variable	Mean	St. Deviation	P-value (SW test)	P-value (KS test)
Wind speed	1.00	0.78	<0.010	0.000
Wind direction	197.26	79.06	<0.010	0.000
Temperature	18.11	9.48	<0.010	0.000
Relative humidity	66.82	11.45	<0.010	0.000
Solar radiation	288.87	114.71	<0.010	0.000
NOx	42.10	47.61	<0.010	0.000
CO	0.67	2.21	<0.010	0.000
$PM_{2.5}$	10.70	8.52	<0.010	0.000

5.5 Frequency distribution of traffic data

This section uses average hourly data of traffic flow (vehicles/hr) and vehicle speed (km/hr) from Kirkstall monitoring site during November 2007 to October 2009. The density plot of road traffic characteristics (speed and flow) for various vehicle categories are shown in Figure 5.7. The colour scheme is the same for each vehicle category whether it is showing speed or flow: Cars (red), buses (orange), vans (green), articulated lorries (pink), motorcycles (purple) and trailers (black). Both total flow and average speed are shown by blue colours. There are clear deviations from the hypothetical normal curve in both flow and speed data. The flow data in particular are heavily right skewed (Figure 5.7, botttom-right) for some vehicle categories. The speed data although seem closer to normal distribution curve but statistical tests (Kolmogorov-Smirnov and Shapir-Wilk test) show that these are not normally distributed (p-value < 0.01).

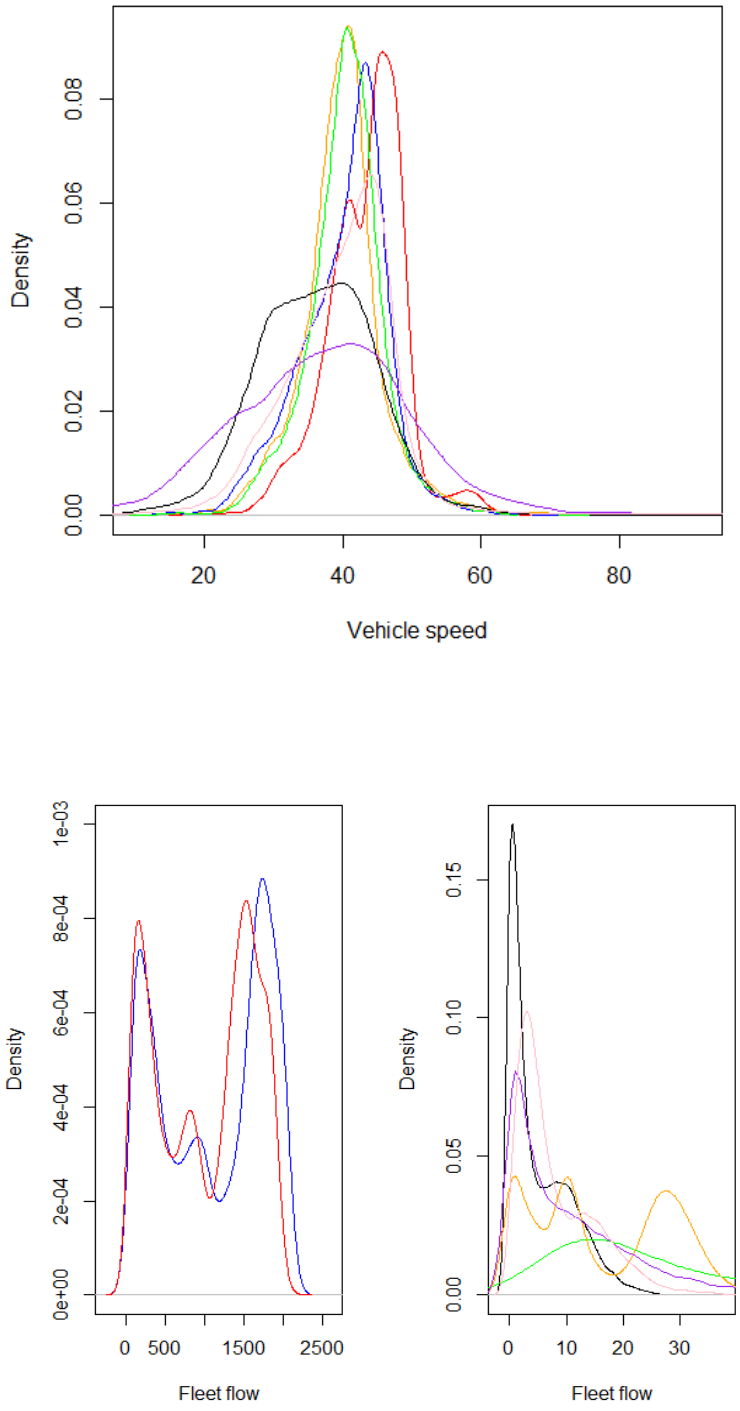


Figure 5.7. Density plots of vehicle speed (km/hr, top) and traffic flow (vehicles/hr, bottom). The colour scheme is the same for each vehicle category whether it is showing speed or flow: Cars (red), buses (orange), vans (green), articulated lorries (pink), motorcycles (purple) and trailers (black). Both total flow and average speed are shown by blue colours. The hurly average data are collected at Kirkstall roadside monitoring site, November 2007 to October 2009.

5.6 Temporal variations of ozone

Ground level ozone exhibits a typical diurnal cycle in the UK and has been described by several authors (e.g., Coyle et al., 2002; AQEG, 2009). Ozone concentrations in rural areas show a mid-afternoon maximum and night-time minimum (Coyle et al., 2002). The afternoon peak in ozone concentration is produced by photochemical ozone production and the descending of ozone from the free troposphere. The former is caused by NOx and VOCs reactions in the presence of solar radiation, whereas the latter is caused by turbulent mixing induced by both wind shear and thermal convection (AQEG, 2009). In urban areas the ozone diurnal cycle shows different characteristics and is controlled by the level of NO, which reacts with ozone and produces NO_2. Therefore, the minimum ozone concentrations are normally observed during the morning and evening traffic peak hours, while the maximum concentrations are observed at night (due to low traffic) and in the mid-afternoon (due to photochemical ozone formation) (Coyle et al., 2002).

In this section ozone data from four monitoring sites (Leeds centre, Harwell, Marylebone, and Strath Vaich) have been analysed to estimate ozone daily, weekly and seasonal cycles. The four monitoring sites have different topographical and meteorological characteristics. The aim here is to obtain a broad picture of ozone variations at roadsides, urban centres, rural and remote areas. Ozone concentrations seem to have been affected by both meteorological conditions and sources of fresh NO (as explained below). Figure 5.8 shows the time variation plots of ozone for 2008 at Leeds centre, Harwell, Marylebone, and Strath Vaich. Generally ozone concentrations are found to be higher at rural and remote sites (Harwell and Strath Vaich) and lower at urban and roadside monitoring sites (Leeds and Marylebone). The lowest ozone concentrations are exhibited by Marylebone monitoring site which is located approximately one meter from the edge of Marylebone road (A50). This road has six lanes and has a flow of 80,000 vehicles per day (UK-AIR, 2012). Most probably titration of ozone by fresh NO emitted by road transport keeps ozone concentrations low at this site.

Ozone concentrations at all sites follow a typical twenty four hours cycle i.e. lower during night-time and early morning hours and higher during day times (Figure 5.8, bottom-left). The highest concentrations are achieved during the afternoon from 12:00 to 14:00 hours, most probably caused by photochemical ozone formation as a result of higher amount of ultraviolet (UV) radiation during these hours. Harwell and Strath Vaich sites have slightly different daily cycles than Marylebone and Leeds. At Marylebone and Leeds in addition to night times low, there is a further reduction in ozone concentrations in the morning (about 06:00), which cannot be observed at the other two sites. This effect is most probably caused

by the early morning traffic which emits NO that quickly reacts with ozone and further reduces its concentrations.

On a weekly basis generally weekend and Monday exhibit higher, whereas Wednesday and Thursday show relatively lower ozone concentrations (Figure 5.8, bottom-right panel). For instance, mean ozone concentrations ($\mu g/m^3$) at Marylebone site were 20 and 12 and at Harwell site were 47 and 55 on Sunday (weekend) and Thursday (midweek), respectively. High level of ozone during weekend is a well known phenomenon and is referred to as 'ozone weekend effect (OWE)' in the literature, e.g. Jenkin (2008) and the references therein. Low levels of traffic during weekend is considered to be the main cause of OWE, as low levels of fresh NO reduce local ozone removal. Compared to other weekdays, higher level of ozone on Monday is probably due to the carry over effect of ozone from weekend. At Strath Vaich monitoring site the difference in ozone concentrations during different days is negligible, probably because the site is remote and is not affected much by road traffic emissions.

Ozone concentrations show a clear seasonal effect. Ozone concentrations are higher during March, April and May and lower during autumn and winter months at all four sites (Figure 5.8, bottom-middle). For instance, monthly mean ozone concentrations ($\mu g/m^3$) at Marylebone site were 35 and 7 and at Leeds site were 79 and 17 for May and December, respectively. Cloudy and cold weather conditions during winter months result in very low UV radiation in the UK, which reduce photochemical ozone formation. Ozone titration by NO and low tropospheric – stratospheric exchange of ozone caused by the stagnant atmospheric conditions further reduces ground level ozone concentrations, which explain low level of ozone in the winter months. In spring when UV radiation increases, it increases photochemical ozone formation and hence ozone level increases in the atmosphere.

The point which needs further attention is that UV radiation are generally higher in June, July and August, however Figure 5.8 shows that after May ozone levels, despite the fact that UV radiation are there, decrease gradually and in August ozone level decreases to a level which is normally observed in winter months. The reason for this probably is that for photochemical ozone formation, in addition to UV radiation, the presence of ozone precursors (e.g., VOCs) is required whose oxidation by hydroxyl radicals in the presence of NOx leads to ozone formation. To elaborate on this further, hydrocarbon data for two monitoring sites Marylebone (a roadside monitoring site in London) and Harwell (a rural monitoring site in Oxfordshire) were obtained. Hydrocarbons data are not available from many AURN monitoring sites, therefore these two sites were selected to represent urban and rural environment. Some changes in hydrocarbon concentrations at different monitoring

sites will be expected; however, here the aim is to show general trends (seasonal or monthly variations) in hydrocarbon concentrations, rather than the absolute levels.

About thirty hydrocarbons are monitored at both Harwell and Marylebone monitoring sites. The hydrocarbons monitored are: 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-butadiene, 1-butene, 1-pentene, 2-methylpentane, 3-methylpentane, benzene, ethane, ethyl-benzene, ethene, ethyne, isoprene, propane, propene, toluene, cis-2-butene, cis-2-pentene, iso-butane, iso-octane, iso-pentane, mp-xylene, n-butane, n-heptane, n-hexane, n-octane, n-pentane, o-xylene, trans-2-butene, trans-2-pentene. Here the focus is not on individual hydrocarbon, the aim is rather to investigate the general trend in various hydrocarbon concentrations, therefore instead of analysing all 30 hydrocarbons average concentration of these hydrocarbons was calculated and considered for trend analysis. Monthly average hydrocarbon concentrations at Harwell and Marylebone monitoring sites for year 2008 are shown in Figure 5.9. Hydrocarbon levels at Marylebone are much higher than at Harwell, therefore normalised levels are applied to make the comparison easy. 'Openair package' simply divides the variable(s) by their mean values to calculate the normalised levels.

The one year data considered show that hydrocarbon concentrations are generally higher in colder months (January, February, October, November, and December) and lower in warmer month (e.g., June, July, August). It seems like hydrocarbons accumulate in the atmosphere during winter months and reach the highest level in February. In March when the level of UV radiation increases, this consumes hydrocarbon concentrations through photochemical ozone formation and hydrocarbons levels gradually decrease. In August in spite of relatively high level of UV radiation, photochemical ozone formation is restricted by the limited availability of hydrocarbons. This probably explains why ozone levels are low in August.

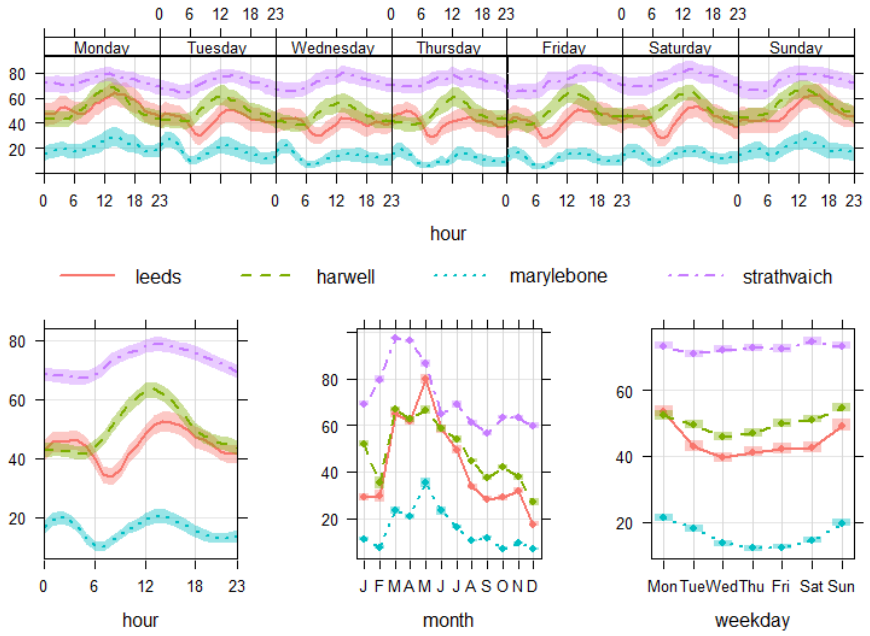


Figure 5.8. Time variations of ozone at four different monitoring sites (Leeds, Marylebone, Harwell and Strath Vaich) in the UK, 2008.

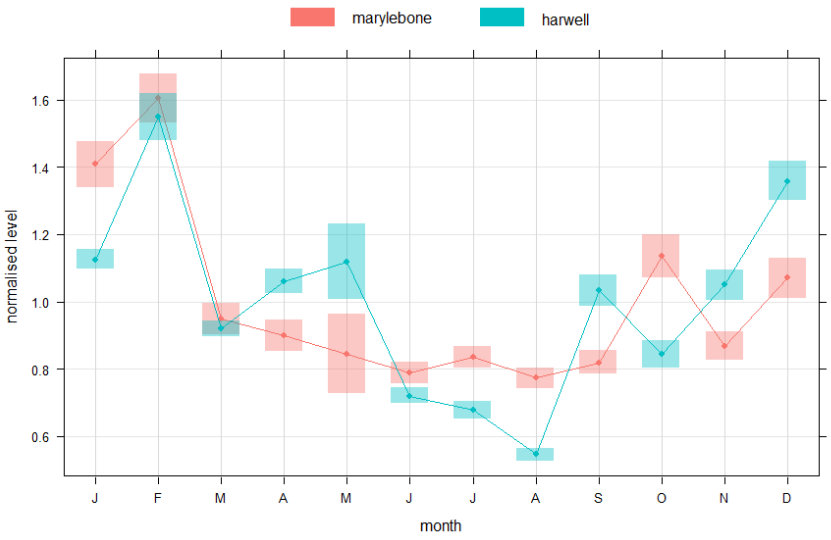


Figure 5.9. Normalised monthly mean concentrations of hydrocarbons in 2008 at Harwell and Marylebone monitoring sites.

5.7 Cluster analysis of ozone diurnal cycle

In this section data from Kirkstall road are analysed to further elaborate ozone diurnal profile during different seasons and months of the year and compared them with those profile obtained using cluster analysis.

5.7.1 Ozone diurnal cycle and seasonal variations

It is observed that the diurnal cycle of ozone concentrations varies during different seasons of the year due to changes in meteorological characteristics (e.g., temperature or the level of solar radiation). Therefore diurnal cycle of ozone varies during spring, summer, autumn and winter, as shown in Figure 5.10. It can be observed in Figure 5.10 that average ozone concentration is highest during the spring season (March, April, May), followed by summer (June, July, August). Ozone photochemical formation and hence its concentration in the atmosphere is directly related to the levels of ozone precursors (e.g., NOx and VOCs), solar radiation and temperature as explained in Munir et al. (2012). As mentioned above ozone diurnal cycle in urban areas is mainly controlled by the level of NO, which depletes ozone and the level of solar radiation which gives rise to ozone formation. The combination of these two results in ozone concentration being highest in the afternoon and lowest during the morning traffic peak hours (Figure 5.10). Furthermore, the day-night variation in ozone concentration is considerably higher in spring than in winter. In winter due to low levels of solar radiation hardly any photochemical ozone formation takes place and most probably due to this reason ozone concentration in the afternoon is almost the same as during night time (Figure 5.10). In Figure 5.11 the diurnal cycle of ozone for each month is shown. The highest concentrations (top 3 lines) are shown for March, April and May and lowest for December (the bottom line, marked by blue squares having a summation signs inside). December shows ozone concentrations during day time significantly lower than night time, which is most probably due to the lack of ozone formation during day time and ozone being further depleted by the freshly produced NO. On the other hand during night time due to low level of road traffic flow, ozone depletion by NO is minimal and hence ozone concentrations are higher than day time. In Figure 5.11, June (black colour) and July (yellow colour) exhibit considerably greater day-night variation most probably due to the high level of solar radiation in these months. It is worth re-emphasising that average ozone concentrations in these months are still lower than that in March – May, which is probably more to do with the level of ozone precursors than solar radiation. The rest of the months make a group (in the middle) showing characteristics of a typical urban diurnal cycle.

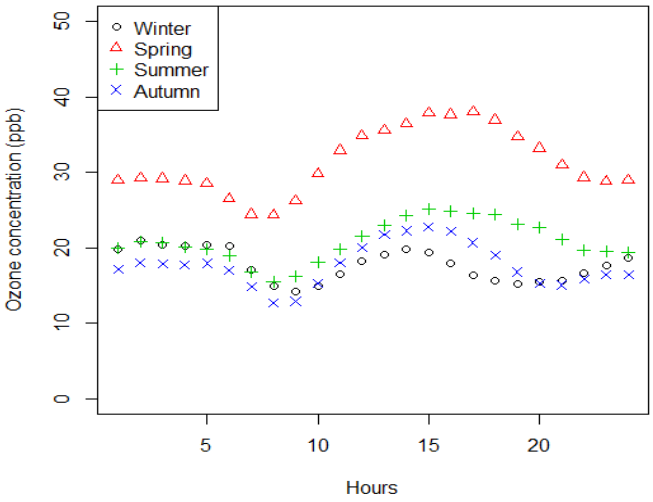


Figure 5.10. Ozone diurnal (24 hour) cycle for each season (winter – December, January, February; spring – March, April, May; Summer – June, July, August; autumn – September, October, November). The data used are for 2008 at Kirkstall monitoring site.

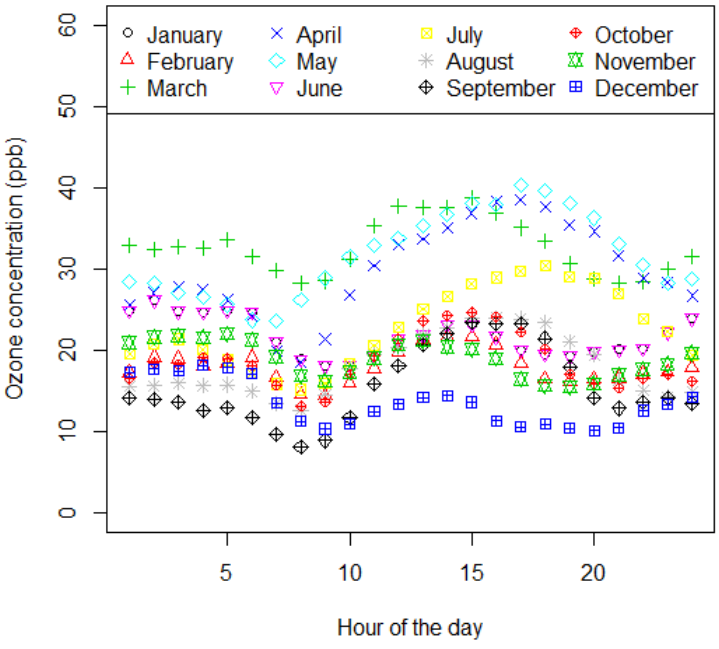


Figure 5.11. Ozone 24 hour cycle for each month. The data used are for 2008 at Kirkstall road monitoring site in Leeds.

5.7.2 Ozone diurnal cycle using cluster analysis

In this section k-means clustering analysis is applied to divide the diurnal cycle of ozone concentrations (ppb) for 2008 into various clusters and analyse their similarities or dissimilarities with the seasonal or monthly cycle of ozone. Firstly ozone data for 2008 are divided into 365 diurnal cycles and then using k-means these are grouped (clustered) into 4 (shown in Figure 5.12) and 12 (shown in Figure 5.13) clusters. The reason for selecting 4 and 12 clusters was to make comparison easy with seasonal and monthly diurnal cycles.

As shown in Figure 5.12, the diurnal cycles for the 4 clusters vary considerably in some aspects from the seasonal diurnal cycle (as shown in Figure 5.10). The diurnal cycles of the 4 clusters (Figure 5.12) are evenly distant from each other, whereas those in Figure 5.10 show two distinct groups. Spring is totally away from the rest of the 3 seasons, which seems closely related. Cluster 1 and cluster 4 look almost the same as winter and spring, but the rest of the two clusters (cluster 2 and 3) exhibit different characteristics from summer and autumn. Cluster 2 show ozone concentration during day time lower than the early morning hours (0 to 5 am) and looks more like a typical winter urban diurnal cycle (as that of December in Figure 5.11), whereas cluster 3 has very high afternoon peak ozone concentration compared to early morning hours and looks more like a typical summer urban diurnal cycle (as that of July in Figure 5.11).

Figure 5.13 shows the diurnal cycles of 12 clusters and it can be seen that these diurnal cycles vary from those of monthly cycles. Within the 12 clusters (Figure 5.13), 4 distinct groups can be identified. For instance, the yellow colour shows a very low ozone concentration during the morning peak traffic hours and relatively higher concentration during the early morning and afternoon, however the afternoon concentration is considerably lower than the blue line (square with '+' sign inside). The blue line (square with '+' sign inside) show much more variation in morning and afternoon hours than any other cluster; the concentrations (ppb) in the morning is less than 10, whereas it reaches over 40 in the afternoon. There are some other distinct clusters, such as pink (inverted triangles) and red (triangles), which are significantly different from each other (Figure 5.13).

This analysis shows that apart from seasonal and monthly variation in the diurnal cycles of ozone there are some mixed days that show different characteristics within the same season. Therefore probably cluster analysis is better suited for analysing ozone diurnal cycle than just seasonal variation.

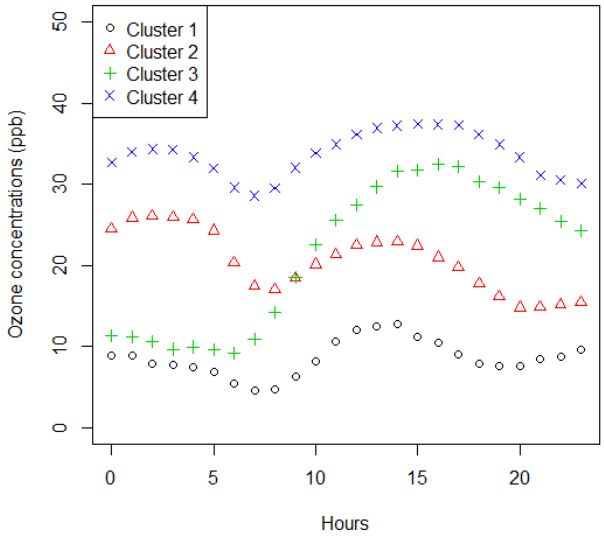


Figure 5.12. Ozone diurnal cycles using 4 clusters. The data used are for 2008 at Kirkstall road monitoring site in Leeds.

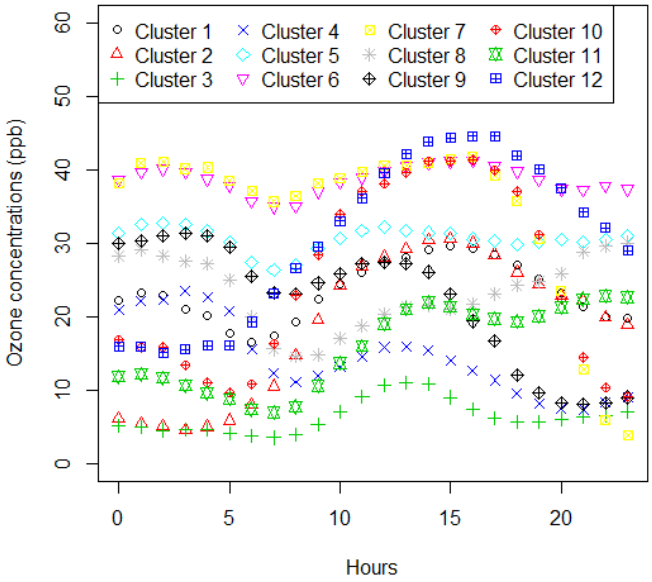


Figure 5.13. Ozone diurnal cycles using 12 clusters. The data used are for 2008 at Kirkstall road monitoring site in Leeds.

5.8 Summary

This chapter investigates the frequency distribution of ozone in details and demonstrates that ozone distribution is not normal. Ozone distribution is not a fixed phenomenon and

rather it varies both spatially and temporally, for example ozone distribution varies during different months of the years and at various monitoring sites in the UK. The distribution shows very high frequency at ozone concentration less than 5 ppb, its validity was further investigated and seems to be a result of low ozone concentration during unfavourable atmospheric conditions, particularly at urban and roadside locations. Furthermore, the distributions of other air pollutants (e.g., CO, $PM_{2.5}$), meteorological variables (temperature, solar radiation, relative humidity, wind direction and wind speed) and traffic characteristics (traffic flow and speed) were investigated with the help of graphical presentations and statistical tests (Shapiro-Wilk and Kolmogorov-Smirnov). Both graphical presentation and statistical tests showed non-normal distribution of these variables. It is concluded that classic parametric statistics might not be suitable for investigating ozone, air pollutants, meteorological variables and traffic characteristics data, therefore non-parametric or distribution free statistics should be used for their analysis.

Temporal variations of ozone concentrations are analysed using data from various monitoring sites (Harwell, Strath Vaich, Leeds Centres, and Marylebone). Ozone diurnal profile at Kirkstall monitoring sites in Leeds has been further elaborated with the help of cluster analysis (k means), using 4 and 12 clusters. These clusters have been compared with seasonal and monthly ozone cycles. It is shown that some groups have distinct characteristics and vary considerably from the seasonal and monthly diurnal cycles of ozone, which highlights the fact that even in a single season or month the diurnal cycle of ozone may vary; or in other words, diurnal cycle of ozone may resemble in different seasons or months of the year depending on meteorological conditions and the presence of ozone precursors (e.g., NOx and VOCS) and sinks (e.g., NO).

In this chapter it is found that ozone distributions are not only dependent on meteorological variables but also on the concentrations of other air pollutants. Next chapter (ozone and other air pollutants) further investigates the association of ozone with traffic related air pollutants (e.g., NOx, CO, PM_{10}) and describes how ozone concentration is affected by the levels of these pollutants.

CHAPTER 6: THE RELATIONSHIP OF OZONE WITH TRAFFIC RELATED AIR POLLUTANTS

6.1 Introduction

Ozone is not emitted directly by combustion processes; rather it is formed photochemically from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NOx) in the atmosphere and is therefore considered as a secondary air pollutant. Ozone concentrations are not only dependent on meteorological variables (e.g., solar radiation, temperature) but also on other air pollutants (e.g., NOx, VOCs). These pollutants can contribute positively (e.g., NOx and VOCs act as ozone precursors) or negatively (e.g., nitric oxide (NO) acts as a sink) to ozone concentration. Ozone chemistry and its involvement in various chemical reactions with other air pollutants are described in chapter 2. The full pathway of ozone formation and its reaction with other chemicals is summarised in Figure 2.2 (chapter 2).

The concerning factor about ozone is that although the concentrations of other pollutants including NOx, sulphur dioxides (SO_2) and VOCs have been declining for the last 20 years or so, ozone does not seem to suggest a declining trend. Background ozone concentrations have rather increased since about 1990 in the UK (Derwent et al., 2007). The increasing trends in ozone concentrations are most apparent at urban sites, but which to a less extent also influences the observations at the majority of rural locations (AQEG, 2009). The increasing trend in ozone concentrations can be attributed to long distance migration of ozone from across the North Atlantic (AQEG, 2009) or to reduction in local-scale removal of ozone by direct reaction with fresh NO (Jenkin et al., 2008), a trend that is now widely attributed to on-going improvement in vehicle NOx emission regulations and associated progressive policy practices. The levels of some pollutants have declined, however ozone concentration has particularly increased in urban areas, indicating a change in pollutants proportions and their chemistry, therefore it is important to analyse the association of ozone with these pollutants.

Several authors (e.g., Jenkin, 2004, Tidblad et al., 2002; Paschalidou et al., 2008) have investigated the association of ozone with other air pollutants, especially NO and NO_2. Some of the studies (e.g., Jenkin, 2004) are laboratory based, which are useful in understanding the basic chemistry of the air pollutants and ozone; however these studies fail to represent the actual atmospheric environment. Secondly, the majority of previous studies (e.g., Soja and Soja, 1999; Pont and Fanton, 2000; Paschalidou et al., 2008) have employed

linear regression approaches, which are based on several assumptions (e.g., normality and linearity), however, air quality data are not normally distributed and the association between different air pollutants is not linear. Therefore, several authors (e.g., Baur et al., 2004; Gardner and Dorling, 2000) have suggested that these types of models are not suitable for ozone modelling. This project addresses the above issues by: (a) employing a quantile regression model that can successfully address the normality and linearity problem; (b) analysing the effect of covariates on various quantiles, especially on extreme values of ozone concentrations; (c) using observed (monitored) hourly data of both ozone and the other air pollutants (e.g., NOx, CO, $PM_{2.5}$ and HCs).

6.2 Methodology

This chapter is based on mean hourly and 24 hour data of ozone (ppb), HC (ppb), NOx (ppb), NO (ppb), NO_2 (ppb), $PM_{2.5}$ ($\mu g/m^3$) and CO (ppm). The data were obtained from two monitoring sites: Kirkstall and Marylebone air quality monitoring sites (see chapter 4, section 4.3 for details of monitoring sites). These sites are categorised as urban traffic (roadside) monitoring sites and therefore the air pollutants considered in this chapter, except ozone, are considered to be mainly emitted by road traffic. Some data are used from Harwell, a rural monitoring site, for comparing purpose. The statistics used (e.g., Spearman correlation analysis, OLS regressions and QRM) are described in chapter 4.

6.3 Results and discussions

6.3.1 Ozone and NOx

NOx is invariably negative correlated with ozone (Jenkin, 2004). The scatter plots between 24 hour mean NOx (ppb) and ozone (ppb) data from the Kirkstall site Leeds is shown in Figure 6.1, and exhibits a clear negative correlation between NOx and ozone and as NOx concentration increases ozone concentration decreases and vice versa. Most probably the negative correlation is due to NO reaction with ozone which destroys ozone molecules and produces NO_2: ($NO + O_3 \rightarrow NO_2 + O_2$).

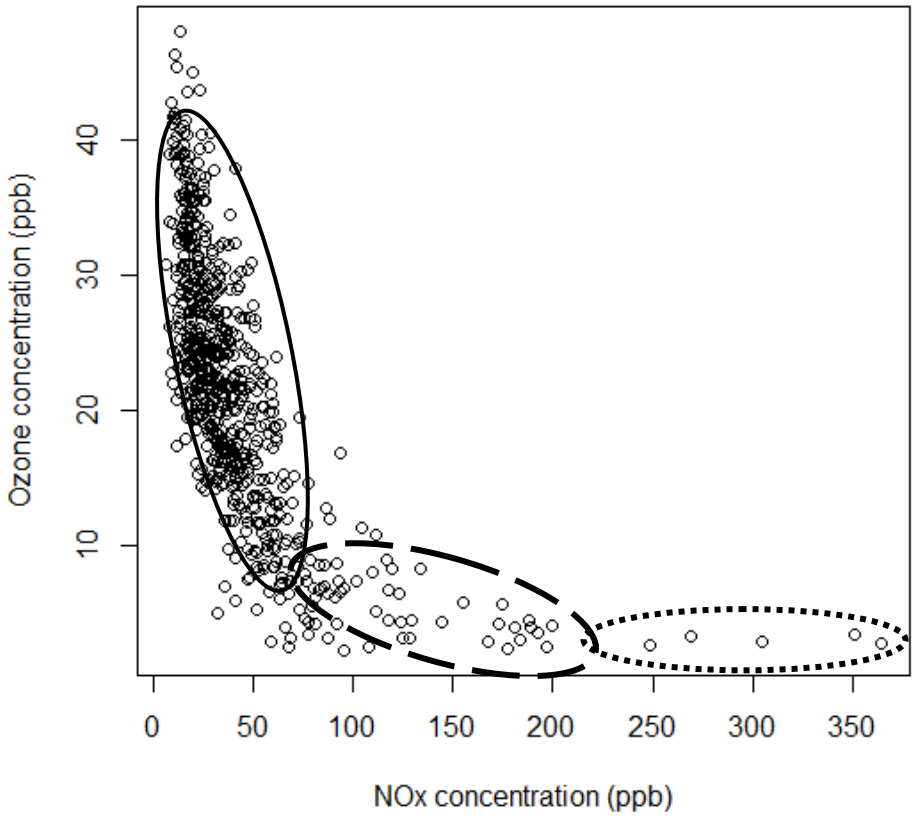


Figure 6.1. Scatter plots of ozone (ppb) and NOx (ppb) 24 h data from Kirkstall site (01/11/2007 to 31/10/ 2009). The overall Spearman correlation coefficient (R) was '-0.78'; however when NOx ppb < 80 (solid-line circle or oval shape) R was '-0.72'; when 80 < NOx ppb < 220, R was '-0.53' (dashed-line circle); when NOx ppb > 220, R was '+0.30' (dotted-line circle).

In Figure 6.1 along the x-axis 3 main segments can be observed, which have been reproduced in Figure 6.2 showing separate diagram for each segment. In the first segment (solid-line circle or oval shape, NOx < 80 ppb) the negative correlation between ozone and NOx is very strong (Spearman correlation coefficient R value is '-0.72') and ozone concentration decreases linearly with increases in NOx concentrations. In this area the data points are dense, as on this monitoring site most data points lie in this segment (Figure 6.2, top left). In the next segment (dashed-line circle, 80 < NOx ppb < 220) the negative correlation is still there but not linear. In this section data points are relatively sparse and the negative correlation is weaker (R value '-0.53') (Figure 6.2, bottom left). In the last segment (dotted-line circle, NOx ppb > 220) the negative correlation between ozone and NOx disappears and the curve becomes almost totally horizontal. The negative correlation turns

into positive correlation (R value '+0.30') (Figure 6.2, top right). The positive correlation between ozone and NOx at atypically high NOx concentrations is most probably due to NO_2 oxidation which gives rise to ozone formation. As this correlation is based on 24 h mean ozone and NOx data, the correlation will be further investigated in section 3.2.1 using 1 minute and hourly data from the Kirkstall monitoring site.

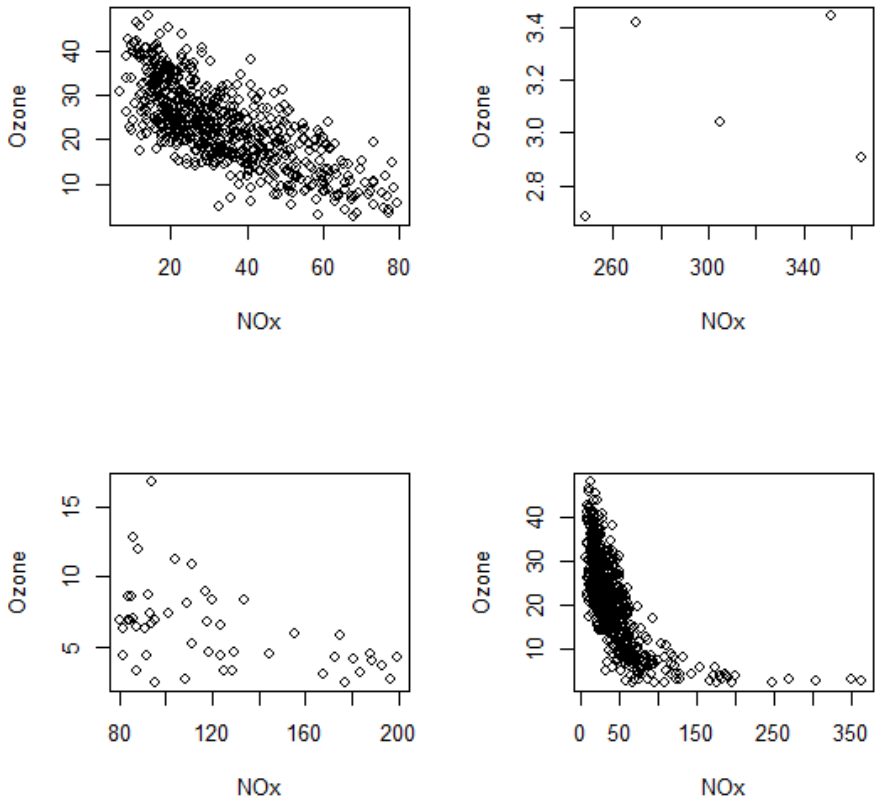


Figure 6.2. Scatter plot between ozone (ppb) and NOx (ppb) 24 h average concentrations (01/11/2007 to 31/10/2009) from Kirkstall site Leeds, when NOx < 80 ppb (top left), NOx > 220 ppb (top right), 80 < NOx < 220 ppb (bottom left), and NOx 0 to 365 ppb (bottom right). The Spearman correlation coefficients were -0.72, 0.3, -0.53 and -0.78 for top left, top right, bottom left and bottom right, respectively.

6.3.3.1 Correlation between NOx and ozone for 1 minute and hourly data

Figure 6.3 shows the scatter plot along with their R values for 1 minute data for the 6 days. Over these days ozone and NOx have positive correlation coefficients, except on 13/12/2007 where the correlation is negative despite the fact that NOx concentration is as high as 304 ppb. During the 6 days (12 – 15 December 2007; and 11 – 12 February 2008)

when daily average NOx concentrations were 365, 304, 250, 200, 271 and 354 ppb, ozone concentrations were 2.9, 3.1, 2.7, 2.6, 3.4, and 3.5 ppb, respectively. This shows that NOx concentrations were high enough to consume almost all the available ozone. Due to low levels of ozone, NOx and ozone chemistry would have been extremely slow, which would have a negligible effect on NOx concentrations. Therefore the negative association between NOx and ozone will disappear. Furthermore, NOx concentration (without having any effect on ozone, which is nearly zero) would increase further due to emission from road traffic and not dispersing due to cold stagnant atmospheric conditions and therefore the generally expected negative correlation would change to positive.

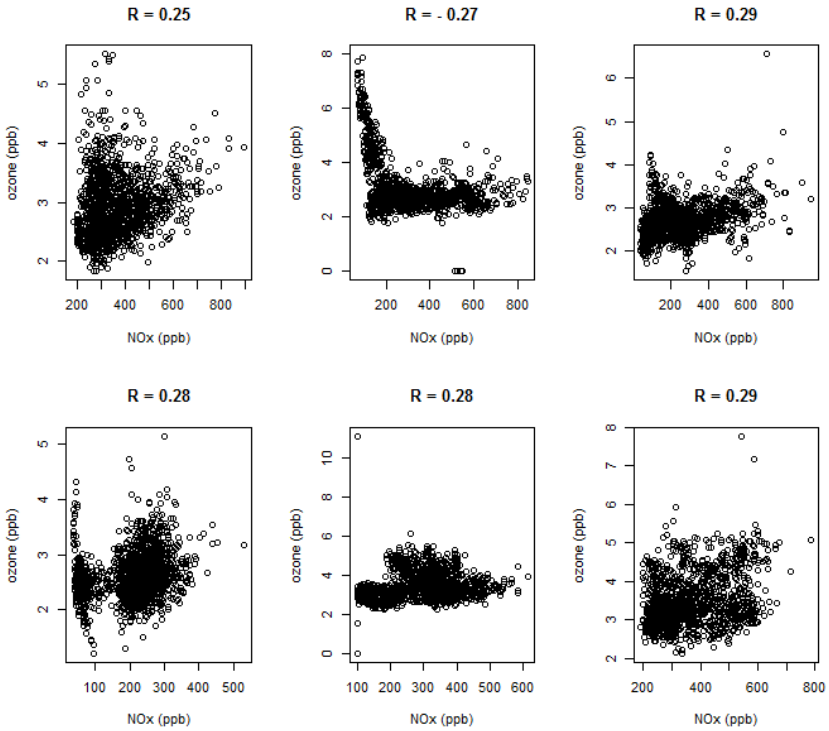


Figure 6.3. Scatter plot of 1minute ozone concentration (ppb) vs. NOx concentration (ppb) for the six days (top-left 12/12/2007, top-middle 13/12/2007, top-right 14/12/2007, bottom-left 15/12/2007, bottom-middle 11/02/2008, bottom-right 12/02/2008), when NOx concentrations were nearly as high as 200 ppb or over and NOx was mostly positively correlated with ozone. R is the value of Spearman correlation coefficient between ozone and NOx concentration.

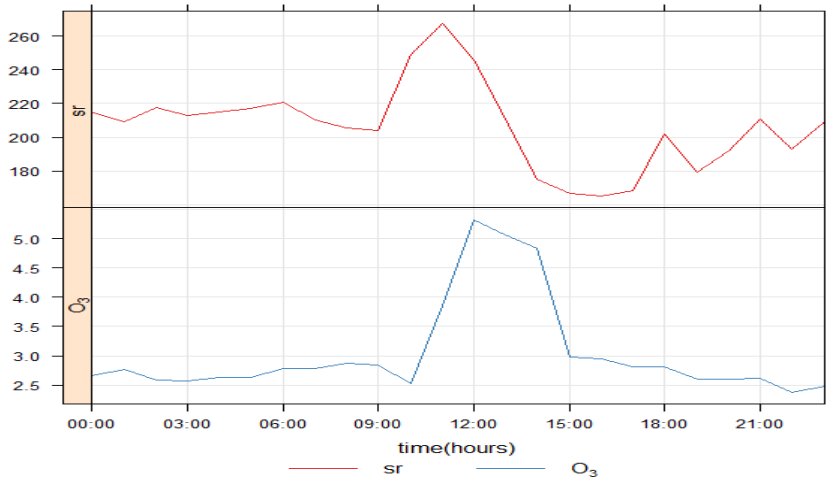


Figure 6.4. Time plot of solar radiation (sr, watt/m^2) and ozone hourly mean concentration (ppb) on 13/12/2007 at Kirkstall site in Leeds.

6.3.1.2 Temporal variations in NOx and ozone

In this section the correlation between ozone and NOx has been analysed using time variation plots (Figure 6.5). These diagrams depict the association of ozone and NOx showing how their concentrations change on average during different hours of the days, days of the week or months of the year.

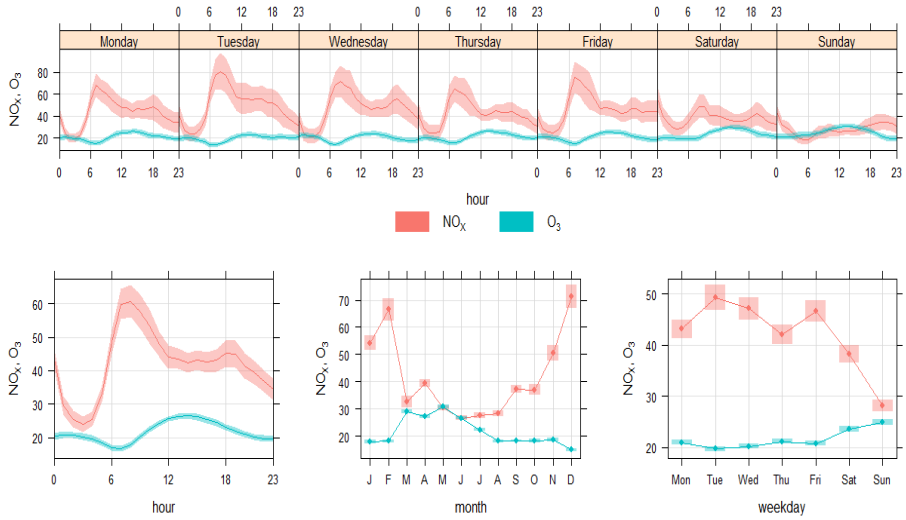
Figure 6.4 reveals that ozone concentrations are normally higher during spring and summer (March, April, May and June) and lower during winter and autumn months (January, February, November and December); whereas NOx concentrations are higher in winter months (January, February, November and December) and lower during summer months (May, June, July and August). In winter the high NOx concentrations are probably due to slow chemical reactions and slower pollutant dilution as a result of stagnant atmospheric conditions; the opposite happens in summer (better chemistry and dilution) (e.g., see Harrison et al., 2006, Jenkin et al., 2002). On the other hand ozone is a secondary pollutant and is only produced in the atmosphere by photochemical reactions of NOx and VOCs driven by solar radiation (Ultraviolet radiation - UV). Therefore in winter because of low UV radiation and temperature ozone production is minimal (if any at all); and whatever ozone is present is consumed by freshly produced NO (remember UV radiation is required for ozone production but not for its destruction). But in summer high UV radiation and temperature are responsible for the relatively higher levels of ozone.

On weekly basis traffic volume seems to be the dominant factor for controlling NOx and ozone concentrations (Jenkin et al., 2002). On Kirkstall road the volume of road traffic is

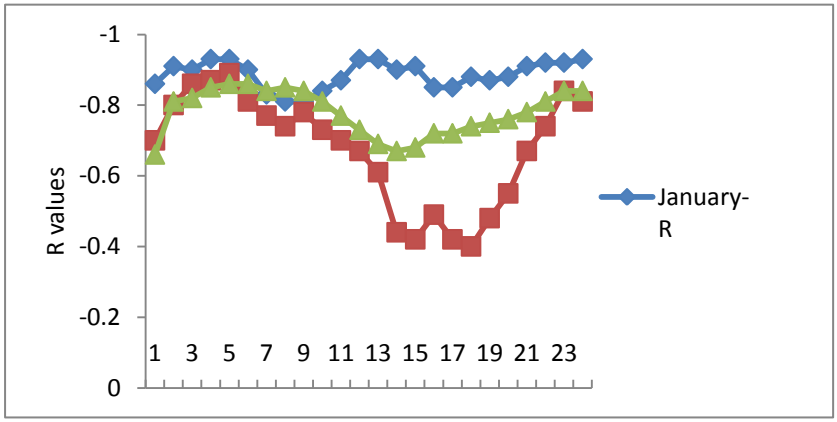
higher during weekdays and lower during the weekend; as many companies and institutes do not operate at the weekend. Figure 6.5 clearly shows the lowest NOx and highest ozone levels on Sunday, followed by Saturday. As on Sunday low traffic volumes produce less NOx which result in less ozone destruction and hence ozone levels are higher. Higher ozone level at the weekend compared to weekdays is called the ozone weekend effect (OWE) and is studied by several authors (e.g. Bronnimann et al., 1996; Pont and Fontan, 2000; Gao et al., 2005).

The diurnal changes in NOx and ozone levels seem to be linked with both traffic volume and meteorology (Jenkin et al, 2002). Although NOx and ozone are strongly correlated and both of them are strongly linked with the volume of road traffic, the diurnal average trend of ozone seems to be dominated by solar radiation. The highest ozone concentrations were observed at 13.00 to 15.00 hour when UV radiation is often at a maximum; and lowest ozone levels at 06.00 to 07.00 am in the morning due to the overnight dry deposition and NOx scavenging effect. NOx levels are strongly linked with traffic volume and reached a maximum level at 08.00 to 09.00 am when roads traffic activity is at peak. After that NOx levels come down but rise again at about 17.00 to 18.00 hours in the evening, probably due to late afternoon traffic peak hours.

It was observed that correlation between NOx and ozone is stronger during winter (R for January was '-0.80') and weaker during summer (R for May was '-0.40'). Figure 6.5 (b) shows the correlation coefficient for different hours of the day during May, January and an 'average of all months'. It can be seen that in May R values decrease during the daytimes (especially from 13:00 to 19:00 hours) when solar radiation and temperature are highest and the atmosphere is turbulent. In January not much difference can be observed in R values during different hours of the day, which is most probably because in January the amount of UV radiation is low and the atmosphere is cold and stagnant 24 hours of 'the day' in the UK. The average for the whole period (including both winter and summer) shows a combine effect of both winter and summer, i.e. the day effect which was dominant in May still can be observed but not as clearly. This reveals that NOx is probably the dominant controlling factor for ozone levels when there is not much photochemical ozone production and as solar radiation and temperature increase they weaken the correlation between NOx and ozone. Therefore for ozone prediction in addition to NOx it is essential to quantify the role of meteorology (described in chapter 8) and traffic flow (described in chapter 7)in controlling ozone levels.



(a)



(b)

Figure 6.5. (a) Time variation plots of ozone (ppb) and NOx concentrations (ppb) hourly mean data from Kirkstall site November 2007 to October 2009; (b) Spearman correlation coefficient (R) between NOx and ozone for each hour during January, May, and 'average of 12 months'.

6.3.2 Ozone vs. NO & NO_2

NO and NO_2 are collectively known as NOx because they are rapidly inter-converted during the day. NO and NO_2 are both generated by combustion processes in the atmosphere. Many years emission measurements show that the major species emitted is NO with a small proportion of NO_2, approximately 5% (AQEG, 2007). However, recent observations show

that the proportion of NO_2 has risen due to penetration of exhaust after treatment technologies for diesel vehicles. A small proportion of NO_2 is directly emitted, known as primary NO_2 particularly by diesel vehicles; however most of NO_2 is formed in the atmosphere by oxidation of NO, for example, by reaction with ozone. Therefore most of the NO_2 is considered as a secondary (formed in the atmosphere) and NO as a primary pollutant (directly emitted). NO_2 is split up by UV light to give NO and an oxygen atom (O), which combines with molecular oxygen (O_2) to make ozone. In rural air, away from sources of NO, most of the nitrogen oxides in the atmosphere are in the form of NO_2, whereas near a source (e.g. a busy road) NO is the dominant species (see Clapp and Jenkin, 2001 and Jenkin, 2004 for details chemistry of NOx). Figure 6.6 shows the ratios between NO and NO_2 24 hour mean concentrations at Kirkstall (roadside, dashed blue line) and Harwell (rural, red solid line) monitoring site for 2008 and confirms that the level of NO is more than NO_2 at the roadside monitoring site; the opposite is true for the rural site. The reason is clear that at roadside traffic vehicles produce NOx which is mostly consists of NO and by the time these gases reach rural areas most of the NO is oxidised into NO_2.

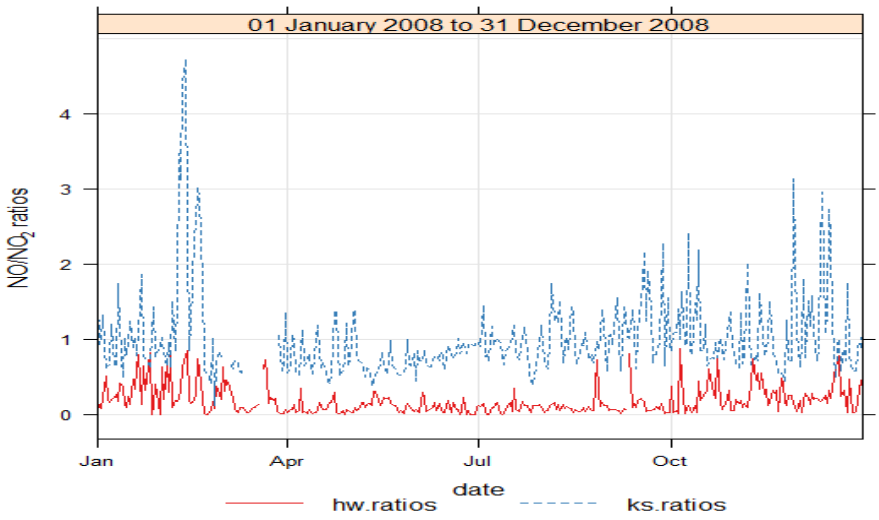


Figure 6.6. The ratios of 24 hour mean NO/NO_2 concentrations (ppb) at Kirkstall roadside (ks) and Harwell rural (hw) monitoring site for the year 2008.

6.3.2.1 Temporal variation of ozone in relation to NO and NO_2

Ozone is negatively correlated with NO and NO_2 at both Kirkstall and Harwell sites having Spearman correlation coefficient of -0.65 and -0.66 at Kirkstall and -0.29 and -0.42 at Harwell site, respectively for hourly mean data. The Spearman correlation coefficients of NO and NO_2 with ozone hourly mean for each month are shown in Figure 6.7. It is shown in Figure 6.7 that the negative correlation between NO_2 with ozone is slightly stronger than the

correlation of NO with ozone at both sites. In addition, the correlation is stronger in winter months than in summer months. The weakest correlation was observed for the month of June and strongest for January, February, November, and December. In summer months there is plenty of sun shine that helps in photochemical ozone formation and the atmosphere is turbulent and well mixed which affect the impact of locally emitted NOx. In contrast in winter, the atmosphere is stagnant and temperature and the amount of solar radiation are low. In these conditions the locally emitted NOx plays the dominant role in controlling ozone concentrations (Harrison et al., 2002). The correlation of NO_2 is stronger than that of NO with ozone at both sites, but at Harwell site the difference is more significant, as it can be observed in Figure 6.7, which indicates that at roadside locations freshly emitted NO play more active role than at rural sites.

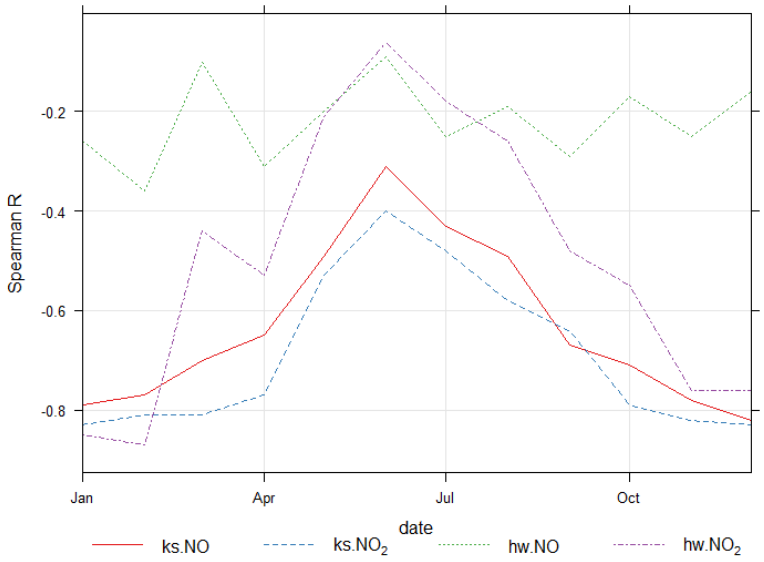


Figure 6.7. The Spearman correlation coefficients (R) of hourly mean NO (ppb) and NO_2 (ppb) with ozone (ppb) during different months at Kirkstall (KS) and Harwell (HW) monitoring sites for 2008.

Figure 6.8 shows the time variation of ozone, NO and NO_2 at Kirkstall (top) and Harwell (bottom) monitoring site, depicting how the average concentrations of these pollutants change during different hours of the day, days of the week and months of year. At Kirkstall site NO and NO_2 have almost the same diurnal cycle, i.e. their concentrations start increasing in the morning with increases in traffic activities and reach the highest level at about 08:00 to 09:00 am and then decrease. In the afternoon probably due to afternoon peak hours traffic activities, the concentrations of NO and NO_2 slightly increase again at about 06:00 pm. The highest NO and NO_2 concentrations were observed on Tuesday and Lowest on Sunday. At this site the diurnal cycle of ozone concentrations seems to be linked with

both the concentration of NOx and meteorological variables. Ozone concentrations are low in the morning at about 08:00 am and then increase as solar radiation increases and reach the highest level in the afternoon about 03:00 pm. In contrast to NOx, ozone concentrations are highest on Sunday and lowest on Tuesday and Wednesday. The highest ozone concentrations on Sunday are probably due to low traffic activities during weekend. NO and NO_2 concentrations were observed to be highest in January, February, November and December and lowest in June in case of NO and August in case of NO_2. On the other hand ozone concentrations were highest in March, April and May and lowest in the winter months.

At Kirkstall site, probably due to changes in traffic activities, the concentrations of NO are generally higher than that of NO_2 and ozone, but sometimes the opposite happens (e.g. over nights and weekend). In contrast, at Harwell which is a rural site, the concentrations of ozone are highest followed by NO_2 concentration at all the times. At Harwell the concentrations of NO and NO_2 do not change much during different hours of the day, days of the week and months of the year, most probably these are not affected by traffic activities and represents the regional background concentrations. Furthermore, ozone concentrations are considerably higher at rural sites (Figure 6.8, bottom) (Jenkin, 2008). The main difference between rural and urban or roadside monitoring sites is the presence of many other air pollutants (e.g. hydrocarbons, CO, NOx, particles) emitted mainly by road traffic. These air pollutants interact with each other and ozone and hence affect the atmospheric chemistry significantly. Figure 6.8 (top and bottom) gives an indications of the nature of these two different environment. Kirkstall site seems more dynamic and there are abrupt changes even on hourly basis, whereas Harwell site is more stable and steady, but still the diurnal and seasonal effect can be clearly observed on ozone concentrations.

Figure 6.8. Time variation plots of NO (ppb), NO_2 (ppb) and ozone concentrations (ppb) at Kirkstall (top) and Harwell (bottom) monitoring sites, depicting hourly mean data for 2008.

6.3.2.2 The association of Ozone with NO and NO_2 described by QRM

In this section the effect of hourly mean NO and NO_2 on ozone concentrations is further analysed with the help of QRM, using data from Kirkstall monitoring site from November 2007 to October 2009. The outputs of the model have been shown in Figure 6.9. The outputs of ordinary least square regression have also been visualised. In ordinary least square regression, only one regression coefficient represents the entire distribution of the explanatory variable (indicated by the red line along with its 95% confident interval); whereas in quantile regression, a quantile regression coefficient is a function of quantiles (τ) and hence several coefficients have been given. In Figure 6.9 regression coefficients have been given for 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 0.99 quantiles (represented by dashed dark line with their 95% confidence intervals). In Figure 6.9 the top part shows the

intercepts and bottom part shows the regression coefficients of explanatory variable (NO and NO_2).The intercept value gradually increases with increases in ozone concentrations i.e. with quantile range from 0.1 to 0.99, the intercept increases from 21 to 50.

Quantile regression exhibits considerably stronger effect of NO_2 than NO on ozone concentrations. The quantile regression coefficients range from '-0.005 to -0.07' for NO and '-0.14 to -0.75' for NO_2. It can be clearly seen in Figure 6.9 that the strength of coefficients for NO and NO_2 follow opposite trends, i.e. for NO the highest correlation coefficients (absolute value) are observed at quantiles 0.1 and 0.99, whereas for NO_2 the weakest coefficients (absolute value) were observed for these two quantiles. In other words, NO has maximum effect whereas NO_2 has minimal effect on ozone concentrations at extreme values (minimum and maximum). At these quantiles the effect is stronger than the mean effect in case of NO, whereas the opposite happens in the case of NO_2. Low ozone concentration occurs in a cloudy cold condition (low solar radiation and temperature), such as winter season, whereas high ozone concentration occurs in favourable conditions (high temperature and solar radiation), such as summer or spring season. In the formal case (unfavourable condition) the photo-dissociation of NO_2 and ozone is low, however NO and ozone chemistry is still active as it s not dependent on solar radiation, which probably leads to stronger and weaker association in case of NO and NO_2, respectively. In contrast, in summer or spring (favourable conditions), photochemistry of NO_2 and ozone is very active and high rate of NO_2 dissociation result in ozone formation, offsetting the negative correlation and therefore overall association is weaker association. The strength of coefficients varies at different quantiles of ozone concentration, however the nature does not change, i.e. the relationship of ozone with NO and NO_2 remains negative (for detailed analysis as to how ozone chemistry is affected by NO and NO_2 levels see Clapp and Jenkin, 2001; and Jenkin, 2004).

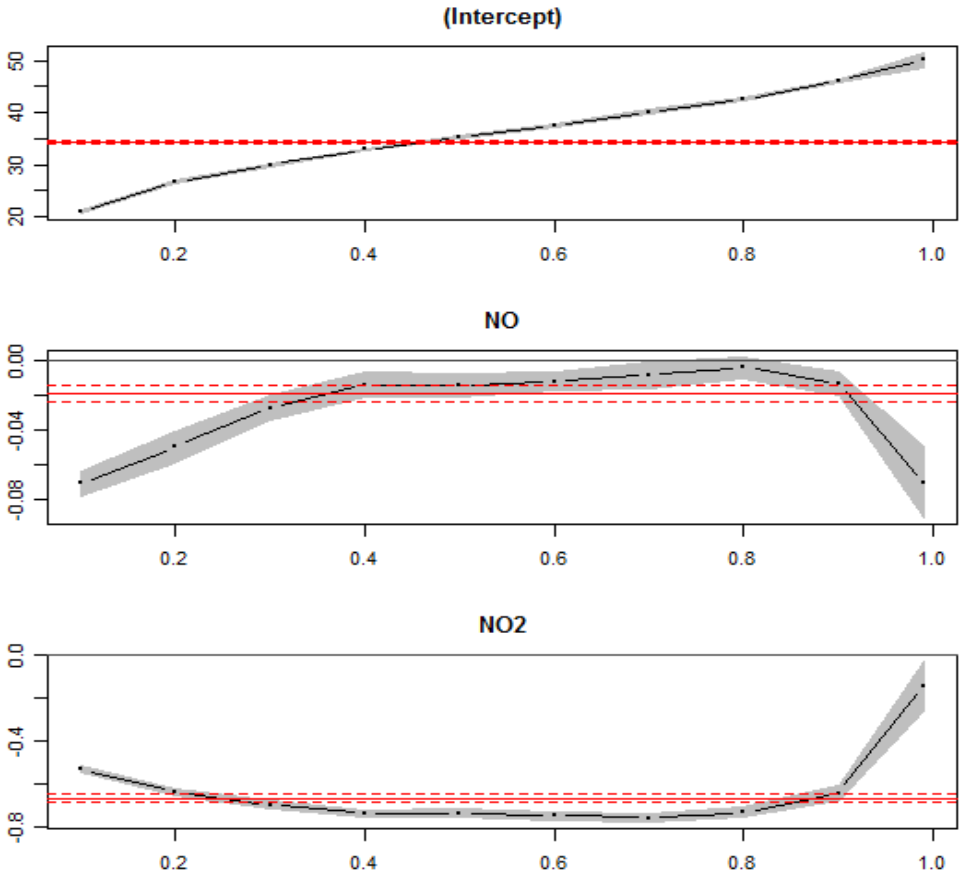


Figure 6.9. The output of quantile regression model, showing the effect of NO and NO_2 on hourly mean ozone concentrations. Quantile regression coefficients (dashed dark line) and ordinary least square regression coefficients (solid red line) are presented with 95% confidence interval.

6.3.3 The relationship of ozone with CO and $PM_{2.5}$

6.3.3.1 Checking for outliers

The CO and $PM_{2.5}$ data from Kirkstall site for a two year periods (November 2007 to October 2009) have been presented in Figure 6.10 as a box plot, where the left panel shows $PM_{2.5}$ and the right panel shows CO concentration. It can be clearly seen that in both $PM_{2.5}$ and CO outliers exist.

In air quality data, the extreme values are more important from human health perspective (Makra et al., 210). The general statistics rules for detecting data outliers may not be applicable to air quality data. The statistical rules (e.g. classic statistics: mean±2*SD (standard deviation); robust statistics: median±2*MAD (median absolute deviation)) normally consider the 2%, 2.5% or up to 5% extreme values as outliers (see Reimann et al., 2008 for details). In the case of atmospheric (air quality) data there might not be any outliers

at all, the high concentrations may be only extreme values and vital for our purpose (health impact or air quality modelling). Therefore this study adopts a cautious approach and investigates atypically high data points whether any explanation could be found for the high levels of pollutants, before deciding on the data points as outliers.

The statistical analysis of $PM_{2.5}$ data reveals that bottom 4% data (677 data points) are negative (i.e. below zero), which cannot be true as negative concentrations of particle is illogical. Furthermore, the 99th percentile of $PM_{2.5}$ is 42 µg/m^3. There are 8 data points above 100 ppb and the maximum is 247 ppb. Further investigation reveals that 7 of the 8 data points occur on 3rd, 4th, and 5th November 2007 and the 8th point which is 247 ppb occurs on 13^{the} May 2009. The $PM_{2.5}$ concentrations on these dates have been presented in Figure 6.11. The 7 data points were recorded on 22:00, 23:00, and 00:00hour of 3rd and 4th and 01:00 hour of 5th November 2007. During the nights of 3rd and 4th November 2007 the $PM_{2.5}$ level generally seems high and there seems to be a similar trend on both nights. Investigation of the other meteorological variables indicates that wind speed was very low on those nights (Figure 6.12) which might have resulted in accumulation of particles in the atmosphere, which were emitted locally. Hence these points seem genuine and will not be removed. However, the $PM_{2.5}$ concentration of 247 µg/m^3 (Figure 6.11, top) clearly seems an outlier, as the concentration on that day is generally quite low (the second highest concentration is 19 ppb). No explanation was found for such a high concentration on the day and therefore it would be discarded, along with the negative values, from the dataset.

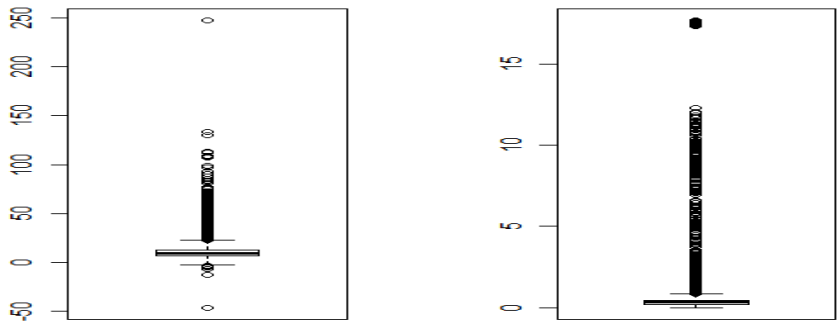


Figure 6.10. Box plot of $PM_{2.5}$ (µg/m^3) (left) and CO (ppm) (right) of hourly mean data from Kirkstall site Oct 2007 to Nov 2009.

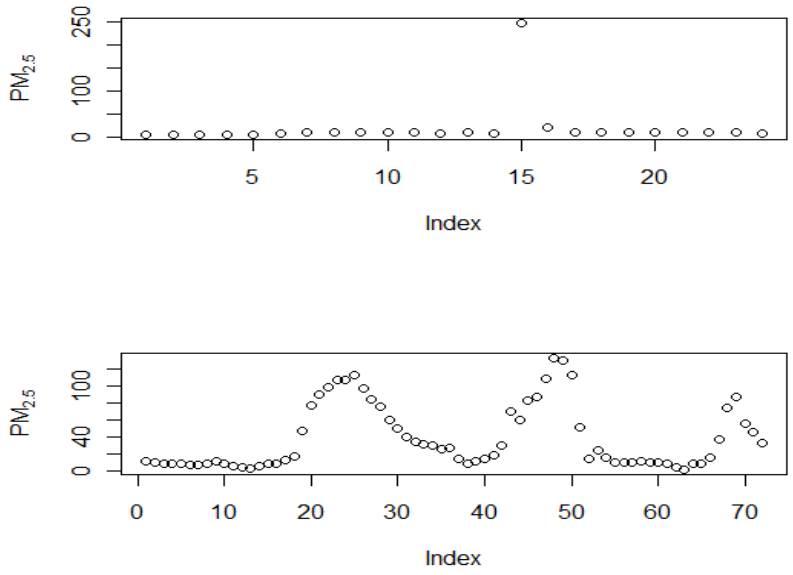


Figure 6.11. $PM_{2.5}$ concentrations (µg/m^3) on 13th May 2009 (top) and 3rd, 4th, and 5th November 2007 (bottom).

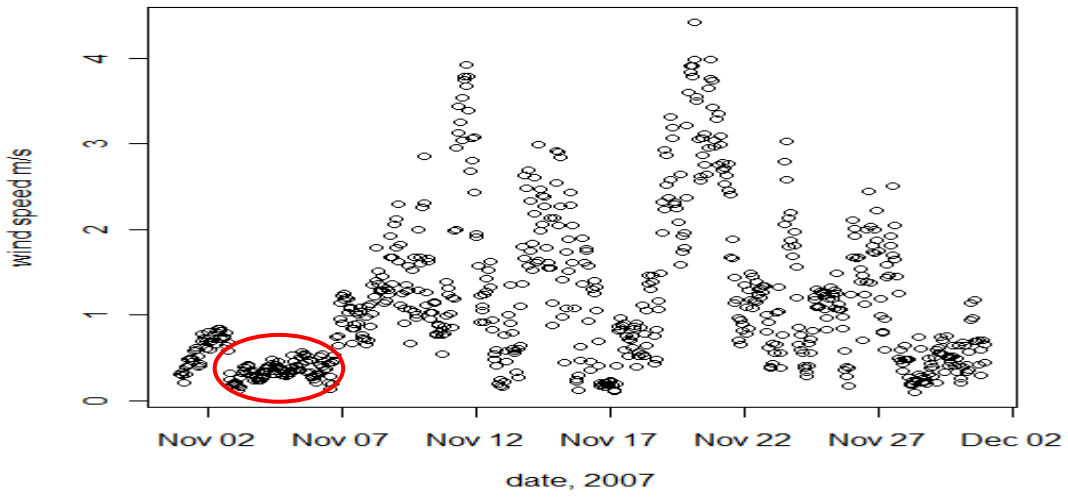


Figure 6.12. Showing wind speed (m/s) in November 2007, highlighting 3rd, 4th, and 5th November as being the cause of high $PM_{2.5}$ concentrations (µg/m^3) on these dates at Kirkstall monitoring site.

The CO data (ppm) demonstrate a minimum concentration of 0, median 0.32, 97th quantile 2.3, 98th quantile 8.47 and maximum 17.69 ppm. Majority (97 %) of CO concentrations are less than 2.3ppm. The top 2% CO that are nearly 10 ppm or higher will be further investigated to decide whether to consider these as outliers or genuine extreme values.

These high CO concentrations occur on 7 to 16 July and 12 to 15 August 2008 (Figure 6.13). The CO concentrations during 7 to 16 July do not exhibit any trend or any consistent trend with time. Further analysis of the meteorological and traffic data does not give any clue why this could have happened. These data points may be the result of an error or artefact. On the other hand the CO concentrations on 12 to 15 August seem to be linked with the rest of observations and are more likely to be real. Further investigation of the related traffic data shows that the flow of heavy vans and minibuses was higher on these days. Figure 6.14 shows the flow of heavy van on 10 to 18 August 2008 and it can be observed that the flow on 13 to 15 august is clearly higher than the other days. Therefore, these data points will not be discarded and will be considered as genuine higher observations.

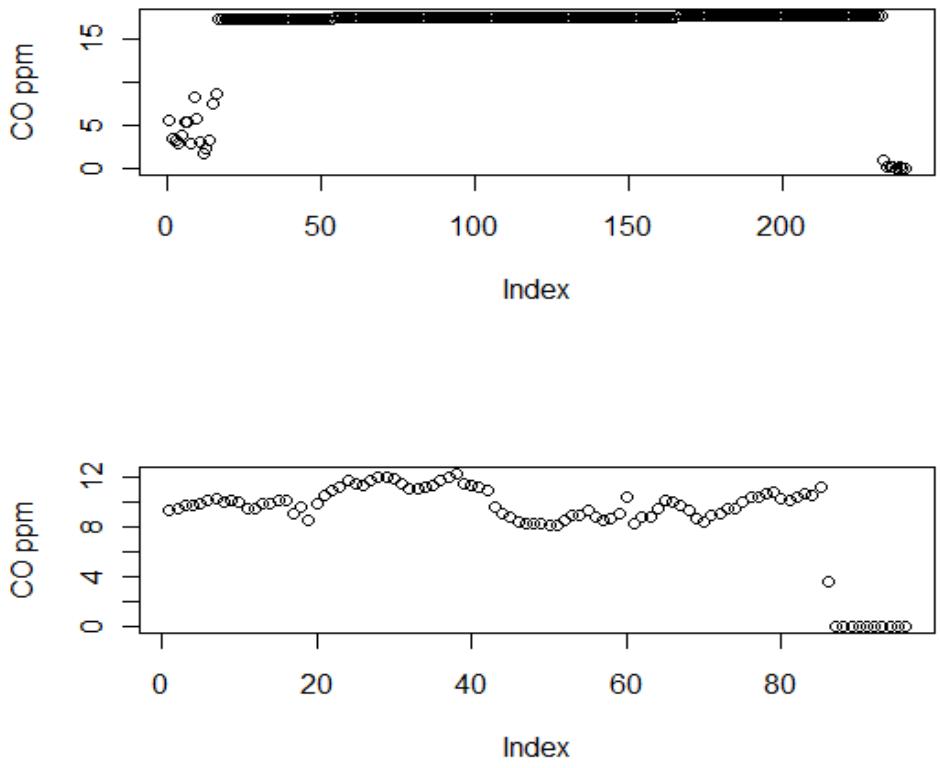


Figure 6.13. Comparing CO concentrations (ppm) for 7 to 16 July (top) and 12 to 15 August 2008 (bottom) at Kirkstall monitoring site.

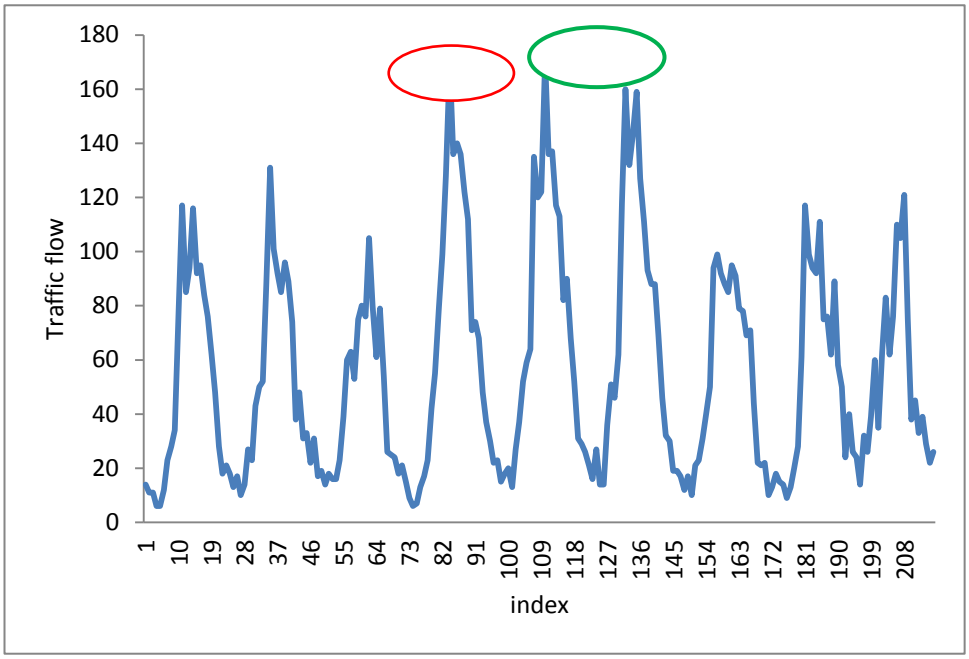


Figure 6.14. Traffic flow (vehicles/hour) for Heavy van and mini-buses on 10 to 18 August 2008 at Kirkstall road Leeds.

6.3.3.2 Time variations of ozone, CO and $PM_{2.5}$

Figure 6.15 shows the normalised time variation plots of ozone, and $PM_{2.5}$. Time variation plots show how concentrations vary during different hours of the day, days of the week and months of the year. To get the normalised value the observed concentration is simply divided by its mean (Carslaw and Ropkins, 2012). The normalised concentrations make comparison easy of different pollutants, which are not at the same scale. The time variations of ozone in comparison with NOx are described in section 6.3.1. The time variations of $PM_{2.5}$ and CO are similar to that of NOx, probably indicating the same source (road traffic). Here we only show $PM_{2.5}$ and ozone to keep the plots simple. Expectedly, low $PM_{2.5}$ concentrations were observed during weekend and higher during weekdays, which can be linked with the traffic levels on different days of the week. Furthermore, the concentrations of $PM_{2.5}$ were higher during winter months, most probably due to cold and stagnant atmospheric conditions that hinder the dispersion of the emitted pollutants. $PM_{2.5}$ concentrations are higher during the morning busy hours (08:00 to 09:00 am) and then again during the late afternoon or evening busy hours and lower after mid night to early morning (before 06:00 am) when traffic flows are low. Ozone shows opposite trends to that of $PM_{2.5}$ and CO and hence confirms the negative association. The Spearman correlation coefficients between ozone and $PM_{2.5}$ were -0.46 (whole dataset), -0.64 (December), and -0.30 (June), whereas between ozone and CO the correlation coefficients were -0.11 (whole dataset), -0.28 (December) and -0.27 (June). The correlation analysis shows that the association of

ozone with other air pollutants is much stronger in winter, when the effect of meteorological variables is minimal (this has also been described in section 6.3.1).

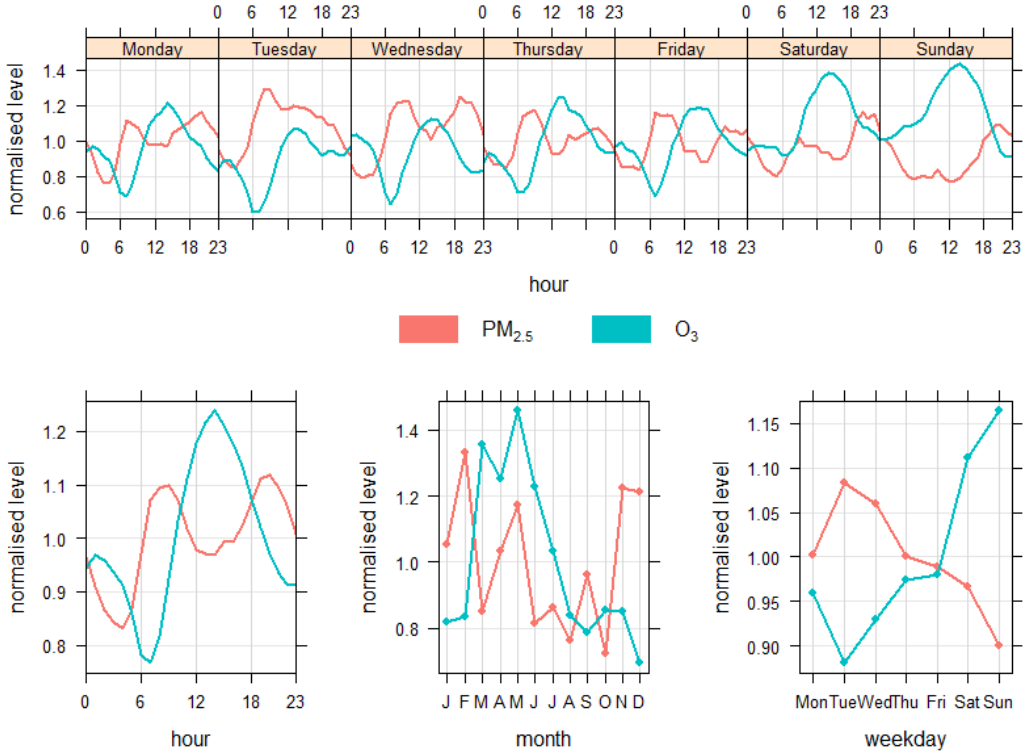


Figure 6.15. Time variations of ozone (ppb) and $PM_{2.5}$ ($\mu g/m^3$) showing normalised concentrations for October 2007 to November 2009 at Kirkstall monitoring site.

6.3.3.3 Ozone vs CO and $PM_{2.5}$ investigated with QRM

In this section the association of ozone with CO and $PM_{2.5}$ has been further investigated using a QRM model. The outputs of QRM are shown in Figure 6.16. The negative quantile regression coefficients indicate that both CO and $PM_{2.5}$ have mostly negative effects on ozone concentrations, except at 0.99 quantile where the effect of $PM_{2.5}$ is positive, although not very strong. The effect of CO at 0.2 to 0.8 quantile is not significantly differently from the mean effect determined by ordinary least square regression, as indicated by the fact that the shaded area of these quantiles overlaps with confidence envelop of the mean coefficient. The magnitudes of estimated coefficients of $PM_{2.5}$ gradually decrease (absolute value) from 0.3 quantile upward. At extreme high ozone concentrations (0.99 quantile) the coefficients become positive.

Like HC and NOx, CO (Munir et al., 2012) is considered as one of the precursors of ozone and photochemical ozone formation consumes CO, therefore ozone concentration will increase and CO concentration will decrease, which explains the negative association.

$PM_{2.5}$ particles may provide a surface for ozone dry deposition (Ding et al., 2013) which reduces ozone concentrations. Furthermore, the negative effect of both CO and $PM_{2.5}$ may be in part due to the fact that the data come from a roadside monitoring site and therefore almost all of CO and $PM_{2.5}$ are emitted by road traffic. Higher concentrations of these pollutants may indicate higher traffic volume and hence higher NO which depletes ozone molecules (e.g., Ding et al., 2013 and references therein). The absolute values of $PM_{2.5}$ decrease with increasing ozone concentrations and at quantile 0.99 turn positive, which might be due to the fact that high ozone concentration indicates high temperature and favourable environment for atmospheric chemistry. High temperature in addition to photochemical ozone chemistry plays an important role in secondary aerosol formation (e.g., Ding et al., 2013), such as sulphate (SO_4^{-2}) and nitrate (NO_3^-), which are formed from sulphur dioxide (SO_2) and NOx. This mechanism probably gradually decreases the negative association between the two species.

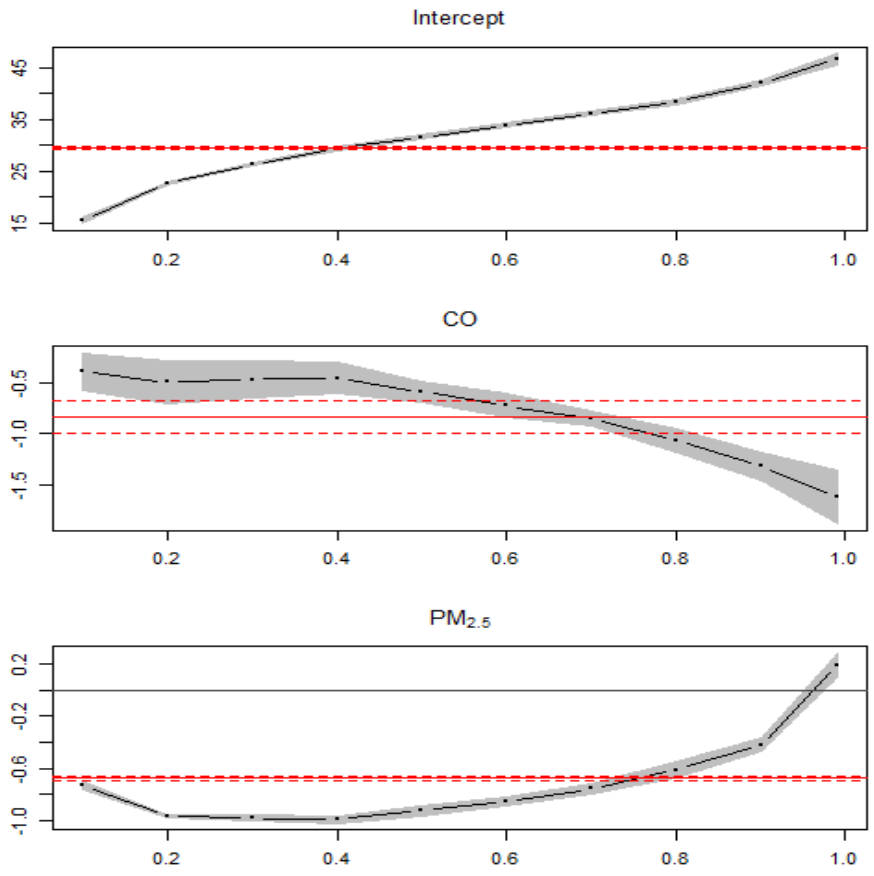


Figure 6.16. The outputs of quantile regression model, showing the effect of CO (ppm, top) and $PM_{2.5}$ ($\mu g/m^3$, bottom) on hourly mean ozone concentrations (ppb). Quantile regression coefficients (dashed dark line) and ordinary least square regression coefficients (solid red line) are presented with 95% confidence interval, using data from Kirkstall site October 2007 to November 2009.

6.3.4 Modelling the collective effect of various air pollutants

In the above section various air pollutants were considered individually or in small group, here all these air pollutants are considered collectively and their effect on ozone concentration is modelled. The performance of the model is assessed with the help of various statistical metrics.

The outputs of quantile regression model have been depicted in Figure 6.17, using ozone as a response variable and hydrocarbon (HC), NO, NO_2, CO and $PM_{2.5}$ as explanatory variables measured at Marylebone road, 2008. Reason for using data from Marylebone site is that HC is not monitored and the concentrations of CO and $PM_{2.5}$ have potential outliers (as explained above) at Kirkstall monitoring site. Furthermore, Marylebone site can provide a good alternative for comparison purposes with Kirkstall site. In Figure 6.17 quantile regression coefficients have been shown for 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 0.99 quantiles (represented by dashed-dotted line with their 95% confident intervals). Quantile regression coefficients have been shown at y-axis and different quantile values (0.1 to 0.99) at x-axis. In Figure 6.17 the top left panel shows the intercepts of the model. The values of intercept (constant) are higher for higher quantiles and vice versa. For instance, the intercept value for 0.1 quantile is about 5, whereas it is about 75 for quantile 0.99.

The effect of HC on ozone concentrations have been presented in Figure 6.17 (top-right), which shows significant effect on ozone concentrations as confidence intervals of the quantile regression coefficients do not overlap with the zero line. Quantile regression coefficients are negative, which shows that HC have negative association with ground level ozone. In other words an increase in ozone concentrations causes a decrease in HC concentrations. HC levels are generally higher in winter months (data not shown here) when ozone concentrations are lower and their concentrations start decreasing in spring as photochemical ozone formation increases, which consumes HC. The strength of the relationship between ozone and HC increases gradually with the increase in ozone concentration and reaches the highest value at quantile 0.99, where the quantile regression coefficient value is '-2.02', which is most probably due to the fact that increasing ozone concentration in spring and summer, consume greater amount of HC. Spearman correlation between ozone and HC was also estimated and had a negative value, the highest correlation coefficient was estimated for the month of March (-0.80) and lowest for August (-0.34). Spearman correlation was employed because it can be used for both normal and non-normal distribution and is therefore best applicable to air quality and ozone data, which normally have non-normal distribution.

The effect of CO on ozone concentrations is shown in Figure 6.17 (middle-left). CO has a negative relationship with ozone concentrations and the effect is significant at all quantiles. The quantile regression coefficients of CO have the same pattern as that of HC. The strength of coefficients increases from quantile 0.1 to 0.99 gradually and range from -0.53 to -10.00. The correlation coefficients are much higher for CO than the other air pollutants, which may be due to the fact that CO concentrations are much higher and therefore measured in ppm; in contrast to the other pollutants which are expressed in ppb. The highest spearman correlation coefficient was shown in March (-0.81) and lowest in August (-0.37). The effect of CO is negative at both Kirkstall and Marylebone, but much stronger at the latter site, most probably due to higher traffic flow and hence higher emissions at the Marylebone site.

The effect of NO (Figure 6.17, middle-right) on ozone concentration is negative and is significant at all quantiles except at quantile 0.99, where the confident intervals overlap with zero. The strength of coefficients slightly increases from quantile 0.1 to 0.5 and then stays almost constant. The effect is not significantly different from the mean effect at most of the quantiles. On the other hand NO_2 (Figure 6.17, bottom-left) has positive effect on ozone concentrations from quantile 0.1 to 0.6 and negative from quantile 0.7 to 0.99 of the ozone distribution. This effect is different to that observed at Kirkstall site as shown in Figure 6.9, which might be due to the interaction of other air pollutants or due to difference in the level of air pollutants, topographical conditions or meteorological conditions, which are expected to vary at the two monitoring sites.

Figure 6.17 (bottom-right) shows the effect of $PM_{2.5}$ on ozone concentrations. Quantile regression coefficients are negative up to quantile 0.8 and positive at quantile 0.9 and 0.99. The effect is significant at all quantiles. Highest correlation coefficient was estimated for the month of March (-0.78) and lowest for the month of August (-0.46) using spearman correlation analysis. The curves of the coefficients at Kirkstall and Marylebone although seem similar, they have different characteristics, e.g. coefficients are much stronger at Kirkstall site; the mean effect is significant at Kirkstall site and insignificant at Marylebone site; and the effect is positive only at quantile 0.99 at Kirkstall site whereas at Marylebone the effect is positive at both quantiles 0.9 and 0.99. This might indicate that the effect of other air pollutants on ozone concentration is site specific and vary from site to site, which is understandable due to changes in local topographical and meteorological conditions. The effects of meteorological and geographical parameters on ozone concentrations are investigated in chapter 8 and 9, respectively.

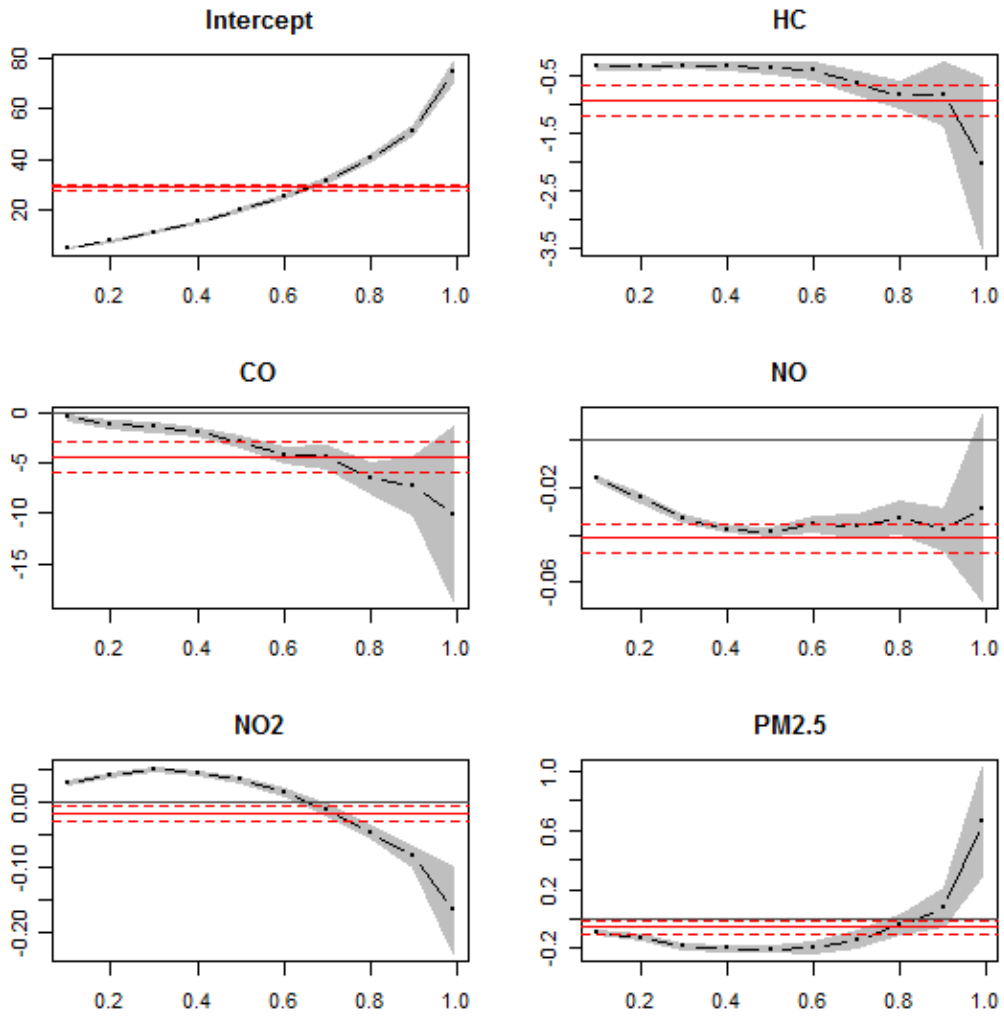


Figure 6.17: The outputs of quantile regression model showing the effect of HC (ppb), NO (ppb), NO_2 (ppb), CO (ppm) and $PM_{2.5}$ (µg/m^3) on hourly mean ozone concentrations (ppb) at Marylebone road site, 2008. Quantile regression coefficients (dashed-dotted line) and ordinary least square regression coefficients (solid line) are presented with 95% confidence interval. Various quantiles are shown on x-axis, whereas their coefficients are shown on y-axis.

6.3.4.1 Assessment of the model performance

The methods of assessment for QRM have been described in details in chapter 4, section 4.5.1. In this section local goodness of fit $R^1(\tau)$ for each quantile is estimated. Furthermore, several statistics metrics are calculated, including global goodness of fit (R^1) to assess the performance of the model. Figure 6.18 shows $R^1(\tau)$ values estimated for different quantiles of ozone concentration. The local goodness of fits are relatively weaker compared to global goodness of fit, which is understandable as the local goodness of fits are calculated for a small portion of the total data. Several other statistical metrics have been calculated for both

QRM and ordinary least square (OLS) regression and are shown in Table 6.1. The statistics metrics clearly show that QRM performs better than OLS.

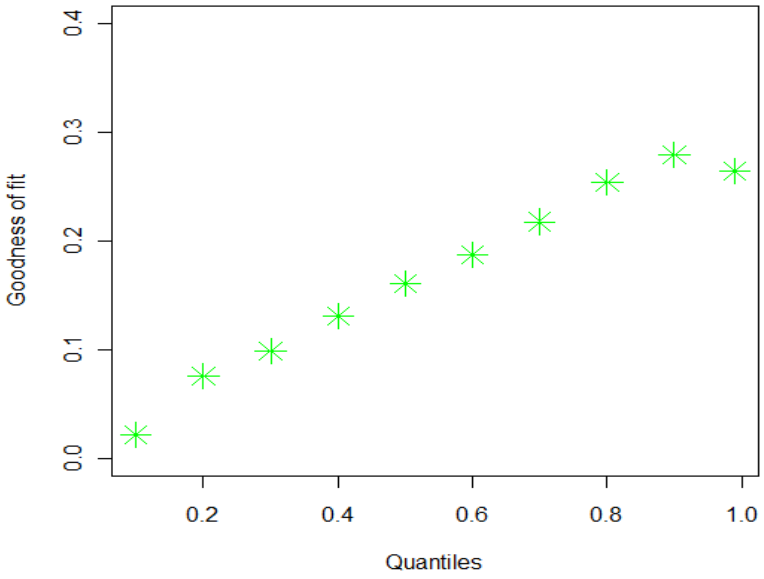


Figure 6.18. Local goodness of fit R^1 (τ) as a function of the ozone quantiles for the quantile regression model at Marylebone road, 2008.

Table 6.1. Showing several statics metrics for both QRM and OLS

Metrics	QRM	OLS
FAC2	0.87	0.65
MB	-2.83	-6.99
MGE	4.70	11.56
NMB	-0.12	-0.29
NMGE	0.20	0.49
RMSE	5.99	15.22
R^1	0.93	0.46

Figure 6.19 depicts predicted ozone versus observed ozone concentrations at Marylebone roadside monitoring site for April 2008. The scatter plots of observed ozone versus predicted ozone by QRM and by OLS are compared. The model lines (dashed lines) show the within factor of two (FAC2) region and it is perhaps worth noting that most of the points for QRM lie with the factor of 2 region (FAC2 = 0.87). For linear regression model relative more points lie outside the FAC2 region, particularly at higher ozone concentrations. Derwent et al. (2010) recommended that a model with a FAC2 value > 0.50 (half or more of the points lying inside the region) should be considered acceptable. It is further recommended (Derwent et al., 2010) that air quality models are considered acceptable if Normalised Mean Biased (NMB) values lie within the range between -0.2 and +0.2 and faulty if not. QRM model fulfil both conditions, whereas the linear model fails the later condition having NMB value of -0.29. Observed and predicted ozone depicted by lines rather than points to simplify the comparison are also shown in Figure 6.19 (bottom panel). Predicted ozone by QRM closely follows the observed ozone, particularly at extreme values where OLS fails to perform. QRM explains more of the ozone variations, represented by coefficient of determination or global goodness of fit (R^1). The values of R^1 were 0.93 and 0.46 for QRM and OLS, respectively. (It should be noted that generally R^2 is used to express coefficient of determination for OLS and R^1 for QRM, however here for the sake of brevity only R^1 is adopted for both cases). This indicates that QRM is explaining significantly more variation in ozone concentration than OLS, particularly at extreme values (right tail of the ozone distribution) OLS fails to follow ozone trend, as a result OLS model under-predicts ozone concentrations in the right tail of the distribution.

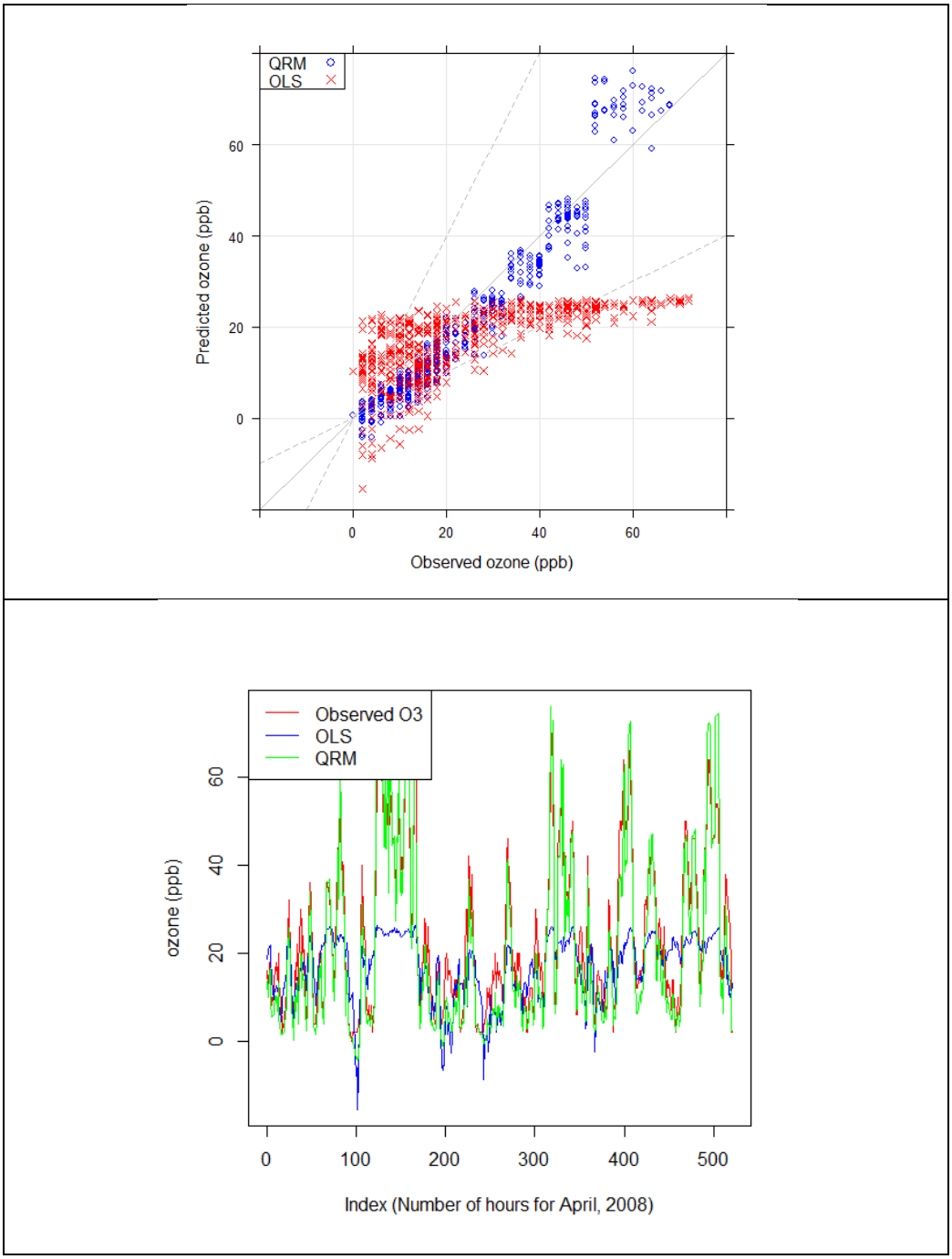


Figure 6.19. Comparison of predicted ozone (ppb) versus observed ozone (ppb) at Marylebone roadside site using AQRM (amalgated quantile regression mode) R^1=0.93 and OLS (ordinary least square) model R^2=0.46 for April, 2008. In the top panel the middle solid line is 1:1, and the above and below dashed lines are 0.5:1 and 2:1, respectively. So, the area between the two dashed lines is the factor of two (FAC2) regions. In top panel different clusters are due to using several quantiles (0.1, 0.2, ..., 0.9 and 0.99).

6.4 Summary

In this chapter the association of ozone concentration with traffic related air pollutants (NOx, NO, NO_2, CO, $PM_{2.5}$ and HC) has been investigated using exploratory data analysis techniques, OLS and QRM. The data come mainly from two monitoring sites: Kirkstall and Marylebone monitoring sites. Some data have been used for comparison purpose from Harwell monitoring site, which is a rural site. These air pollutants have shown negative correlation with ozone concentrations, however it is observed that the strength of the correlation changes with changes in atmospheric conditions and traffic flow, e.g., generally correlation is stronger during colder months. Furthermore, the behaviour and interactions of the independent variables with ozone change at different regimes of ozone concentrations, a characteristic that is normally obscured in the traditional regression models. Comparing the performance of QRM and OLS, it is shown that QRM performs better than OLS, based on the scores of several statistical metrics (e.g., FAC2, NMB, R^2). Better correlation was observed between observed and predicted ozone by QRM, particularly at extreme values as OLS under-predicts ozone concentrations in right skewed tail of ozone distribution.

There are several points in this chapter which are unique in comparison to previous studies. Firstly, it determines that the association of various air pollutants with ozone changes spatially and temporally and therefore it is recommended that in future studies modellers take account of these factors. Secondly, this chapter employs robust modelling techniques that are applicable to non-normal distribution and have the ability to address the nonlinearities in the association of ozone and other air pollutants. Furthermore, it is recommended to model the whole distribution, especially the extreme values of ozone using more robust metrics, such as quantiles, percentiles etc. rather than only mean value which is biased by few larger or smaller data points. Finally, in contrast to Baur et al. (2004) who only used the coefficients of determination for evaluating the performance of QRM and OLS, here several statistical metrics (FAC2, RMSE, MB, NMB, MGE, NMGE and R^2, defined in chapter 4, section 4.7) have been calculated which assess the model performance in more robust way and characterise the errors of the model in a better way.

The levels of various air pollutants are closely correlated with the level of road traffic flow. Therefore local traffic flow affects the concentration of these pollutants, including ozone. In next chapter the association of road traffic flow with ozone concentration is described using hourly monitored data.

CHAPTER 7: THE IMPACT OF ROAD TRAFFIC ON GROUND LEVEL OZONE

7.1 Introduction

Road traffic is both a major source of ozone precursors, such as nitrogen oxides (NOx) and hydrocarbons (HC) and a potential local sink for ozone in the form of fresh nitric oxide (NO) that depletes ozone. Road traffic contributes about 40, 41 and 11 % to the total emission of NOx, CO, and non-methane hydrocarbons (NMHC), respectively in the UK (NAEI, 2011). The amount of road traffic-emitted air pollutants is substantially higher in large urban areas (e.g., London). Numerous researchers have investigated the relationship between road traffic and traffic related air pollutants, for instance NOx and particulate matter (Carslaw, 2005; Carslaw and Beevers, 2005; AQEG, 2004; AQEG, 2005); however very few considered road traffic in conjunction with ozone concentration, most probably because ozone is not emitted directly by road traffic. Berastegi et al. (2001), Pont and Fontan (2000) and Bronnimann and Neu (1996) investigated the effect of road traffic on ground level ozone concentration. Using linear regression and time series analysis Berastegi et al (2001) found that 81% to 99.6% of total variance of long term ozone changes could be associated with road traffic. Pont and Fontan (2000) analysed the variations in weekend and weekdays ozone concentrations in 5 large French cities and concluded that a 40% reduction in road traffic would not have a significant effect on ozone concentration. They have, however not used any traffic flow, speed and fleet composition data and used carbon monoxide (CO) to estimate traffic level. Although CO can be used as a relatively generic marker for traffic flow, modern monitoring practices mean that we can now look more directly at the relationship between different traffic characteristics (e.g. speed, flow and composition) and air quality. Furthermore, Bronnimann and Neu (1996) and Gao et el. (2004) investigated ozone variation during weekend and weekdays in USA. The limitations (e.g., using precursor's data as a surrogate for ozone concentrations) are discussed in the chapter 3, section 3.5.

In this chapter the intention is to analyse synchronised measured hourly ozone concentration (ppb), traffic flow (vehicles per hour), vehicle speed (km/hr) and fleet composition collected at the same site to quantify the impact of local road traffic on urban decrements in Leeds. Most of the existing studies on the topic investigate how ozone concentration varies over weekend and weekdays without using any traffic flow, speed and fleet composition data. However, those studies that used measured traffic data, have neglected the effect of background ozone concentration (Bronnimann and Neu, 1996; Gao et el., 2004). In this

project the background effect on ozone concentration has been addressed to remove the regional effect before applying the model to investigate the effect of local traffic. The intention in the second part of this chapter is to quantify urban decrements (i.e., the rural ozone concentration minus the urban ozone concentration) in the whole UK. Urban decrements are analysed not only for mean values but also at various quantiles of ozone distribution, particularly at both tails of ozone distribution to characterise the difference at extreme ozone concentrations.

Another issue to consider is that most of these previous studies were carried out in USA or European countries and none of them was conducted in the UK. Therefore, this UK based project modelling the association of ozone with road traffic characteristics will provide further insight into the effects of road traffic on ozone concentration. This project is based on synchronised ozone and road traffic data collected at the same monitoring site and employs an advance modelling approach (quantile regression), which is applicable to normal distribution, can handle nonlinearities in the association of ozone and predictors and can model the effect of predictors on the whole ozone distribution, especially on atypically high ozone concentration. High ozone concentrations are important from public health point of view, therefore the characterisation of their behaviour and association with the controlling parameters are important.

7.2 Methodology

In this chapter firstly traffic flow (vehicles/hr), fleet composition and vehicle speed (km/hr) are briefly described at Kirkstall road in Leeds and then their impact on ground level ozone concentration (ppb) is investigated. Cars are the dominant traffic source and make 90 % of the total flow at Kirkstall road. The legal speed limit is 48 km/hr and observed average speed is 40 km/hr. Traffic characteristics i.e. traffic flow (vehicles/hr), fleet composition and vehicle speed (km/hr) were measured using Traffic Detector Loops. The traffic loops were installed by Golden River Limited, as part of a contract to the LANTERN Consortium of the University of Leeds within the SRIF2 Instrumented Junction Project. The consortium included partners in the Institute for Transport Studies, and Departments of Engineering, Chemistry and Computing. The loops were placed in the upper layers of the road surface at both directions i.e. the southeast carriageway towards city centre and the northwest carriageway out of Leeds city centre. The system provides continuous 15 minutes traffic count and vehicle speed estimates for each of the 2 traffic lanes, which are converted to hourly average values. Lane1 (direction 1) is the southeast carriageway, towards city centre and lane 2 (direction 2) the northwest carriageway, out of Leeds city centre. The vehicles are classified into 6 categories according to European 6 bin scheme: (1) motorcycles, (2)

cars (cars or light-vans), (3) trailers (cars with trailers), (4) vans (rigid heavy van or mini-buses), (5) artic (articulated Lorries), and (6) buses (buses and coaches).

The data analysis has been carried out using graphical presentations, correlation analysis and quantile regression models (QRM), which has the capability to be applied to non-normal distributed ozone concentration and models the influence of the predictors on different percentiles of ozone concentration (Koenker, 2005; Hao and Naiman, 2007; Baur et al., 2004). QRM is particularly useful for studying the extreme values of the distribution; where other models (e.g. multiple regression models) fail to perform well, due to their dependence on the mean value of the data, particularly when the distribution is skewed relative to the mean, see chapter 4 for details description of the QRM.

Furthermore, the effect of road traffic on ozone concentration has been investigated in terms of the differences in ozone concentration at urban and rural monitoring sites with the help of QRM, analysing ozone data from 80 monitoring sites (described in chapter 4). Ozone concentration (ppb) hourly data are obtained from the UK automatic urban and rural network (AURN) and are converted to yearly mean or other metrics as required. The 'type' of monitoring sites (urban or rural) is a qualitative or categorical variable and therefore needs to be handled differently from numerical variables. There are seven types of monitoring sites, which are grouped into two main groups i.e. rural (rural background, rural background agriculture, rural background nature, and suburban background) and urban (urban background, urban industrial and urban traffic). Dummy variables are assigned to urban and rural site type. Dummy variable - *proxy variable* is numerical value that stands in for qualitative data in a regression model and can take values of 0 or 1, where 0 indicates absence and 1 indicates presence of urban factor, therefore 1 is assigned to urban and 0 to rural sites. Rural sites with a value of 0 will cause the coefficient of the variable to disappear and urban with a value 1 will cause the coefficient to act as a supplemental intercept in the quantile regression model. The coefficient can be interpreted as the difference in ozone concentration between urban and rural monitoring sites, keeping all other factors the same.

7.3 Results and Discussions

7.3.1 Traffic flow

The fifteen minutes traffic flow (vehicles/hr) and vehicle speed (km/hr) are converted to hourly mean for both traffic flow (volume) and speed. The hourly traffic flow data are presented in Figure 7.1, where it can be seen that cars (green) are the dominant vehicle type at this site and consist of over 90% of the total traffic flow. Hourly mean flow for car is 1021, whereas it is about 11, 5, 57, 8, 16 for motorcycles, trailers, vans, artic and buses,

respectively. In Figure 7.1 (a) the flow of cars hides the details of other vehicle classes therefore the box plot has been re-presented without cars flow in Figure 7.1 (b), which shows motorcycle (red), trailers (blue), vans (grey), artic (purple) and buses (yellow). In Figure 7.1 (c) the flow of cars (green) is compared to the total flow (pink), which reconfirms the fact that cars are the dominant traffic category and it seems probable that cars will be playing a vital role in vehicular emitted air pollutants at the site. The second highest counts (volume) are vans with a mean flow 57 per hour. Heavy vehicles and buses are comparatively less in counts, however they might be important from air quality point of view due to their fuel type (diesel) and larger engine size.

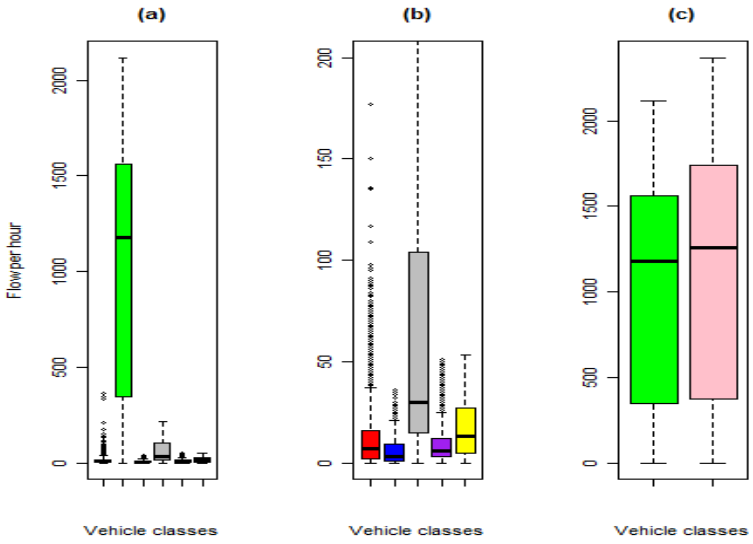


Figure 7.1. Box plots showing flow of different vehicle categories per hour at Kirkstall roadside monitoring site in Leeds for the period of November 2007 to October 2009, the plots represent motorcycles (red), cars (green), trailers (blue), vans (grey), artic (purple), buses (yellow) and total flow (pink). In (a) all six vehicle categories have been shown but due to relatively large flow of cars the details of other vehicles are hidden. (b) Shows all vehicle types except cars and (c) shows only cars and total flows.

7.3.2 Vehicle speed

The speed limit at Kirkstall road where the traffic detector loops are installed is 30 miles per hour (48 km/hr). The observed average speed (km/hr) of motorcycles (red), cars (green), trailers (blue), vans (grey), artic (purple), buses (yellow) and average speed of all vehicles (pink) are presented in Figure 7.2 for about 2 years period (November 2007 to October 2009). Cars have the highest mean speed (43 km/hr), whereas cars with trailers and motorcycles have been observed to have the lowest average speed of 36 and 37 km/hr, respectively. The average speed of artic and buses are about 40 km/hr, which is the average

speed of all categories as well. The minimum, 1st quartile (0.25 quantile), median (0.5 quantile), 3rd quartile (0.75 quantile) and maximum of the vehicle speed are depicted in Figure 7.2.

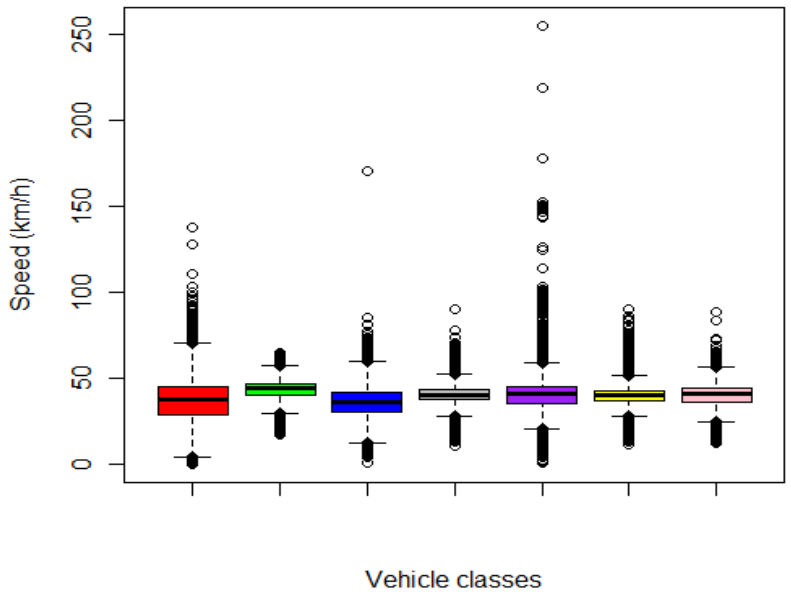


Figure 7.2. Speed of vehicle (km/hr) at Kirkstall site Leeds from November 2007 to October 2009, the plot represents motorcycles (red), cars (green), trailers (blue), vans (grey), artic (purple), buses (yellow) and average speed (pink).

7.3.3 Time variations of traffic volume

The time variations of total traffic and car flow have been depicted in Figure 7.3. As the volume of cars is comparatively higher and if presented in the same plot it will hide the details of other vehicles categories. Therefore the volume of cars is presented in a separate Figure (7.3) along with total traffic flow. Figure 7.4 represents a comparison of the monthly flow in 2008 and 2009. The flow of motorcycles, trailers, vans, artic, and buses have been depicted in Figure 7.5.

Car flows and total flows show exactly the same trends. Generally as expected the traffic flow is higher during day time and lower during night times. Figure 7.3 shows that on daily basis the traffic flow can be divided into four sub-phases: (a) midnight to early morning (about 05:00 am) – low traffic flow with some variation; (b) early morning to morning peak hours (about 08:00 am) – faster increase in traffic flow; (c) morning peak hours to afternoon peak hours (about 18:00 pm) – a high traffic flow with some variation; and (d)

afternoon peak hours to midnight – faster decrease in traffic flow. In other words, there is a low (night flow), high (day flow) and a transitional phase (morning and evening). This is the average pattern and obviously hides daily, weekly and monthly variations. On weekly basis our data show (Figure 7.3, bottom-right) lowest traffic volume on Sunday followed by Saturday and highest on Friday. The low traffic volume on weekend is understandable as most of the educational institutes and working places remain closed on Saturday and Sunday in the UK. The diurnal cycles of traffic flow on different days also vary as Saturday and Sunday show midday maximum flow, in contrast to the other days where flow decreases slightly during this time of the day. There is no clear difference in traffic volume between summer and winter months, however lowest traffic flow is shown in March, August and December and highest in November. When the data were analysed separately for 2008 (Figure 7.4, top) and 2009 (Figure 7.4, bottom) they show a different picture. In 2008 (Figure 7.4, top) the lowest total flow was recorded in February and highest in October, whereas in 2009 (Figure 7.4, bottom) the lowest flow was recorded in August and highest in July and October. This shows that the highest and lowest flows during different months vary in different years and no clear conclusion can be drawn from our data as to which month observes the highest or lowest total traffic flow at this site. The same is true for some of the other traffic categories (motorcycles, cars with trailers, vans, artic, and buses) (Figure 7.5). In Figure 7.5 the variation in the flow of vans between weekend and weekdays is much greater than the other traffic categories. This might be due to the vans being used for deliveries during the weekdays.

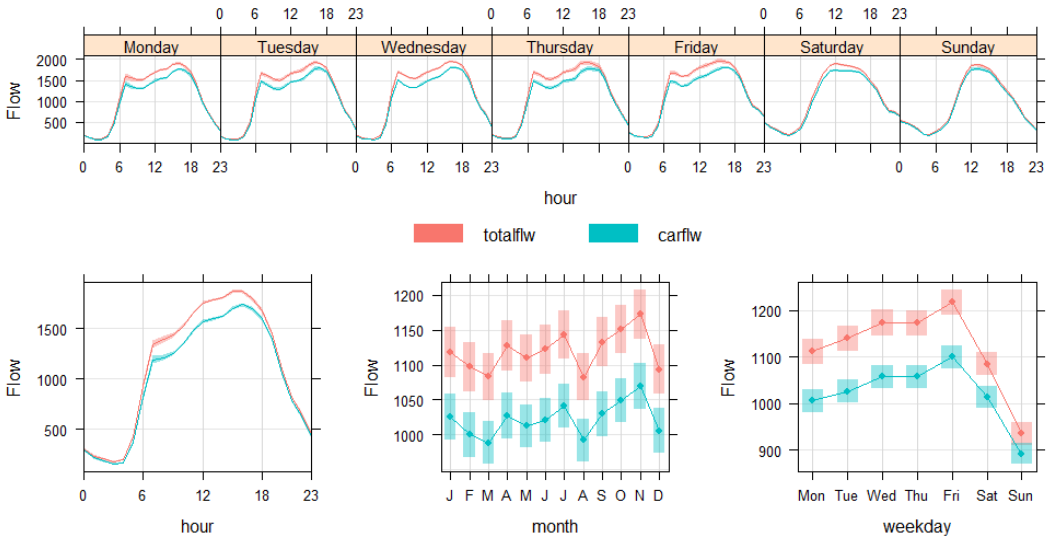


Figure 7.3. Time variation plots of cars flow (cars/hr) and total flow (vehicles/hr) mean hourly data from Kirkstall site Leeds, November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

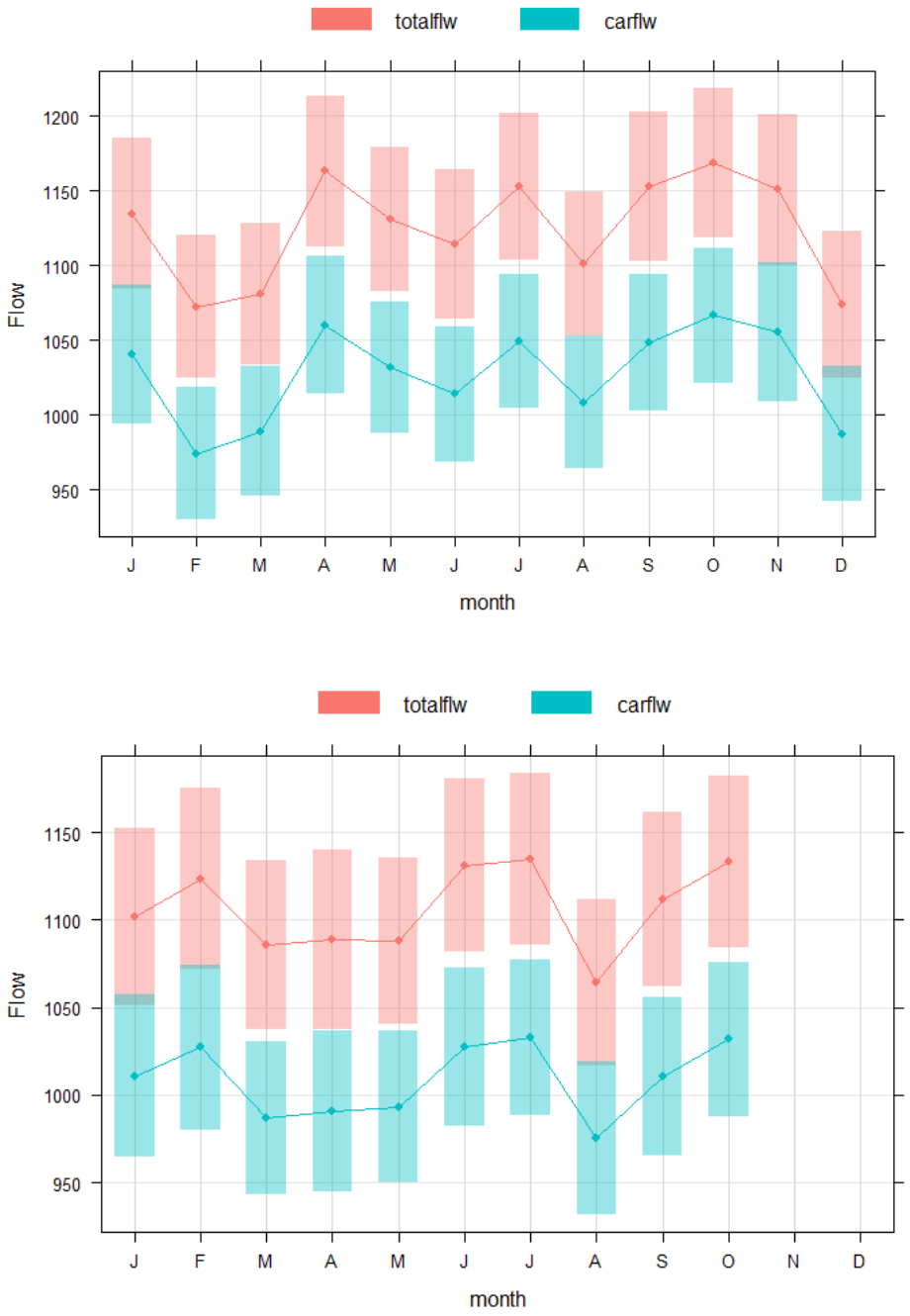


Figure 7.4. Hourly total flow (vehicles/hr) and cars flow (cars/hr) for each month at Kirkstall site Leeds, 2008 (top) and 2009 (bottom). November and December data are missing in 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

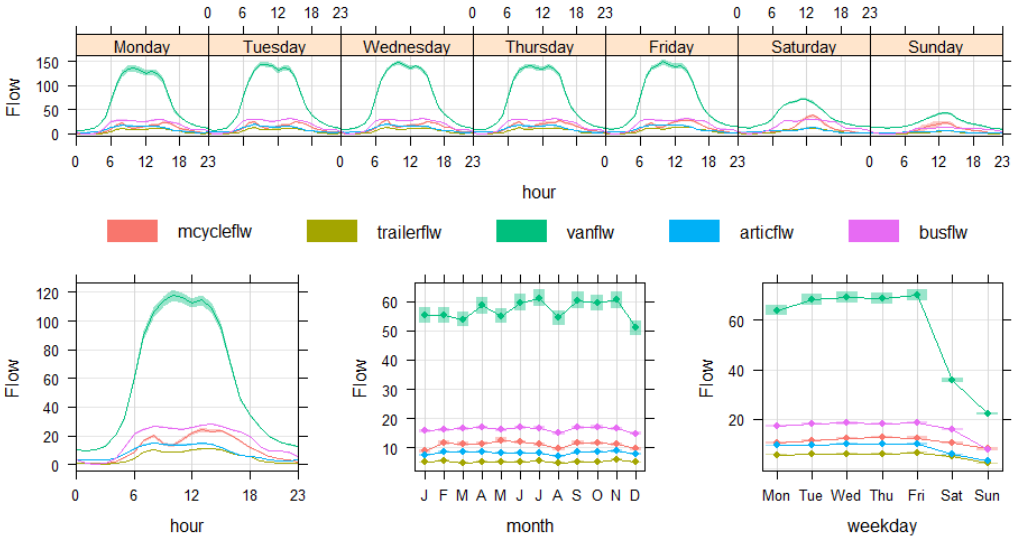


Figure 7.5. Time variation plots of hourly average flow (vehicles/hr) of motorcycles, trailers, vans, artic and buses at Kirkstall site November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

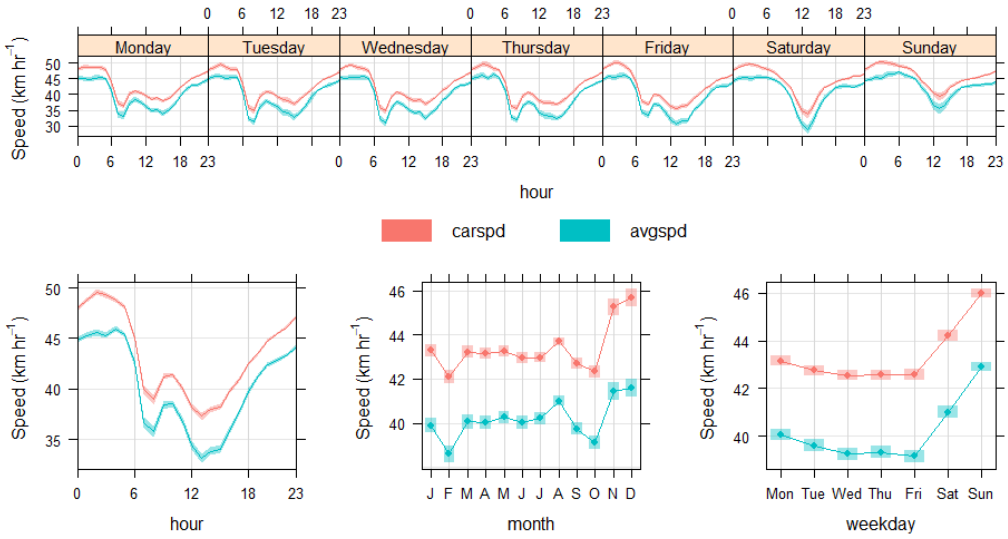
7.3.4 Time variations of vehicle speed

Figure (7.6) shows how average speed and the speed of cars vary over different time periods. Theoretically vehicle speed should be inversely proportion to traffic volume and vehicle speed should decrease as traffic volume increases. Our data also demonstrate negative correlation between speed and volume. On daily basis speed is shown (Figure7.6 a) to be higher over nighttimes and lower during daytimes, most probably higher traffic volume during daytime causes vehicle speed to slow down. Average speed and total flow have been depicted together in Figure 7.6 b, where the negative correlation can be clearly observed, particularly in diurnal and weekly cycle. Total traffic flow and average speed are on different scales and their actual values cannot be presented in the same graph, therefore normalised levels have been depicted in Figure 7.6 b. To get normalised values R (using package 'openair') just simply divide each observation by the mean of the variable.

Figure 7.7 shows the vehicle speed (km/hour) versus traffic flow (vehicles/hour) relationship at Kirkstall road in Leeds. It uses the procedure defined by Bell et al. (2006) and shows four distinct areas of the speed flow curve that relate to different levels of emissions for quiet, free flow, busy and congested traffic conditions. The quiet (not congested) traffic conditions are characterised by traffic speeds not constrained by the flow levels. Free flow (slightly congested) traffic conditions are referred to where the speed is constrained by the flow, particularly with the ability to overtake, but nevertheless traffic flow continues. Busy (moderately congested) traffic conditions occur when the flow is

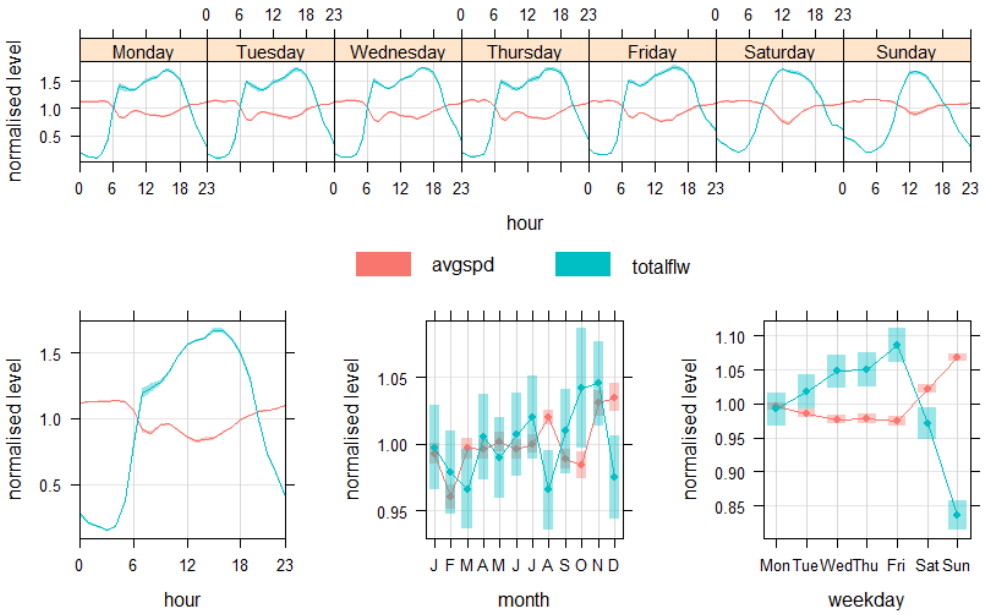
approaching the capacity of the link and the traffic flow is very unstable, causing short shock waves and, for a given traffic volume, large variation in speed with acceleration and deceleration events. Congested (severely congested) traffic conditions are characterised by flow breakdown where speeds are slow and display stop start behaviour. The traffic conditions on Kirkstall during the study period were 29 % quite, 18 % free flow, 46 % busy and 7 % congested.

The Spearman correlation coefficient between average speed and total flow is '-0.76'. The correlation coefficient between cars speed and volume is '-0.80' and cars speed and total traffic volume is '-0.84'. The Spearman correlation coefficients of total flow against the speed of motorcycle, trailer, van, artic, and bus were '-0.49', '-0.54', '-0.61', '-0.54', '-0.70', respectively.



(a)

Figure 7.6 a. Time variation plots of cars speed and average (of all categories) hourly speed (vehicles/hr) at Kirkstall site November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.



(b)

Figure 7.6 b. Time variation plots of normalised speed (km/hr) and flow (vehicles/hour) at Kirkstall site November 2007 to October 2009. Normalised levels are obtained dividing each value by the mean of the variable. The shaded area (bars) show the estimated 95 % confidence intervals.

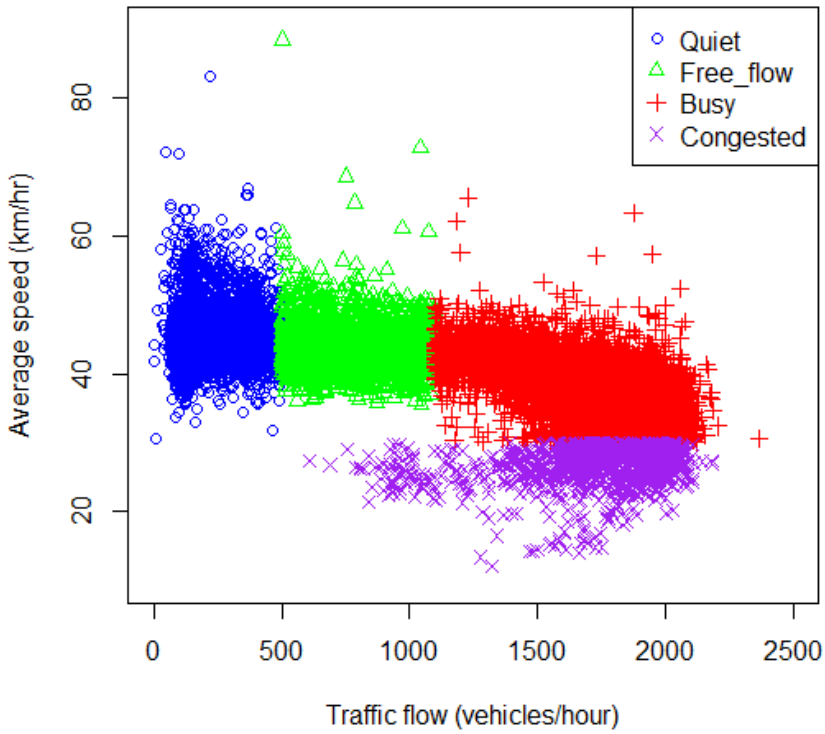


Figure7.7. Scatter plot of average speed (km/hr) versus total flow (vehicles/hour) at Kirkstall site Leeds, November 2007 to October 2009.

7.3.5 Comparisons of the traffic flow and speed at the two directions

At Kirkstall site traffic flow and vehicle speed are measured at both Lanes and directions. Lane1 (direction 1) is the southeast carriageway, towards city centre and lane 2 (direction 2) is the northwest carriageway, out of Leeds city centre. In this section the variation in traffic flows and speeds at both direction and lanes are described.

Total flow and average speed on both directions are not much different, but they have slightly different patterns. Hourly total traffic flow (vehicles per hour) for direction 1 is 548 and for direction 2 it is 563. Direction 1 (Figure 7.8, total flow 1 - red) has higher traffic volume in the morning than direction 2 (Figure 7.8, total flow2 - blue), whereas direction 2 has higher traffic volume in the evening. The reason for this most probably is that comparatively more people travel to Leeds for work, study or other purposes than the one who travel from Leeds to other places. This has been demonstrated in Figure 7.8 where the red line (ttlflw1) is higher in the morning and lower in the evening, crossing at about 12:00. On weekly and monthly basis the traffic flow on direction 1 is slightly lower than direction 2.

The hourly average speed (km/hr) is 40 and 41 for direction1 and direction 2, respectively. Direction 1 (Figure 7.9, avgspd1 – red line) shows lower speed than direction 2 (Figure 7.9, avgspd2 – blue) in the morning peak hours and higher in the evening peak hours. Because direction 1 is busier in the morning and direction 2 is busier in the evening. On weekly and monthly basis the speed on direction 1 is slightly lower than the speed on direction 2, but still shows the same trend. The average speed on weekdays is normally lower during the morning busy hours; whereas on weekend the average speed is lower around 12 hour both on Saturday and Sunday, probably because people normally get up late on Weekend and go for shopping to the Leeds city centre around this time of the day (11:00 to 13:00 hour). On Saturday the average speeds on direction 1 is especially lower at 12 O'Clock (Figure 7.9), which was further investigated to establish if it was caused by a couple of lower observations. Saturday in all months January to December showed the same trends and nothing odd (peculiar) was observed.

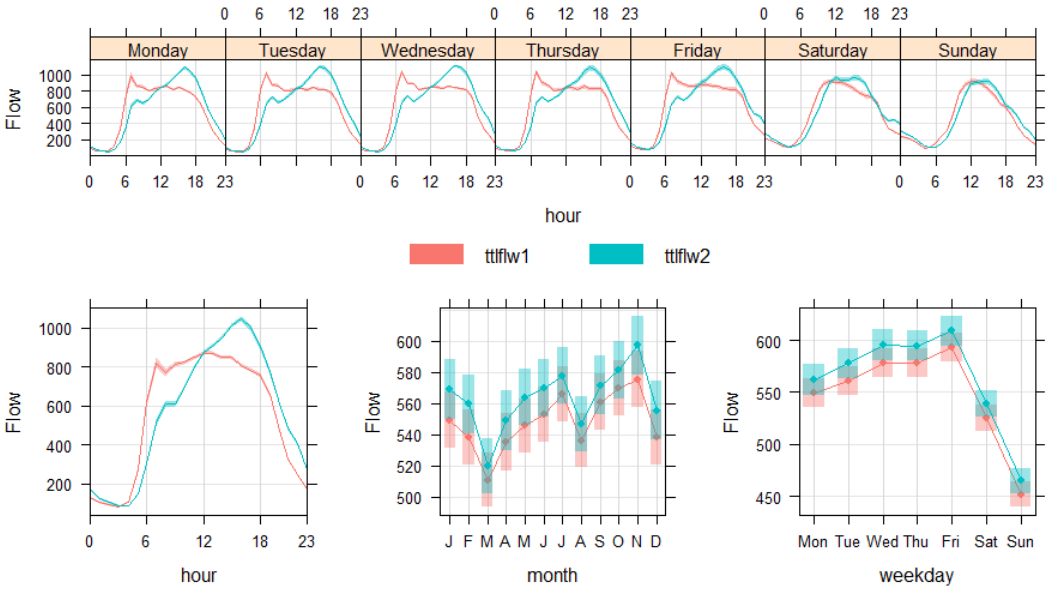


Figure 7.8. Time variation plots of traffic flow (vehicles/hr) at Kirkstall road direction 1(ttlflw1- towards Leeds city centre) and direction 2 (ttlflw2 – out of Leeds city centre), November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

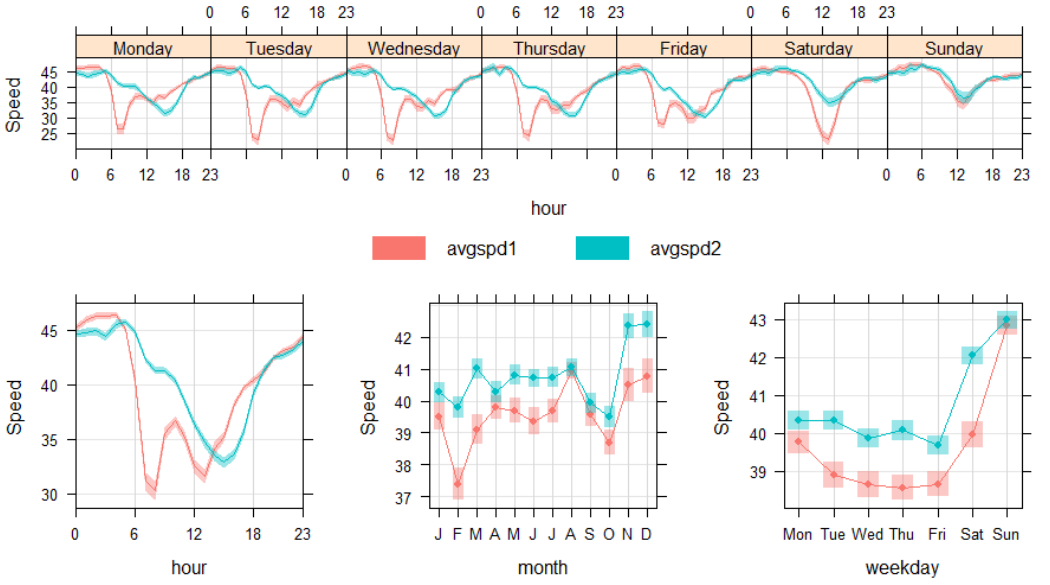


Figure 7.9. Time variation plots of vehicle speed (km/hr) at Kirkstall road direction 1(avgspd1 - towards Leeds city centre) and direction 2 (avgspd2 – out of Leeds city centre), November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

7.3.6 Road traffic flow and its effect on ozone

Road traffics have significant implications for urban air quality. Road traffic is considered to be the main source of NOx, particulate matter (e.g., $PM_{2.5}$), carbon monoxides (CO), and hydrocarbons (HC) (NAEI, 2011). In addition to local urban pollution, road traffics play a vital role in two important regional scale air quality problems – acid deposition and photochemical ozone formation (AQEG, 2009). NOx and certain HC are important precursors of ground level ozone (e.g., Harrison, 2001). Increasing fresh NOx emission is likely to reduce urban ozone concentrations due to scavenging effect, however it might increase ozone concentrations downwind the large urban areas (Jenkin et al., 2002). Chapter 6 analyses the relationship of ozone with some of the traffic related air pollutants in detail. This section explores the associations of road traffic volume and speed with ground level traffic related ozone concentrations.

Using the whole data set (November2007 to October 2009) the correlation between ozone concentration (ppb) and total traffic flow (vehicles/hr) was positive but very weak with a spearman correlation coefficient value of 0.09.The correlation was negative for winter months, e.g., January (-0.05), November (-0.08) , and December (-0.12) and positive for the rest of the months. The strongest correlation between ozone concentrations and total traffic flow was observed for the month of June (0.31) and August (0.32). Furthermore, correlation between ozone and total traffic flow was negative during early morning and night hours (00:00 to 08:00 and 18:00 to 00:00) and positive during day time hours (09:00 to 17:00). This shows that during colder months and hours when atmosphere is relatively stagnant and less turbulent, ozone shows negative correlation with total traffic flow at this site, probably due to less pollutants (particularly NOx) dilution, which depletes ozone.

The correlation between ozone and average speed was negative but very weak having a spearman correlation coefficient of '-0.03' for the whole data set. The correlation coefficient was positive for four months (January, March, November and December) and negative for the rest of the months. The highest correlation coefficient was found for June (-0.20) followed by September (-0.19). P-value was less than 0.05, indicating that the correlation was significant at 95 % confidence interval.

Figure 7.10 depicts normalised time variations plot of ozone, average speed and total flow. Ozone concentrations are shown to decline during night times, most probably due to ozone dry deposition and not replenishing by photochemical ozone production or descending from the stratosphere. Ozone concentrations are further reduced by reaction with fresh NO produced by road traffic and reaches a minimal level early in the morning about 07:00 am, as this is the time when road traffic increases (Figure 7.10). Afterwards in spite of high

volume of traffic, ozone levels start increasing most probably due to photochemical ozone production. Ozone concentrations reach a maximum level in the afternoon (about 14:00) and then decrease. It seems likely that on daily basis ozone levels are more controlled by atmospheric conditions, rather than traffic characteristics. On weekly basis there is a clear relationship between ozone concentrations and road traffic volume, which is nicely demonstrated by the ozone levels and traffic conditions during weekdays and weekend. Sunday shows highest ozone concentrations and lowest traffic volume followed by Saturday. Traffic flow and speed do not demonstrate any clear differences during winter and summer months, whereas ozone concentrations are significantly higher during spring and summer months, probably due to photochemical ozone production. Road speed seems to be more linked with traffic flow rather than ozone concentrations. However vehicle speed does affect pollutant emission, which is further elaborated in later sections. Although ozone levels are affected by road traffic flow, the effect is hidden by atmospheric conditions and therefore sometimes the effect of road traffic becomes less obvious.

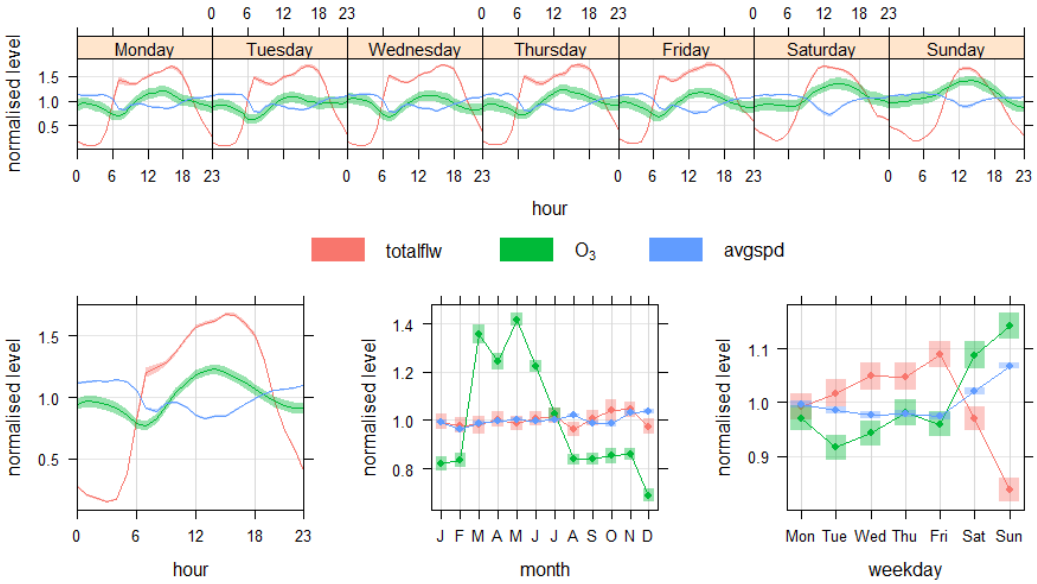


Figure 7.10. Time variation plots of ozone concentration (ppb) versus average speed (km/hr) and total flow (vehicles/hr) at Kirkstall road Leeds, November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

7.3.7 Ozone and car flows

Figure 7.11 shows the association of ozone concentration with flow and speed of cars. The negative correlation between the number of cars and speed is also demonstrated here. As expected, the speed is higher over night hours and lower during day hours, due to traffic flow. As cars are over 90% of the total flow, the effect of flow and speed on ozone is almost

the same as for total flow and average aped (Figure 7.10). Car flow and ozone concentrations show positive correlation for the whole dataset, with spearman correlation coefficient of '0.11'. However, when correlation coefficient was estimated between car flow and ozone for the 3 winter months (November, December and January) the correlation coefficient changed to negative (-0.07). For three month in summer (May, June, July) the correlation was positive (0.26). This might indicate that in summer photochemical ozone production during day times upset the negative correlation; as high traffic flow and photochemical ozone production occur at the same times. On the other hand in winter very little, if any at all, photochemical ozone formation takes place in the UK due to cold and cloudy conditions and whatever ozone is present is further reduced by NO reaction produced by traffic that results in negative correlation between ozone and traffic flow.

The correlation between ozone and car speed appears negative on daily and weekly basis; for instance, ozone levels are higher during day time and lower during night time, whereas car speed shows the opposite trend. The correlation coefficient was '-0.05' between car speed and ozone concentration. This negative correlation probably exists due to a third factor, which is cars flow that is affecting the speed.

7.3.8 Ozone versus vans, buses and artic flow

Figure 7.12 depicts normalised flow of vans, buses, artic and ozone concentrations. It can be observed that on 24 hour cycle flow of buses follows the same pattern as that of cars i.e. their flow reaches the highest level at about 08:00 and then with little decrease stays at that level until 18:00, whereas the flow of vans and artic on the other hand decrease abruptly after 14:00; probably because most of the deliveries take place before this time of the day.

Diesel and petrol vehicles have different emission characteristics (NAEI, 2011)and therefore should have different impacts on air quality and photochemical ozone formation. However, it is difficult to observe any significant differences between the effects of different vehicular categories on ozone levels using graphical presentation and correlation analysis, therefore this is further investigated with the help of QRM in section 7.3.10.

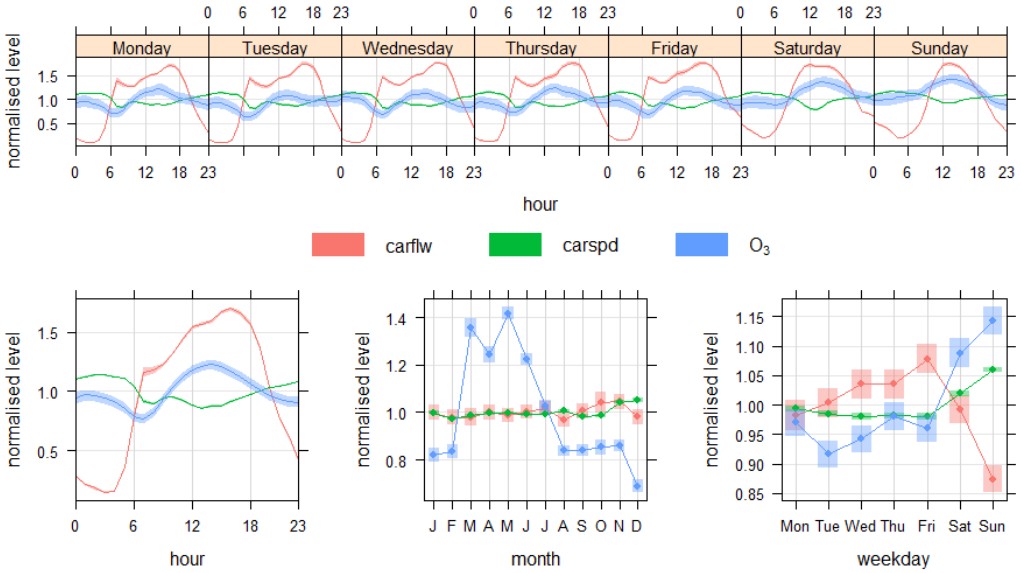


Figure 7.11. Time variation plots of car speed (km/hr), car flow (cars/hr) and ozone concentrations (ppb) at Kirkstall road Leeds, November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

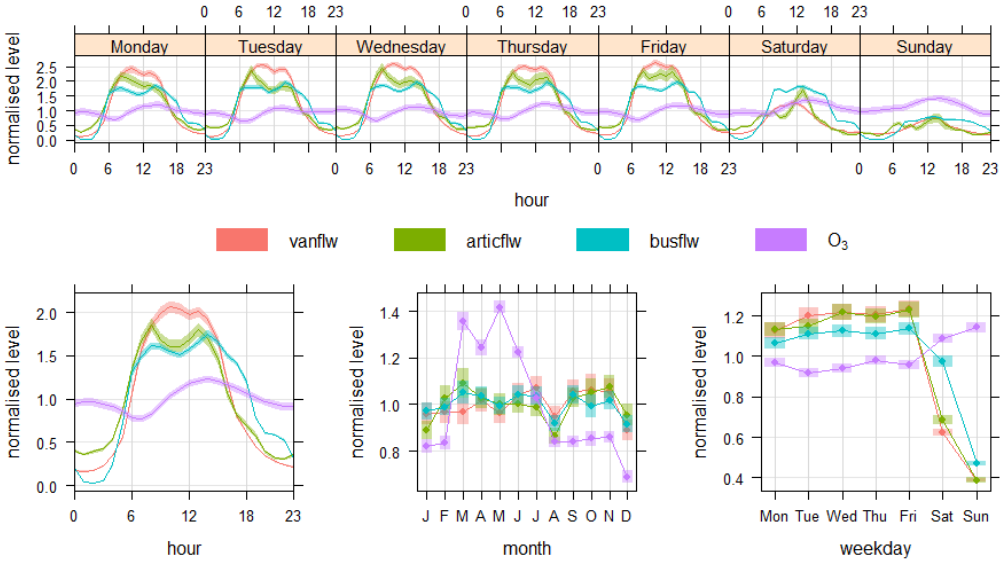


Figure 7.12. Time variation plots of vans, buses and artic flow (vehicles/hr) versus ozone concentrations (ppb) at Kirkstall road Leeds, November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

7.3.9 NOx and road traffics

Combustion processes in the vehicle engine produce NOx, which is made up of NO and NO_2 (explained in chapter 6). Therefore NOx concentrations have positive correlation with

traffic flow, i.e. as the number of vehicles increase NOx levels increase as well and vice versa. Time variation plots of NOx, average vehicle speed and total traffic flow are shown in Figure 7.13, which clearly demonstrates positive correlation between NOx and traffic flow and negative correlation between NOx and vehicle speed. Our data (Figure 7.13) show higher level of NOx during day times and lower during night times. NOx levels start increasing at about 05:00 am in the morning probably due to increasing activities of traffic and reach maximum levels at about 08:00 am. Our data show that after 09:00 am although traffic levels seem to stay at this level or slightly increase further until about 15:00, the NOx levels decrease probably due to ozone formation which consumes NOx, or atmospheric dilution as atmosphere becomes more turbulent during day times. On weekend there seems to be weak correlation between NOx and traffic flow. Furthermore, on monthly basis traffic flows do not show much difference in traffic volume during winter and summer months, whereas NOx concentrations are much higher during January, February, November and December. These observations clearly indicate that although NOx is positively correlated with traffic flow, atmospheric conditions interfere in their relationship and make the correlation weaker.

The Spearman correlation coefficient between NOx and total traffic flow was '0.33' and between NOx and average speed was '-0.33'. According to Highway Agency (HA, 2005) NOx emissions are highest at lowest cruise speeds and decrease considerably until speeds reach about 60 to 70 km/hr. Beyond 70 km/hr NOx emissions tend to increase slightly. This is further discussed in later sections.

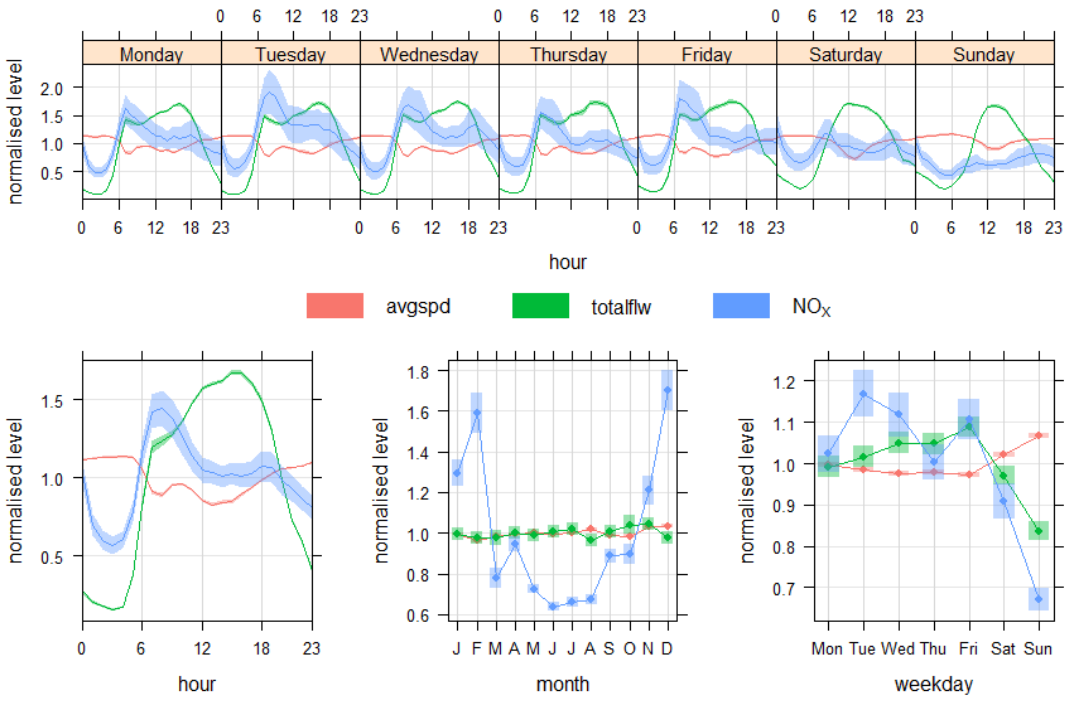


Figure 7.13. Time variations plots of average speed (km/hr), total flow (vehicles/hr) and NOx concentration (ppb) at Kirkstall road Leeds, November 2007 to October 2009. The shaded area (bars) show the estimated 95 % confidence intervals.

Table 7.1 compares Spearman correlation coefficients between average speed, traffic flow, ozone and NOx at direction 1 and direction 2 during both winter and summer. As expected, the effect of direction does not seem much difference on both NOx and ozone. For instance, traffic flow has positive correlation with NOx during winter and the correlation coefficients are 0.39 and 0.36 for direction 1 and 2, respectively. The effect of traffic flow during winter and summer is much clearer on ozone than on NOx. Traffic flows show positive correlation with ozone during summer and negative during winter on both direction 1 and 2. In contrast ozone shows negative correlation with average speed during summer and positive during winter on both direction 1 and 2.

Table 7.1. Spearman correlation coefficients of NOx (ppb) and ozone (ppb) with traffic flow (vehicles/hr) and speed (km/hr) during winter and summer for both directions 1 and 2 at Kirkstall site, November 2007 to October 2009.

R^2	NOx		Ozone	
	Winter	Summer	Winter	Summer
Direction 1 flow	0.39	0.44	-0.08	0.14
Direction 2 flow	0.36	0.35	-0.08	0.30
Direction 1 speed	-0.34	-0.42	0.10	-0.11
Direction 2 speed	-0.26	-0.30	0.09	-0.17

7.3.10 Modelling the effect of road traffic on ozone concentration using QRM

Road traffic is considered to be the main source of NOx, particulate matter (e.g., $PM_{2.5}$), carbon monoxides (CO), and hydrocarbons (HC). NOx and certain HC are important precursors of ground level ozone and cause to increase ozone concentration by taking part in photochemical ozone formation. However, increasing fresh NOx emissions are likely to reduce urban ozone concentrations due to scavenging effect. The effect of various air pollutants on ozone has been analysed in Chapter 6. Here the effect of road traffic characteristics (flows of cars, buses, vans, artics, motorcycles and trailers and average speed) on ground level is investigated employing a Quantile Regression Model. Hourly ozone and traffic data used in this study are from Kirkstall roadside monitoring site in Leeds

from January 2008 to May 2009. Ozone in measured in ppb, road flows are measured in number (counts) of vehicles per hour and vehicle speed is expressed as km / hour. The predictors traffic characteristics) and response variables (ozone) are of significantly different magnitudes. Therefore, the predictors were standardised (each observation was centred by subtracting mean from it and then scaled multiplying by standard deviation). This sort of standardisations make the coefficients of the regression model comparable and make the interpretation easy, especially in cases where the data are not on the same scale, as is the case here.

Traffic flow of each category of vehicles (e.g., cars or buses) was included in the model separately, however, in case of vehicle speed only average speed of all categories was used. This was because when the speed of each vehicle category was included in the model, it did not improve the model performance (model fit) and the model was much larger. It is worth mentioning that smaller models are always better in terms of computer memory requirement, data availability and result interpretation, if they explain the same variation in the modelled variable as the counterpart larger model. As mentioned above, cars were the dominant vehicle type at Kirkstall road and accounted for over 90% of the total traffic flow. Vans flow was about 5% and other categories all together were roughly 5% of the total flow. The speed limit at Kirkstall road, where the traffic detector loops were installed, was 30 miles per hour (48 km/hr), whereas observed average speed was 40 km/hr. Background ozone is mainly affected by regional emissions of precursors, inter-continental movement of ozone and Strato – Tropospheric Exchange (STE) of ozone, therefore it is important to remove the effect of background ozone before analysing the effect of local road traffic on urban decrement. Addressing the effect of background ozone is discussed in the next section.

7.3.10.1 Accounting for background effect

Ozone concentration at a particular location can be represented by a regional component and an urban ozone decrement (for details see Clapp and Jenkin, 2001, and Jenkin, 2004). According to AQEG (2009) the urban ozone decrement is the difference between the values of the ozone concentration at the urban location and the surrounding rural site, taken to be representative of the regional component. Therefore ozone concentration at the Kirkstall site was subtracted from that of the background site to obtain the urban ozone decrement.

Selecting an appropriate background site is the next important step. For this purpose two monitoring sites Ladybower and High Muffles were selected, situated about 45 km southwest and 75 km northeast of Leeds, respectively. These are both rural background nature sites. According to DEFRA rural sites are characterised by low NOx levels and the

air sampled is representative of air quality in a surrounding area of at least 1000 km^2 (UK-AIR, 2012). For further precaution ozone concentrations at Ladybower and High Muffles are averaged to account for local topographical effect (e.g. altitude) of each site.

Temporal variations of ozone urban decrement (ud) are shown in Figure 7.14. Urban decrement is higher during day and lower during the early hours of the morning. The morning peak hours exhibit highest urban decrement that reaches about 10 ppb or higher during weekdays. Weekend, especially Sunday exhibits a different trend. During different days of the week (Figure 7.14, bottom-right) urban decrement is minimal over the weekend, indicating low traffic flow on Saturday and Sunday. Annual cycle shows no clear variations in urban decrement, except during April and May when the urban decrements are exceptionally high. Further investigation showed (data not shown) that during April and May ozone concentrations were higher at both sites (background and the Kirkstall site); however the increment was relatively higher at the background sites, which might suggest higher rates of photochemical ozone formation at rural sites during April and May. The effect might be due to NO_2/NOx ratios which are generally higher at rural sites and their oxidation can positively contribute to ozone formation under favourable conditions.

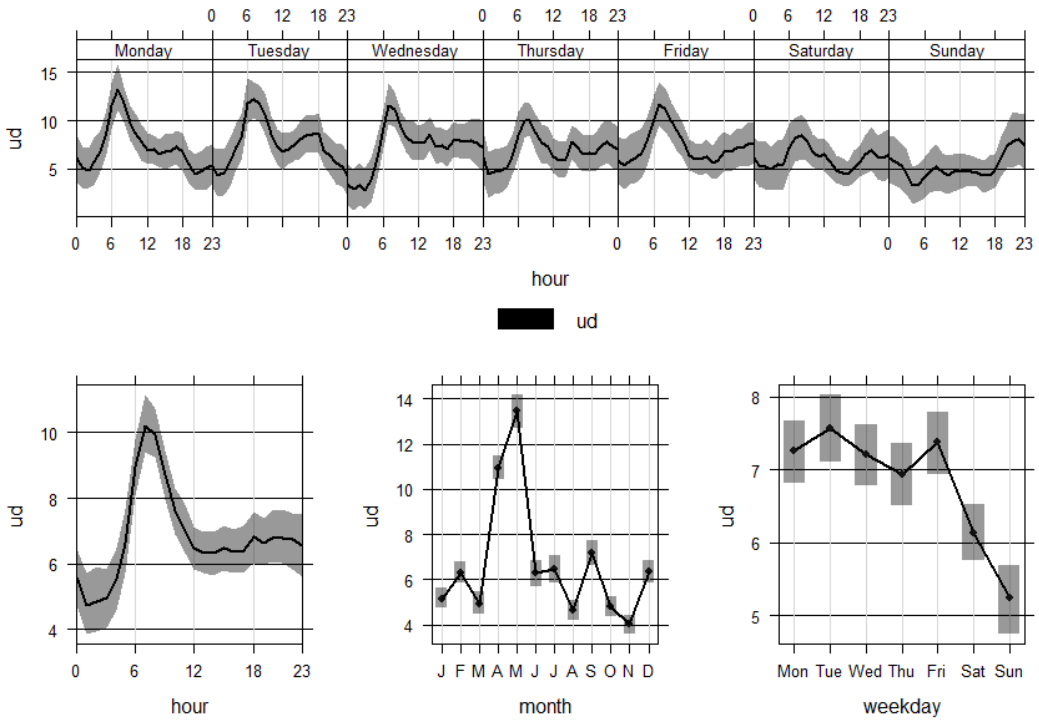


Figure 7.14. Temporal variations of urban decrements (ud, ppb) over different time periods at Kirkstall site using ozone data from January 2008 to May 2009. Hourly mean ozone concentration (ppb) at Kirkstall site is subtracted from hourly mean background ozone concentration (ppb) to obtain urban decrement.

7.3.10.2 QRM outputs

As mentioned above the covariates were standardised to have zero mean and unit standard deviation. The urban decrement is kept in original units (ppb). The standardisation of covariates in this way makes comparison of the impact of each variable feasible (Baur et al., 2004).

Figure 7.15 shows the outputs of the QRM. The red (horizontal solid) line along with its 95% confident intervals depicts the coefficients of least square regression. The line is also referred to as mean line. Quantile regression coefficients have been estimated for 10 quantiles, which are represented by dashed-dotted dark line with their 95% confident intervals. The quantiles have been shown on x-axis and their estimated quantile regression coefficients on y-axis. Positive coefficients indicate positive effect of the predictor on urban decrement, negative coefficients indicate negative effect and where confidence intervals overlap with the zero line, the effect is considered to be insignificant. Furthermore, if confidence intervals of a coefficient overlap with mean line, it means the effect is not significant differently from the mean effect. In this model the flows of cars, vans, buses, artic, cars with trailers, motorcycles and average speed are used as independent variables and urban decrement as dependent variable. The outputs of QRM (Figure 7.15) reveal that the effect of traffic flow on urban decrement is non-linear and changes over different quantiles. For some variables the nature (positive or negative) of coefficients remains the same and only the strength changes, for other both nature and strength change. The coefficients of intercepts are shown in Figure 7.15 (a) and range from -3 to 31 for quantile 0.1 and 0.99, respectively; the coefficients increase gradually from quantile 0.1 to 0.99. According to UK-AIR (2012) rural sites are not significantly affected by a particular local emission source, hence it can be assumed that the background ozone concentration is not significantly affected by the traffic flow at Kirkstall road.

The quantile regression coefficients for cars (Figure 7.15 - b) are positive and decrease from quantile 0.1 to 0.3. For quantile 0.4, 0.5 and 0.6 the coefficients are insignificant as the confidence intervals overlap with the zero line. Coefficients are negative at quantile 0.7, 0.8, 0.9 and 0.99; however the effect is insignificant at quantile 0.99. Car flow shows a positive effect on ozone urban decrement at lower quantiles and the effect is negative at higher quantiles. The effect is not significant at the middle quantiles (0.4 to 0.6), as the confident bands overlaps with zero line. The effect of vans flow (Figure 7.15 - c) is insignificant at most of the quantiles, except at 0.1 and 0.2 quantiles, where the effect is positive. The confidence band of the rest of the coefficients overlaps with zero line and hence the effect is not significant. The effect of buses flow (Figure 7.15 - d) is shown to be positive on urban decrement and is significant at all quantiles. For artics (articulated heavy

vehicles) (Figure 7.15 - e) the positive effect is significant at most of the quantiles, except at upper and lower extremes i.e. quantiles 0.1 and 0.99. The mean effect for artics is significant and has a regression coefficient of about 0.5. The flows of trailers (Figure 7.15 - f) have negative coefficients at most of the quantiles, except at quantile 0.1. The effect is not significant at the lower tail of the distribution. Motorcycle flows and average speed (Figure 7.15 – g & h) show insignificant effect at almost all quantiles of ozone distribution.

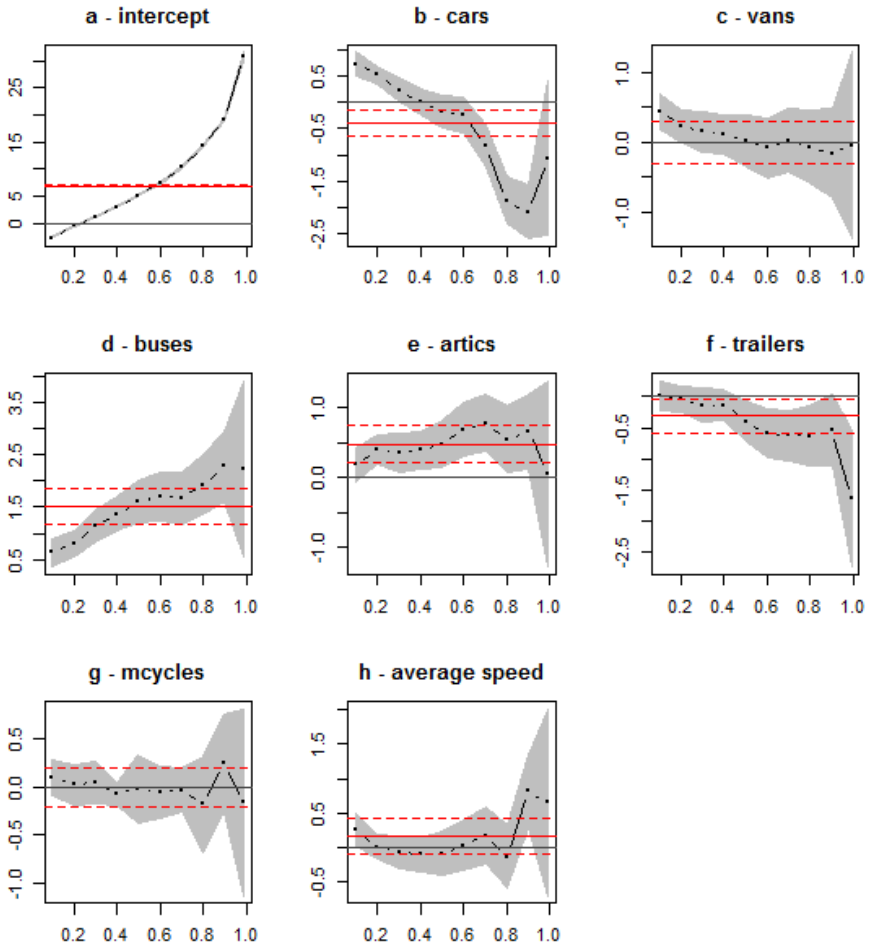


Figure 7.15. The outputs of QRM showing the effect of the flow of cars, vans, buses, artic, cars with trailers, motorcycles and average speed on urban decrement. Quantile regression coefficients (dashed dark line) and ordinary least square regression coefficients (solid red line) are presented with their 95% confidence interval.

According to Highway Agency (HA, 2005) NOx emissions are highest at lowest cruise speeds and decrease considerably until speeds reach about 60 to 70 km/hr. Beyond 70 km/hr NOx emissions tend to increase slightly (HA, 2005). However, more recent empirical studies confirmed that for modern vehicles high emissions of NOx are associated with transients (acceleration and deceleration events) rather than the average speed. Examples

include a tunnel study by Boulter et al., (2007) which monitored and analysed NOx emissions from different vehicle categories, and a driving behaviour study with an instrumented car (2003 Ford Mondeo - Euro III, 1.8, petrol) by Bell et al., (2006). The findings of this study seem to be in agreement with the idea that vehicle speed does not have significant effect on NOx concentrations and hence on ozone levels.

It is interesting to see that some of the traffic categories (e.g. cars) show a mixed effect i.e. the effect is positive at lower and negative at upper quantiles. In other words, cars act as a sink of ozone at lower tail causing urban decrement to increase, whereas they act as a source causing urban decrement to decrease at upper tail of the distribution (Figure 7.15 – e). Trailers show a closer pattern to that of cars with little deflection at some of the quantiles (see Figure 7.15 – f for detail). Buses and articulated heavy vehicles have positive effect at all quantiles of urban decrement, although buses have stronger quantile regression coefficients and smaller confident intervals indicating stronger effect. In other words, buses and artics act as a sink for ozone, which increase the difference between background and roadside concentrations. Buses on average seem to deplete 1.5 ppb ozone at the Kirkstall road; the amounts vary at different quantiles i.e. about 0.5 ppb and 2 ppb at quantile 0.1 and 0.99, respectively. Heavy goods vehicles cause about half a unit ozone decrement at most of the ozone quantiles. It is well established that buses and articulated heavy vehicles emit larger amount of gaseous NOx (e.g. Carslaw et al., 2011; Boulter et al., 2007), which scavenges ozone. Moreover, it is shown that the emission of diesels cars and diesel trucks have higher proportion of NO_2/NOx than petrol vehicles (Boulter et al., 2007). The negative impact of buses and articulated vehicles on urban ozone concentration might suggest that the emission of NOx plays more important role than the NO_2/NOx ratio on ozone concentration.

Six scenarios, based on the flow of buses, cars and articulated heavy vehicles were developed. Table 7.2 shows the scenarios and how they may affect ozone urban decrement compared to the present scenario at selected quantiles (0.5 and 0.99). In present scenario the road traffic has been taken as in May 2009, which had flow (vehicles/hr) of cars, buses and articulated vehicles as 738943, 12033, and 6032, respectively. To obtain the flows for other scenarios theses values can be simply multiplied or divided by 2 as required (scenarios shown in Table 7.2). Scenario 1 observes the highest whereas scenario 2 observes the lowest traffic flow. Traffic flows in other scenarios are in between these two scenarios. As expected, when the flows of buses, cars and articulated heavy vehicles were doubled, the urban decrement increased relative to the present scenario and vice versa. This is most probably related to the amount of NOx emitted by the road traffic, which scavenges ozone. For all scenarios the effect is more dominant at quantile 0.5 (median) than at quantile 0.99.

When the flow of buses was doubled, the urban decrement increased by about 13% at quantile 0.99 and was not significantly affected by the other two traffic categories. The highest urban decrement difference between present and future scenario was observed when the flow of buses and articulated heavy vehicles was doubled and that of cars was reduced to half; however the most practical scenario in terms of ozone level (and probably other air pollutants) seems to be the one which reduces the flow of cars and articulated heavy vehicles to half and double the flow of buses. This scenario suggests more public transport (e.g. buses) and reducing the number of taxis, cars and heavy goods vehicles in large cities of the UK.

Table 7.2. Various traffic scenarios and their impact on the ozone urban decrement (ud). Percent difference for quantile 0.5 and 0.99 was calculated as [(future scenario – present scenario)*100]/present scenario. Q stands for quantile in the table.

Future scenario	ud in present scenario		ud in future scenario		% diff. for Q 0.5	% diff. for Q 0.99
	Q 0.5	Q 0.99	Q 0.5	Q 0.99		
Buses flow*2, Cars flow*2 Artic flow*2	5.21	30.94	7.74	30.20	48.55	4.8
Buses flow/2, Cars flow/2 Artic flow/2	5.21	30.94	3.94	30.20	-24.27	-2.4
Buses flow*2, Cars flow/2 Artic flow/2	5.21	30.94	7.32	34.88	40.47	12.74
Buses flow*2, Cars flow/2 Artic flow*2	5.21	30.94	8.15	34.98	56.53	13.04
Buses flow*2, Cars flow/2 Artic flow	5.21	30.94	7.60	34.91	45.82	12.84
Buses flow*2, Cars flow Artic flow	5.21	30.94	7.45	34.06	43.16	10.09
Buses flow/2, Cars flow Artic flow	5.21	30.94	4.08	29.38	-21.58	-5.04

7.3.10.3 Assessment of the model

In Figure 7.16 local goodness-of-fit $R^1\tau$ (define in chapter 4) are shown for the QRM model. Local goodness of fits range from 0.01 to 0.05 for quantile 0.2 and 0.99, respectively. The model was developed for January 2008 to April 2009 and tested for May 2009. Several other statistics metrics: FAC2, RMSE, R2, MB, NMB, MGE, and NMGE were calculated

(Defined in chapter 4) (see e.g., Derwent et al., 2010; Carslaw, 2011). The values are shown in Table 7.3.The metrics estimated show good performance of the QRM model and over performs the multiple regression model. FAC2 of 0.78 for QRM shows that 78 % percent points lie within the factor of 2 region, the minim acceptable standard for a model is 50 %. OLS fails this standard (FAC2 < 0.50). Other metrics for instance, NMB (0.07) and R^2 (0.90) indicate good performance of the QRM model, which is significantly better than OLS. Figure 7.17 depicts the predicted ozone concentrations by both QRM and OLS versus observed hourly ozone concentrations at Kirkstall road Leeds for the month of May, 2009. QRM particularly performs better at extreme values. Baur et al., 2004 and Sausa et al., 2008 have also reported highly better performance of QRM against OLS.

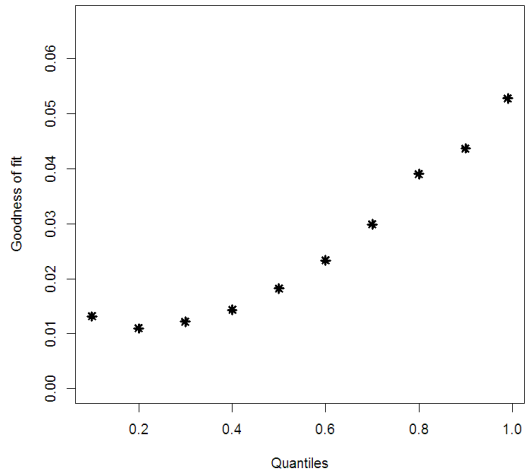


Figure 7.16. Local goodness of fit R^1 (τ) as a function of ozone quantiles for the quantile regression model at Kirkstall site Leeds.

Table 7.3. Comparison of statistics metrics for QRM (Quanitle regression model) and OLS (ordinary least square) models. These metrics have been defined in chapter 4. R^1 shows global goodness of fit for QRM and R^2 shows coefficients of determination for OLS.

Metrics	QRM	OLS
FAC2	0.78	0.49
MB	1.85	-0.35
MGE	2.94	5.91
NMB	0.07	-0.05
NMGE	0.43	0.82
RMSE	4.26	8.08
R^1/R^2	0.90	< 0.50

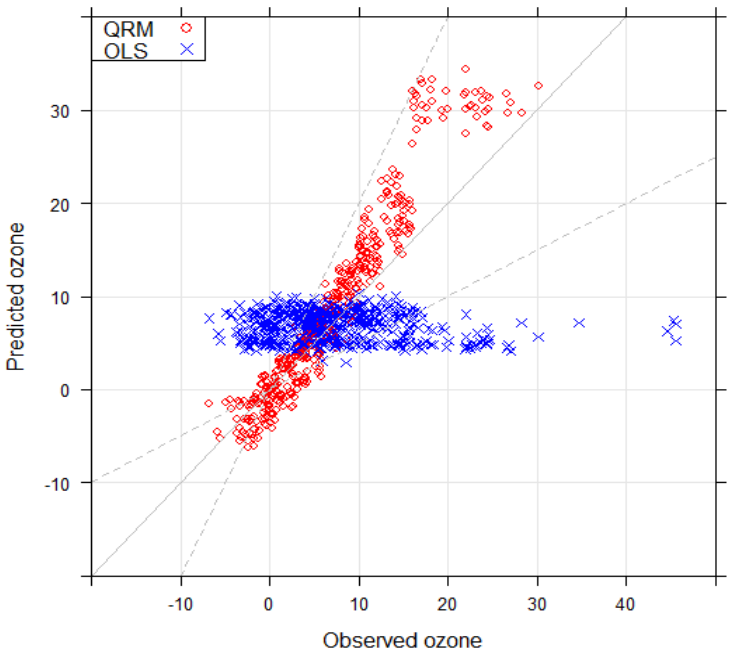


Figure 7.17. Observed versus predicted urban decrement (ppb) at Kirkstall site for May 2009 using AQRM (R^1=0.90) and OLS (ordinary least square regression, R^2 < 0.5).

7.3.11 Urban influence

In this section data from 80 ozone monitoring sites are used to compare ozone concentrations (ppb) at urban and rural sites using a dummy QRM model. Figure 7.18 shows the outputs of dummy QRM. Regression coefficient of the least square regression model is shown by horizontal dashed red line, whereas the quantile regression coefficients for 10 quantiles are represented by dashed-dotted dark line. The quantiles have been shown on x-axis and their estimated quantile regression coefficients on y-axis. In this model 5 years (2007 to 2011) mean ozone concentration (ppb) was used as dependent variable and site type (rural and urban) as independent variable. The dummy variable 0 represented urban and 1 represented rural sites.

In Figure 7.18, the top-panel shows ozone concentration (ppb) at urban sites, and the bottom-panel shows the amount by which ozone concentration in urban areas is less relative to the rural sites at various quantiles. The urban decrement varies at different quantiles of ozone concentration and ranges from 5.25 ppb (25%) to 10.78 ppb (30%) for quantile 0.1 and 0.99, respectively. From quantiles 0.2 to 0.8 the urban decrement do not seem to change much from the mean urban decrement, which is about 7 ppb (26%) estimated by OLS.

Urban and rural ozone concentrations along with urban decrement averaged over 5 years (2007 to 2011) at different quantiles are shown in Figure 7.19. From quantile 0.2 to 0.8 the difference in rural and urban concentrations is about 6.5 ppb. At both extremes (lower and upper tails) the difference is higher. At minimum and maximum ozone concentrations the difference is 9 and 11 ppb, respectively.

Highest ozone concentration (5 years mean in ppb) was recorded for Mace Head (36.5) and Strath Vaich (34) and lowest for London Marylebone (8.25). Mace Head and Strath Vaich are both rural sites, whereas London Marylebone is an urban traffic site. Mace Head is a coastal site and is characterised by comparatively low dry deposition rate at water surfaces (Entwistle et al., 1997) and minimal ozone titration by NO. Strath Vaich is one of the remote (rural background nature) sites and has low level of NOx. On the other hand Marylebone site is located next to a very busy road that is subject to frequent traffic congestions. Traffic flows of over 80,000 vehicles per day pass the site on six lanes (UK-Air, 2012) that emit large amount of NOx that scavenge ozone molecules. Annual average NOx concentration in year 2011 was 21, 23 and 305 $\mu g/m^3$ for Strath Vaich, Mace Head and Marylebone, respectively. Rural monitoring sites are located more than 20 km away from agglomerations (large urban areas) and more than 5 km away from other built-up areas, industrial installations or motorways or major roads, so that the air sampled is representative of air quality in a surrounding area of at least 1000 km^2 (UK-AIR, 2012). Due to these

characteristics rural sites are generally characterised by low traffic flow and hence low NO and most probably that is the reason why rural sites have higher ozone concentrations than urban sites.

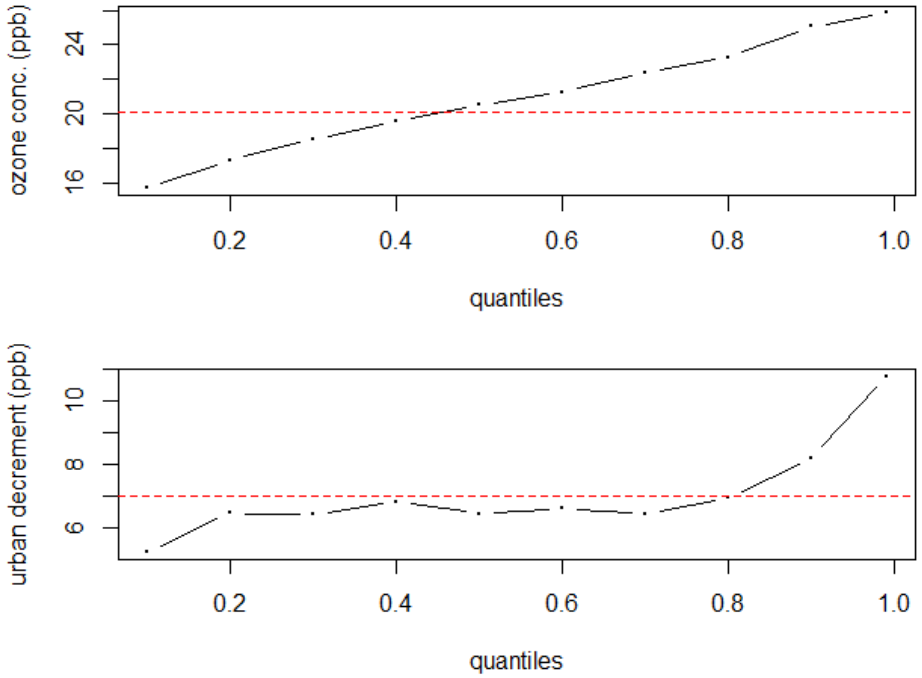


Figure 7.18.The outputs of QRM using dummy variable for monitoring site type (urban and rural), using 5 years (2007 to 2011) mean ozone concentration (ppb) from eighty ozone monitoring sites. Top – panel shows ozone concentration (ppb) at urban sites and bottom – panel shows the urban decrement at various quantiles.

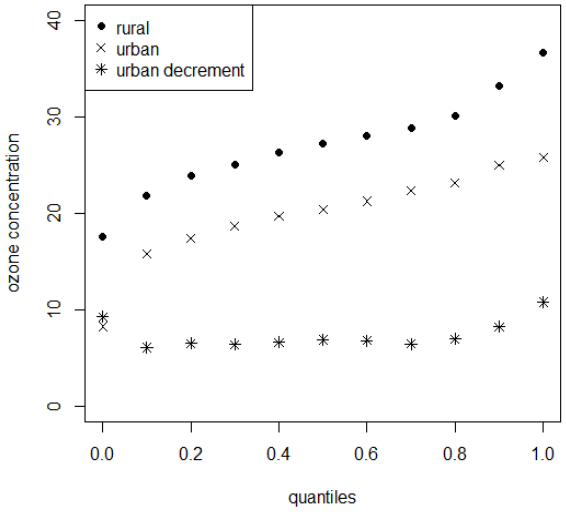


Figure 7.19.Comparing rural and urban ozone concentrations, and their differences (urban decrements) at various quantiles (0.01, 0.1 - 0.9, 0.99) for year 2011 from 80 ozone monitoring sites.

7.4 Summary

This chapter characterises the effect of road traffic characteristics on ozone concentration (ppb) in urban areas using a QRM model. Firstly traffic characteristics, such as traffic flow (vehicles/hr), speed (km/hr) and composition are described at the Kirkstall monitoring site with the help of time variation plots. Car is the dominant traffic category at the Kirkstall road making about 90% of the total flow, followed by van (5 %) and the rest were buses, artic, motorcycles and cars with trailers. The speed limit at the road is 48 km per hour and observed average speed was 40 km per hour. The effect of road traffic characteristics on ozone concentrations has been investigated in three different ways: Using graphical presentation, correlation analysis and quantile regressions. Using QRM model it is shown that both strength and nature of the relationship between ozone concentration and traffic characteristics changes at different quantiles. The results of QRM show that up to 90% ozone variations between rural and urban sites can be explained with the help of road traffic characteristics. Buses are shown to have the strongest positive effect on urban decrement. In other words buses act as a strong sink for ozone concentrations at urban sites. Various traffic scenarios and their effects on ozone concentrations have been investigated. The findings favour the use of public transport (e.g. buses) in urban areas for better air quality management, especially ground level ozone.

It is worthwhile briefly re-emphasising the novelty and implications of this chapter. Firstly, this chapter employs a modelling technique (QRM), although well established in some other areas, which is applied for the first time to investigate the association of ozone and road traffic characteristics. The model successfully addresses nonlinearities in the association of ozone and road traffic, is applicable to non-normal ozone distribution, and models the effects of road traffic characteristics on the whole ozone distribution, most notably using QRM to separately model the extreme values that conventional mean based models more often ignore. Secondly, the dummy model developed to compare rural and urban monitoring sites, again using a QRM approach, provides an amenable approach for modelling urban decrement without any need for traffic or meteorological parameters data. Thirdly, this chapter improves the modelling methodology by addressing the background concentration and recommends that background concentration must be deducted before modelling the effect of road traffic on ozone concentration at local level. The background ozone is the sum of STE (Stratospheric-Tropospheric Exchange), regional and inter-continental contribution, and therefore cannot be accounted for by local traffic. This is ignored in the previous studies, which would add to the uncertainties of the models produced in those studies.

Furthermore, ozone concentrations at rural and urban sites are compared using data from 80 monitoring sites for over 5 years (2007 to 2011). The model results show that ozone concentrations on average are lower at urban monitoring sites by 7 ppb (26%) than at rural sites. The differences vary at different quantiles, for instance at quantile 0.1 and 0.99 the difference is 5.25 ppb (25%) and 10.78 ppb (30%), respectively. This difference is referred to as urban decrement and can be linked with freshly emitted NOx by road traffic, which is an effective ozone scavenger.

As the legal speed limit is 48 km/hr and observed average road speed is 40 km/hr at Kirkstall road, therefore it is suggested to further investigate the relationship of ozone with vehicle speed using traffic data from a site where a much broader range of speeds are encountered. Moreover, the effect of different fuel types (particularly petrol and diesel), vehicle age and drivers behaviour cannot be identified from our dataset; therefore further research is required to study the effect of these factors on ozone concentrations, which can help in better understanding of the relationship of ozone with road traffics and their future implication for policy makers.

Meteorological conditions (e.g., temperature, solar radiation, wind speed) play a vital role in controlling ozone variations, which needs to be considered for detail ozone modelling. Next chapter characterises the effect of meteorology on ozone concentrations.

CHAPTER 8: GROUND LEVEL OZONE AND METEOROLOGY

8.1 Introduction

A decrease or increase in air pollution concentration is the result of an imbalance between air pollutants production rates (emission of primary pollutants from sources and formation of secondary pollutants in the atmosphere) and air pollutants removal rates (dispersion/dilution and loss from the atmosphere). Meteorology plays a vital role in photochemical ozone formation (e.g., temperature and solar radiation) and ozone removal or dilution (e.g., wind). Meteorological factors such as temperature, solar radiations, relative humidity, and wind speed can influence the transport, dispersion and chemical reactions of air pollutants. Substantial variations in meteorological conditions can exert a large impact on ozone concentration and often mask long term trends in ozone concentration (Duenas et al., 2002; Gardener and Dorling, 1999). Summer and spring time high ozone episodes are caused by the high level of solar radiation and temperatures in the UK and elsewhere (AQEG, 2009).

Long range transport, chemical and physical transformation and deposition of air pollutants are strongly dependent on meteorological conditions and vary considerably from year to year due to variation in meteorological conditions. Consideration of meteorological variability on different timescales, from hours to decades is, therefore, necessary when trying to understand trends in various air pollution components or when assessing and detecting the consequences of emission reductions aimed at improving air pollution levels. For more details on the effect of meteorology on ozone concentration see: Andersson et al. (2006); Baur et al. (2004); Cardenas et al. (1998); and Duenas et al. (2002). A brief critical analysis of these studies can be found in chapter 3.

Ozone is a secondary air pollutant and is formed in the atmosphere by photochemical reactions of VOCs and NOx in the presence of solar radiation. Other atmospheric parameters play a vital role in the photochemical ozone formation, horizontal and vertical movement, ozone destruction and dry deposition. This is probably why many researchers have investigated the effect of meteorological variables on ozone concentration. However, there are several issues that need further investigation, which this chapter intends to address: (a) Very often ozone and meteorological parameters used in the models are not measured at the same monitoring site. The reason for this is that generally, particularly in the UK, air quality monitoring stations do not have facilities for monitor meteorological parameters (e.g., wind speed, wind direction, temperature etc.). It is shown in the previous chapters that

ozone exhibits considerable spatial variability in the UK due to changes in local geographical conditions or rural – urban factors, therefore if meteorological and ozone data are not collocated at the same site this can introduce a degree of uncertainty in the model; (b) Ordinary linear regression is the most widely used approach to model the effect of meteorology on ozone concentrations. This approach is based on certain assumptions (e.g., normal distribution and linearity of the association between dependent and independent variables) and if the data do not meet these assumptions, the outcome of the model could be biased; (c) Most of the models used for investigating the effect of meteorology on ozone are mean oriented i.e. they model the mean effect of the predictors on response variable. Mean could be biased by outliers or skewed distributions, which is the case in ozone concentration. Therefore more robust approaches based on median or quantiles may be more suitable for analysing the association between ozone and meteorology. Quantile Regression Model (QRM) is employed in this chapter, which is applicable to both normal and non-normal distribution and can handle the non-linearities in the association of ozone and meteorological parameters. Furthermore, QRM helps investigate the effect of meteorology on various quantiles of the ozone distribution including both extremes, especially the right tail which is more important from public health perspective.

8.2 Methodology

In this chapter the effects of meteorological variables data, such as wind speed (m/s), wind direction (degrees from the north), temperature (^{o}C), solar radiation (watt/m^{2}), and relative humidity (%) on ozone concentration (ppb) have been investigated, using hourly mean data of these variables for a period of nearly two years (November 2007 to October 2009) which have been collected at Kirkstall roadside monitoring site in Leeds (described in chapter 4). Data from Marylebone monitoring site in London for year 2008 are also used, which is part of the UK Automatic Urban and Rural Network (AURN) (Described in chapter 4). This chapter uses correlation analysis, graphical presentations (e.g., scatter plots and time variation plots) and QRM model (described in chapter 4). Several statistical metrics (e.g., RMSE, MB, FAC2, see chapter 4, section 4.7 for details on these metrics) are calculated to assess the performance of the model. The model performances at Kirkstall and Marylebone sites are compared. All statistical analysis is performed using R programming language (R Development Team, 2012), and two of its packages: Openair (Carslaw and Ropkins, 2012) and Quantreg (Koenker, 2012).

8.3 Results and Discussions

8.3.1 Temperature

The air quality monitoring instruments used at Institute for Transport Studies are supplied by Enviro-technology and they use the following analysers for measuring air pollutants:

- CO – Infrared analyser (API M300E);
- NOx – Chemiluminescent analyser (API M200A) ;
- Ozone – Ultraviolet (UV) analyser (API M400E) ;
- HC – Photo ionisation gas chromatograph (syntech spectras GC955-603).

In addition, temperature sensor, relative humidity sensor, solar radiation sensor, and anemometer are used for meteorological observation. The data are stored in a computer at ITS, where the data was validated before use. At the Institute for Transport Studies, University of Leeds to ensure the quality of data is maintained, automatic nightly calibrations of gaseous analysers, and fortnightly manual zero and span calibration using calibration gases CO, NO, and NO_2 are performed routinely for air quality monitoring instruments. After collection the data go through verification, a process to clean-up the initial data. The data are archived in ITS for future use as and when required. Before analysis data were further investigated to check for any abnormal data.

Firstly hourly mean data of temperature from Kirkstall site have been presented as a histogram to observe its distribution and detect outliers, if any. Figure 8.1(a) shows the histogram of temperature data for nearly a two years period and clearly indicates that there are some outliers at temperature 30^{o}C or above. There are about 7000 observations showing temperature greater than 40^{o}C and over 5000 observations showing measured temperature 50^{O}C, which obviously cannot be right, as in the UK temperature never reaches this level. As shown in Figure 8.1 and 8.2, the temperature data at the Kirkstall monitoring site are not reliable and a significant proportion of the data are suspicious. The air quality technician, responsible for the maintenance and routine visit of the air quality network confirmed that the temperature sensor (thermometer) was not working properly during the period where abnormal readings are shown. The data were also compared with another monitoring site (Marylebone) to see the pattern in temperature observation. The assumption was that there would be a consistent pattern in observed temperature at the both monitoring sites, expecting temperature to be slightly higher at the Marylebone site due to ‘urban heat island’ effect. Based on this assumption only four months (November 2007, July, August and September 2009) data were considered acceptable for the PhD project and were used for graphical presentation and correlation analysis. However, these data were not used in the QRM model which was develop for 2008 for Kirkstall monitoring site. To investigate the effect of temperature on ozone using QRM, this project used data from the Marylebone monitoring site.

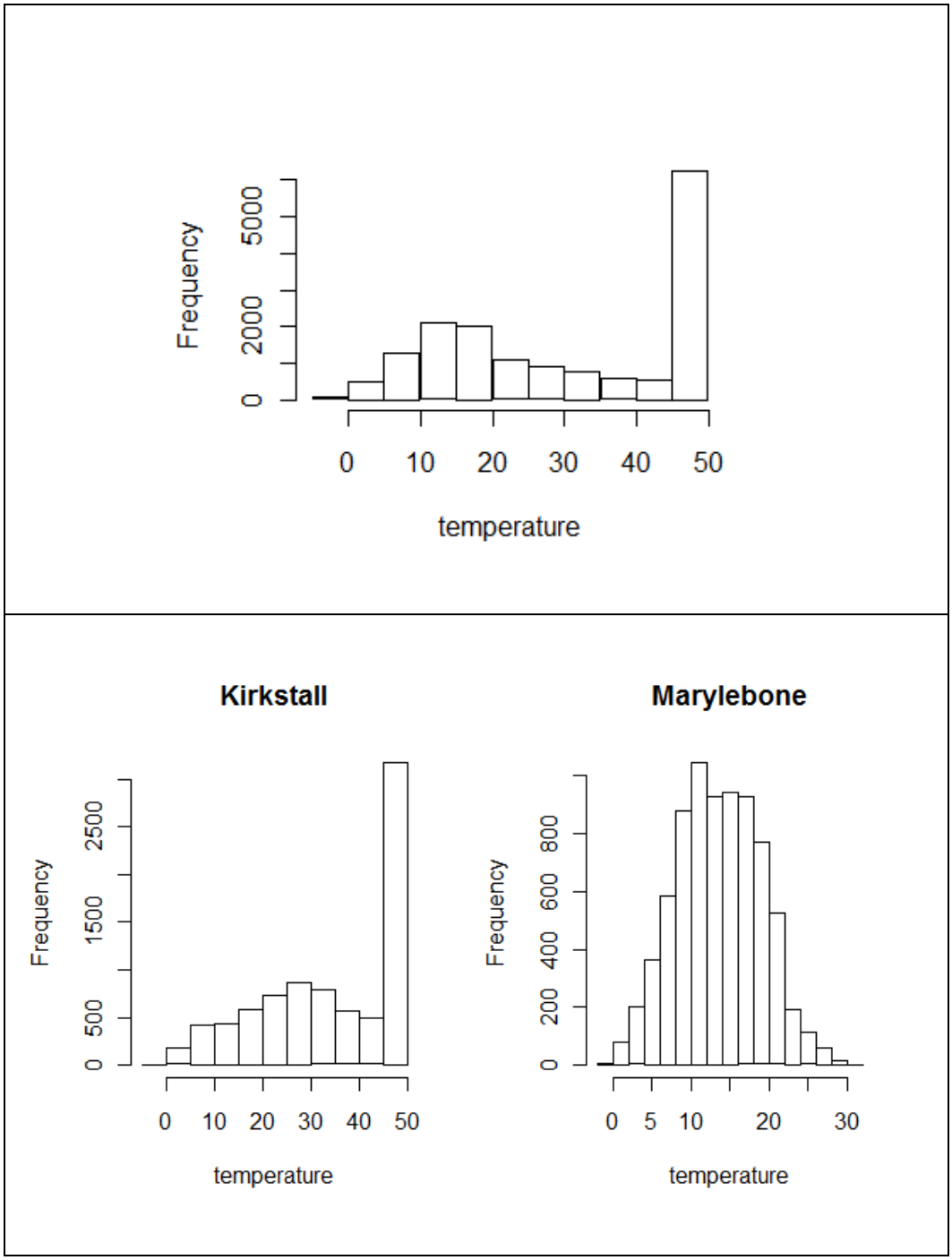


Figure 8.1. Histograms of hourly mean temperature data Kirkstall site for November 2007 to October 2009 (top); Marylebone 2008 (bottom-right), and Kirkstall 2008 (bottom-left).

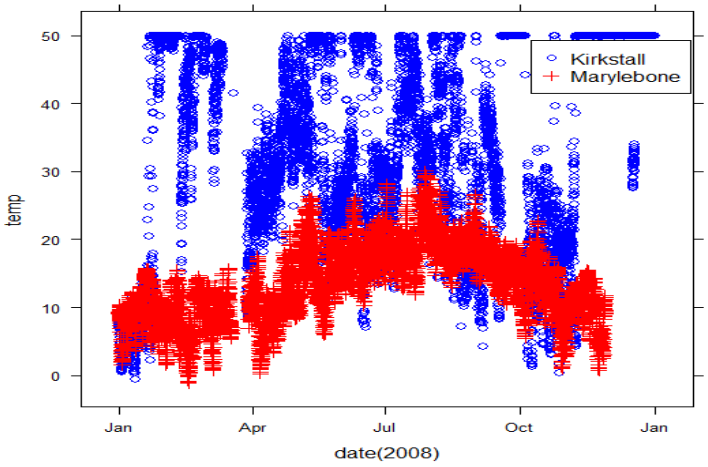


Figure 8.2. Comparison of temperature observations at Kirkstall (blue circle, o) and Marylebone (red plus-sign, +) monitoring site for year 2008.

8.3.1.1 Ozone and temperature

Figure 8.3 provides a graphical presentation of both ozone and temperature for year 2008 at Marylebone site. Generally both temperature and ozone concentration are lower during winter months and higher during summer months, however the highest ozone concentration is recorded in May, whereas highest temperature is recorded in July (Figure 8.3-b). Ozone concentration starts increasing after February and therefore March and April show considerably higher ozone concentrations compared to winter months, whereas observed temperature is still considerably low in these months. The month of May shows the highest ozone concentration and after that ozone concentration starts declining and reaches to the baseline level in August. Temperature on the other hand still increases after May and reaches highest level in July and August. Mean temperature in September is nearly as high as in May, however ozone concentration in this month is nearly as low as in winter months. Therefore although ozone and temperature are positively correlated, there seems to be some other factors which weaken the correlation. These other factors might be solar radiation, wind speed or ozone precursors, e.g. nitrogen oxides (NOx) and volatile organic compounds (VOCs). The Spearman correlation coefficient between ozone and temperature was 0.40, which shows positive association but not very strong.

Figure 8.3 (c and d) show the diurnal and weekly cycle of temperature and ozone concentration. On weekly basis the relationship of the two variables is very weak. There is no clear pattern in temperature level and mean temperature remains flat during different days of the week, which is expected. On the other hand ozone concentration is higher during weekend and lower during weekdays, most probably due to road traffic levels which are lower during weekend. The diurnal cycle of temperature and ozone concentration have a

close relationship. Both ozone concentration and temperature level increase in the morning after 06:00 and reach their maximal levels in the afternoon about 15:00. Thereafter temperature and ozone concentrations start declining again. The diurnal cycle of temperature and ozone concentration at Kirkstall and Marylebone monitoring sites for the months of July, August and September have been compared in Figure 8.4 and they show almost the same correlation, except that ozone concentration is higher at Kirkstall site whereas temperature is slightly higher at Marylebone site. Lower concentration and slightly different diurnal cycle of ozone at Marylebone site is most probably due the higher traffic flow at Marylebone road, compared to Kirkstall road. The Spearman correlation coefficient is significantly higher for the Kirkstall site. The correlation coefficients values for the three months were 0.14 and 0.39 for Marylebone and Kirkstall site, respectively. Marylebone road is a very busy road and has a traffic flow over 80000 per day. In addition it is considered as a street canyon location where recirculation of air pollutants may play an important role in ozone concentration. These extra contributions from high road traffic flow and complex location probably weakens the correlation between ozone and temperature at Marylebone site.

The three months (July – September, 2009) data from Kirkstall site were further analysed (Figure 8.5). It can be seen that the ozone concentration is higher in the start of July (1, 2, and 3 of July), which is reproduced in Figure 8.5 (top-right) and it is shown as to how closely the ozone higher concentration relates with temperature. The correlation coefficient between ozone and temperature for these three days was 0.65. To see how the effect of temperature on ozone concentration changes during hours of the day (light) and night (dark), ozone and temperature data were separated into day hours (06, 07, 08, 09, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20) and night hours (21,22, 23, 00, 01, 02, 03, 04, 05). As in July the sun rises at about 05:00 in the morning and sets about 21:00 hour in the evening in the UK. The correlation coefficients for the day hours was much stronger (0.84) than the night hours (0.12), which is expected as high temperature accompanied by high level of solar radiation during day time increases photochemical ozone formation and hence both have stronger association. The scatter plots between temperature and ozone concentration for the day and night hours are shown in Figure 8.5 (bottom). Although the data come from a roadside monitoring site where fresh NO emitted by local road traffic may be scavenging a significant amount of ozone, still photochemical ozone formation caused by high temperature and solar radiation results in high ozone levels and shows a very strong positive correlation with temperature, particularly during the summer afternoon. Many authors (e.g., Duncan et al., 2009) have shown that biogenic isoprene emissions, which lead to ozone formation, are a strong function of temperature. Therefore in addition to direct effect on ozone photochemical formation, temperature indirectly affects ozone concentrations by

influencing the emissions of its precursors, particularly from biogenic sources.

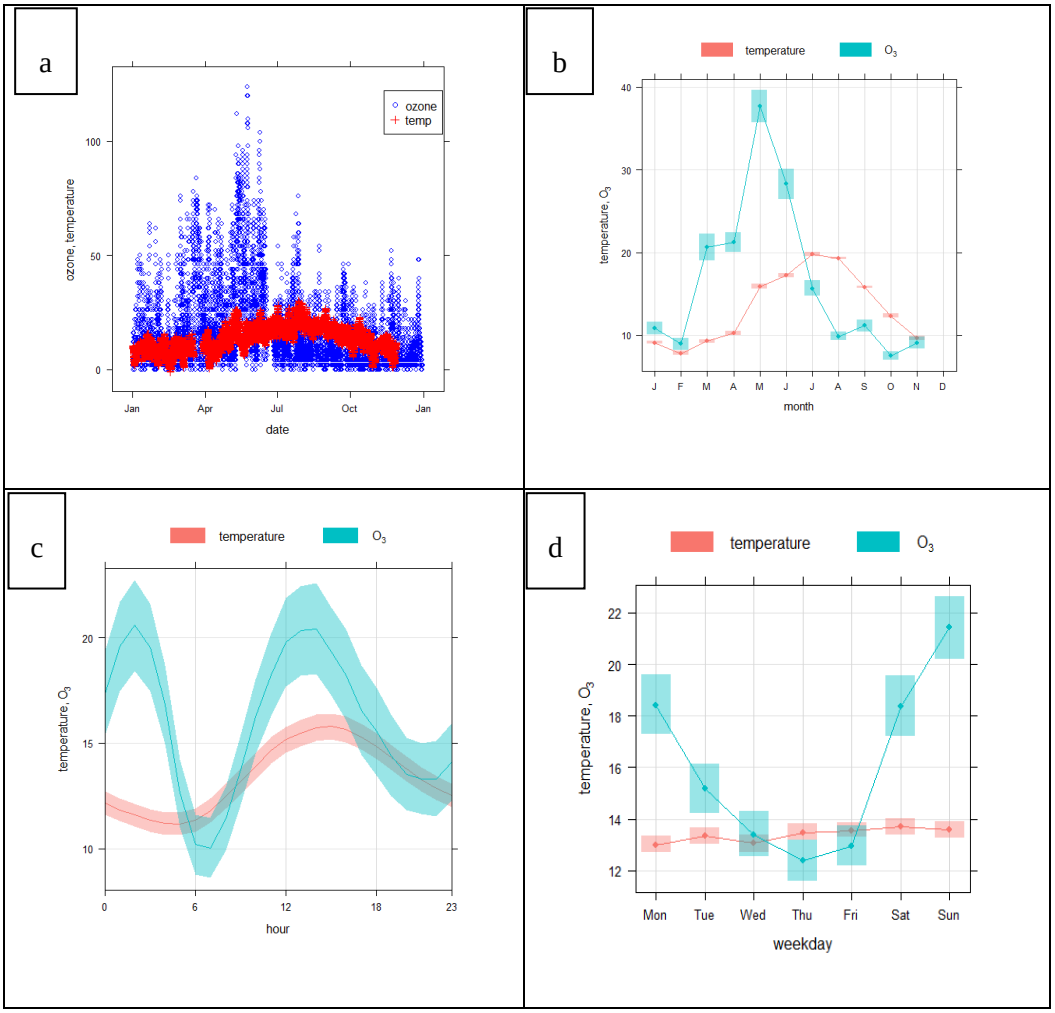


Figure 8.3. The relationship of ozone concentration (ppb) with temperature (^{o}C) for the year 2008 at Marylebone monitoring site in London (a) hourly mean data, (b) monthly mean data, (c) diurnal cycle, and (d) weekly cycle.

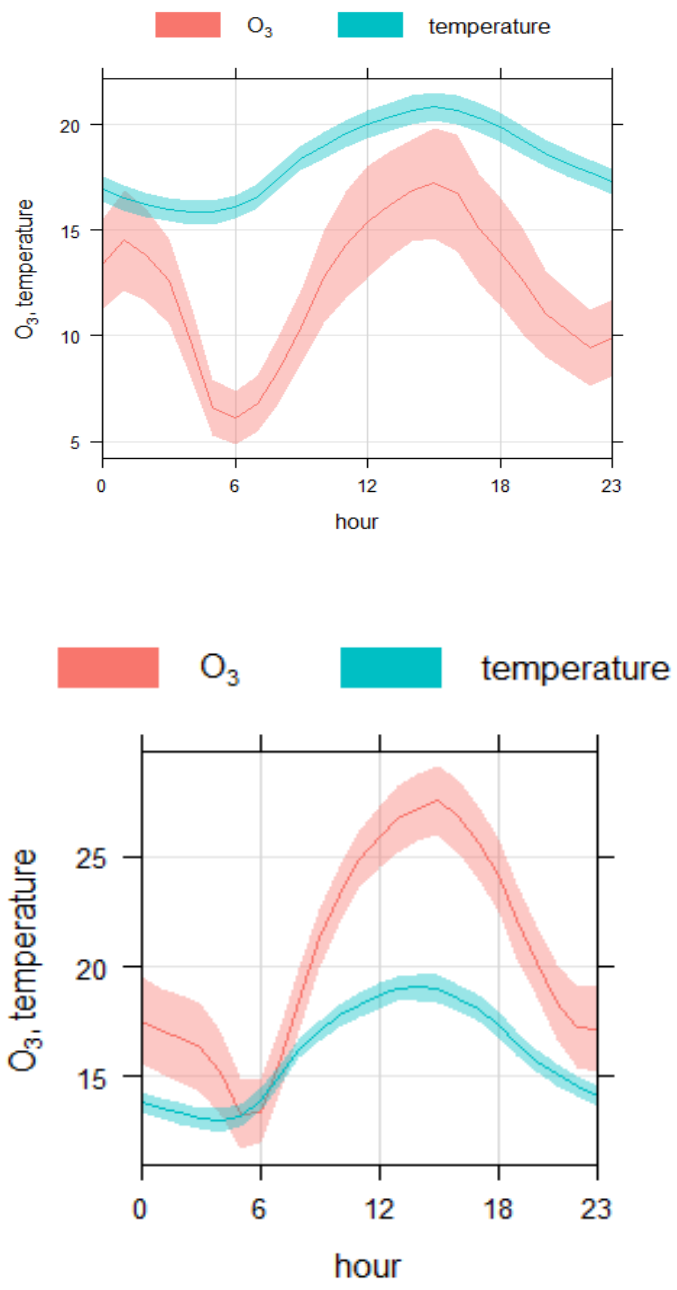


Figure 8.4. The relationship of ozone and temperature for the months of July, August and September 2008 at Kirkstall (bottom) and Marylebone (top) monitoring site.

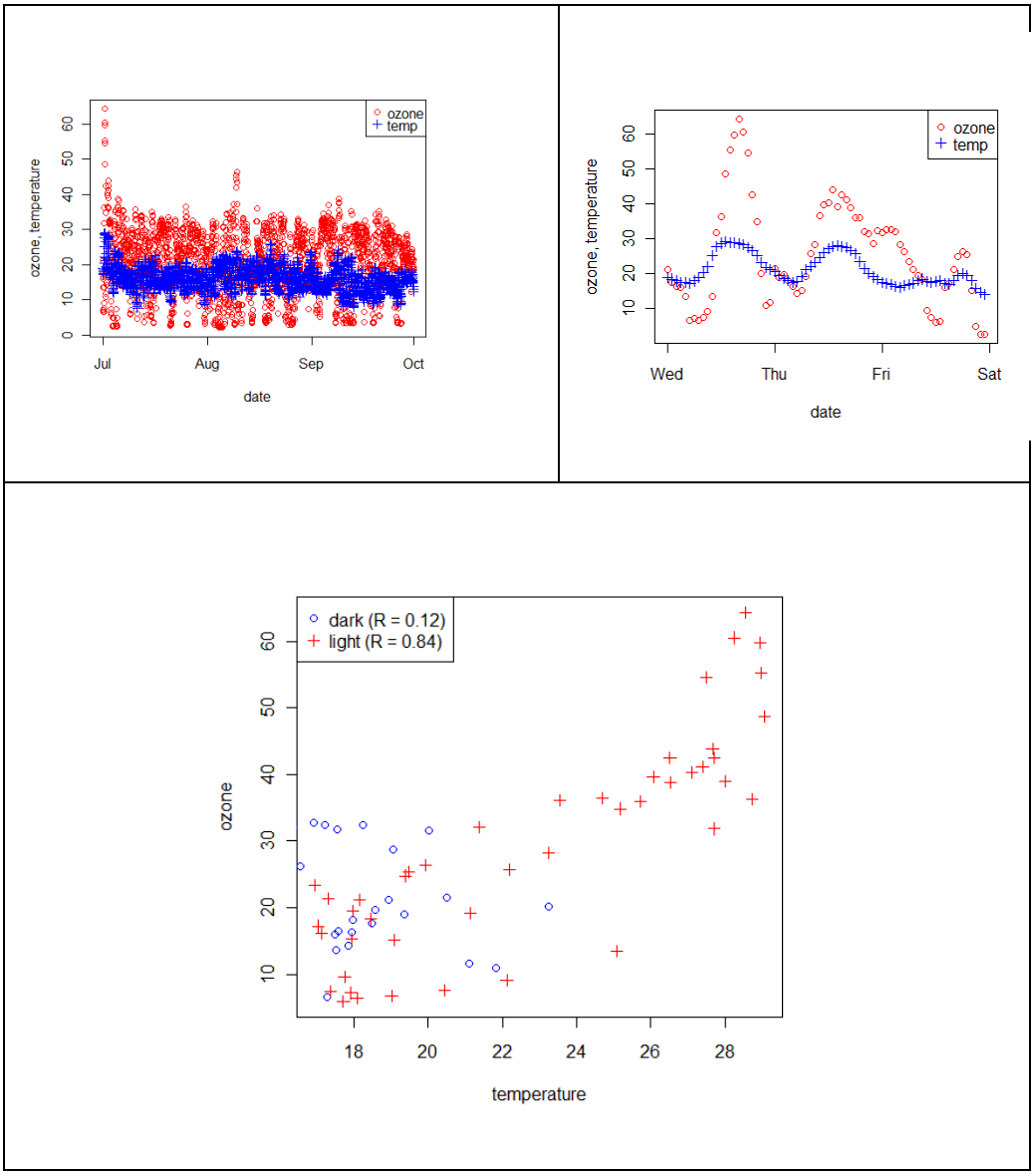


Figure 8.5. Temperature (^{o}C) and ozone concentration (ppb) for July – September 2009 (top-left) and 1-3 July 2009 (top-right) at Kirkstall site. Scatter plot (bottom) showing correlation between ozone concentration (ppb) and temperature (^{o}C) during day (06:00 to 20:00 hour, when Spearman correlation coefficient (R) was 0.84) and night hours (00:00 to 05:00, 21:00 to 23:00 hour, when R value was 0.12).

8.3.2 Solar radiation

Radiation having wavelengths up to 0.24 µm has enough energy to break oxygen molecules (O_2) into oxygen atoms (O). The atomic oxygen liberated in the process is vital for stratospheric ozone production. The ultraviolet (UV) radiation up to 0.31 µm of wave length is absorbed by ozone which causes ozone to dissociate into molecular and atomic oxygen. This process is vital for protecting living things from the harmful effects of the strong UV radiation. Most of the solar radiation having wave length longer than 0.31 µm successfully

reaches the earth surface. These are between ultraviolet and infrared radiation and are known as visible light or visible part of the electromagnetic spectrum (0.39 to 0.76 µm) . (Figure 8.6). Photodissociation of NO_2 ($NO_2 + h\nu \rightarrow NO + O^3P$) can take place in the wavelength range from ultraviolet to visible light spectrum. The atomic oxygen produced then reacts with oxygen molecule and form an ozone molecule ($O_3P + O_2 \rightarrow O_3$).

In Figure 8.7 (left) a histogram shows the frequency distribution of solar radiation and can be observed that the distribution is not normal and is right skewed. The highest frequency is shown when the solar radiation level is from 200 to 300 (w/m^2). The minimum, mean, median and maximum observed solar radiation level was 158, 288, 256 and 978 w/m^2, respectively. The median is smaller than mean value, which shows that the mean is affected by the few larger observations in the right end of the distribution. Figure 8.7 (right) shows higher solar radiation in June and July; and lowest in January and February. On the other hand ozone levels were highest in March – May and Lowest in November – December.

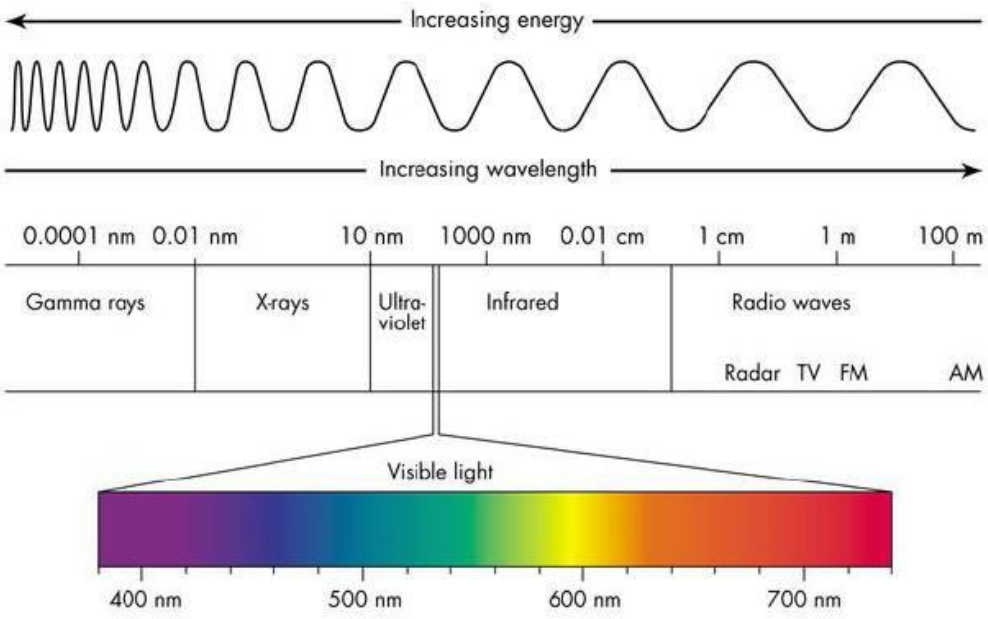


Figure 8.6. Electromagnetic spectrum.

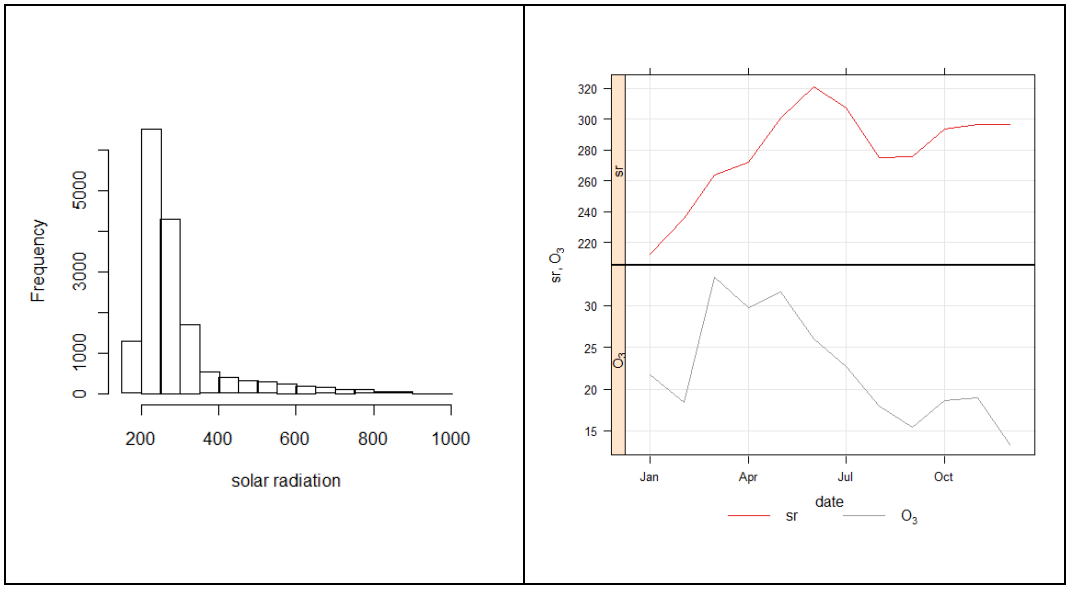


Figure 8.7. Solar radiation (sr) plots histogram of hourly data for November 2007 to October 2009 (left), monthly mean solar radiation and ozone for 2008 from Kirkstall road in Leeds (right).

8.3.2.1 Solar radiation and ozone

Solar radiation (watts / m^2) hourly data for nearly 2 year period (November 2007 to October 2009) from Kirkstall road in Leeds are analysed in conjunction with ozone hourly mean concentrations. The scatter plot of ozone versus solar radiation is shown is Figure 8.8, as the dataset is large and there is considerable over-plotting of the data points, therefore hexagonal binning technique (hexbin) has been used to bin the data. The numbers of points have been colour coded on the right side of the Figure 8.8. For more details on 'hexbin' see Carslaw and Karl (2012). Figure 8.8 (a) shows a positive correlation between ozone and solar radiation and the value of spearman correlation coefficient for the whole dataset was 0.24. Figure 8.8 (b) shows scatter plot between ozone and solar radiation for 4 different seasons of year 2008 i.e. spring (March, April, May), summer (June, July, August), autumn (September, October, November) and winter (December, January, February). The correlation coefficient significantly varied for different seasons. The strongest correlation was observed for the months of summer (0.49) followed by autumn (0.39). The weakest correlation was found for winter (0.01) followed by spring (0.28). The correlation was significant for all four seasons.

As can be observed in Figure 8.7 (right) the level of solar radiation is higher in summer. Similarly highest temperature was observed in summer (Figure 8.3), whereas the highest level of ozone is observed in spring. The highest levels of solar radiation, temperature and ozone do not occur in the same month (explained later). Figure 8.9 shows the scatter plot of solar radiation vs. ozone, colour coded by temperature for July, August, and September

2009 at Kirkstall road Leeds. It can be seen that the relationship of solar radiation and ozone is temperature dependent. The 5 hours when the ozone concentration is highest (55.26, 59.72, 64.27, 60.52, and 54.57) in the 3 months dataset correspond to highest temperature (as shown by the dark red colour) and not to highest solar radiation. The mean temperature on these days was 28^{o}C and mean solar radiation level was 352, which is not one of the highest levels as the highest solar radiation level recorded was 956 and median was 256. Therefore the highest ozone levels correspond to the median solar radiation (when temperature was high) rather than to the highest solar radiation.

Figure 8.9 (right) shows the diurnal cycle of ozone, solar radiation and temperature. Normalise levels of these variables are shown, which have been obtained by dividing each variable by its mean (Carslaw and Ropkins, 2012). The important factor about the diurnal cycle of these variables is that solar radiation reaches the highest level at 12:00 hour, whereas temperature and ozone obtain the highest level at 14:00 and 15:00 hour, respectively. On the other hand temperature and solar radiation do not show much time lag in the morning, whereas ozone concentration starts increasing about an hour later than both solar radiation and temperature.

The seasonal variations of temperature, solar radiation and ozone concentration indicate that there is another factor involved which increase ozone concentration in spring rather than in summer when both solar radiation and temperature are at the highest levels. That factor is most probably the concentrations of ozone precursors, particularly volatile organic compounds (VOCs). For photochemical ozone formation in addition to UV radiation, the presence of VOCs is essential whose oxidation by hydroxyl radicals in the presence of NOx leads to ozone formation (AQEG, 2009). Hydrocarbons accumulate in the atmosphere during winter months and reach the highest level in February. In March when the level of UV radiation increases, this consumes the hydrocarbons through photochemical ozone formation and hydrocarbons levels gradually decrease (e.g., see DEFRA, 2005). In summer months (June, July, and August) in spite of relatively high level UV radiation, photochemical ozone formation is restricted by the limited availability of hydrocarbons and therefore ozone concentrations in the atmosphere decline. This has been demonstrated by Munir et al. (2012) using VOCs and ozone data from Harwell and Marylebone monitoring sites for year 2008.

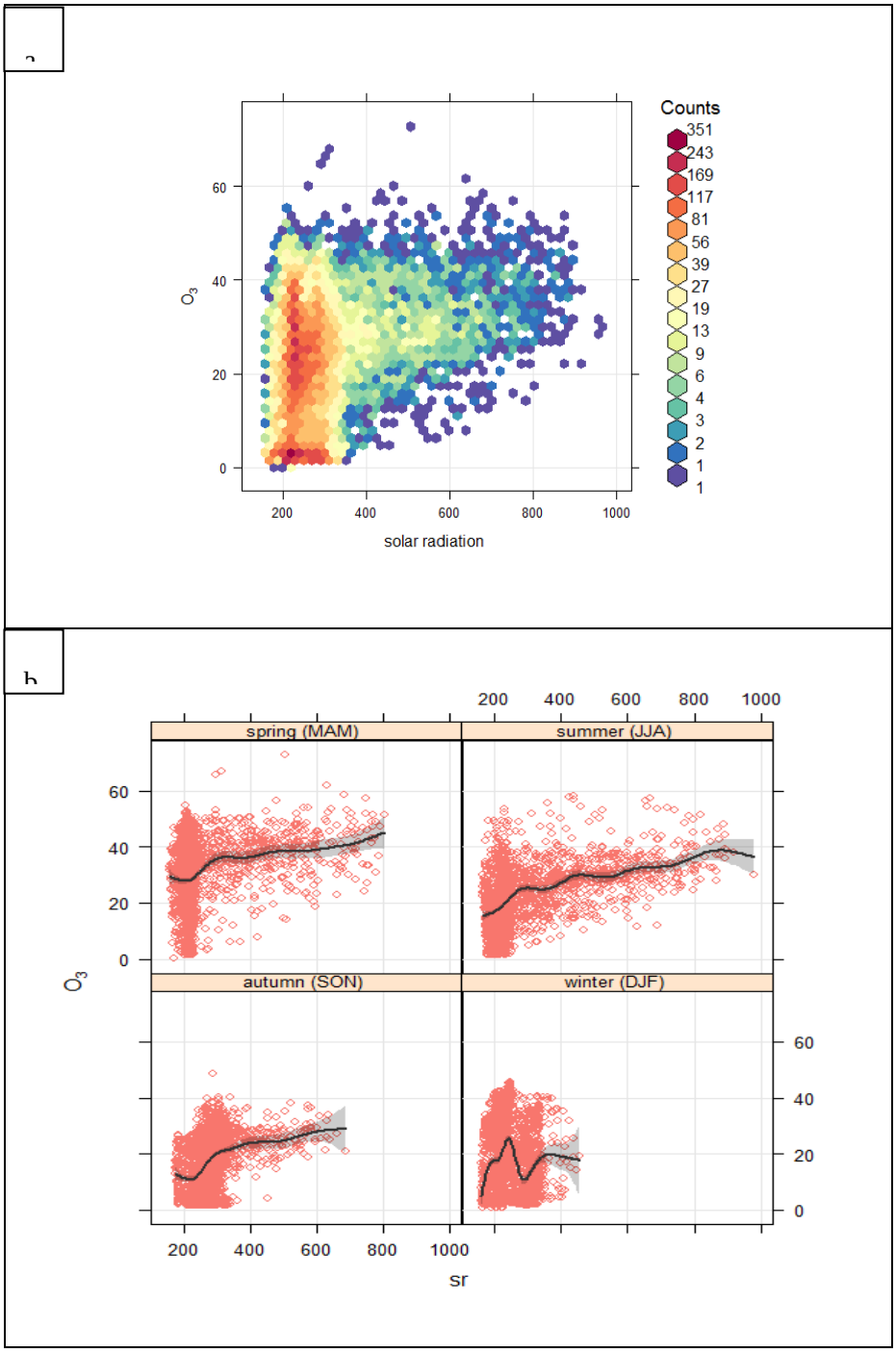


Figure 8.8. Scatter plots of ozone and solar radiation using hexagonal binning technique (a) and dividing the data by season (b), where stand for MAM March, April, May; JJA for June, July, August; SON for September, October, November; and DJF for December, January, February. Smooth lines (black solid curves) with 95 % confidence intervals show non-linear relationship between ozone and solar radiation.

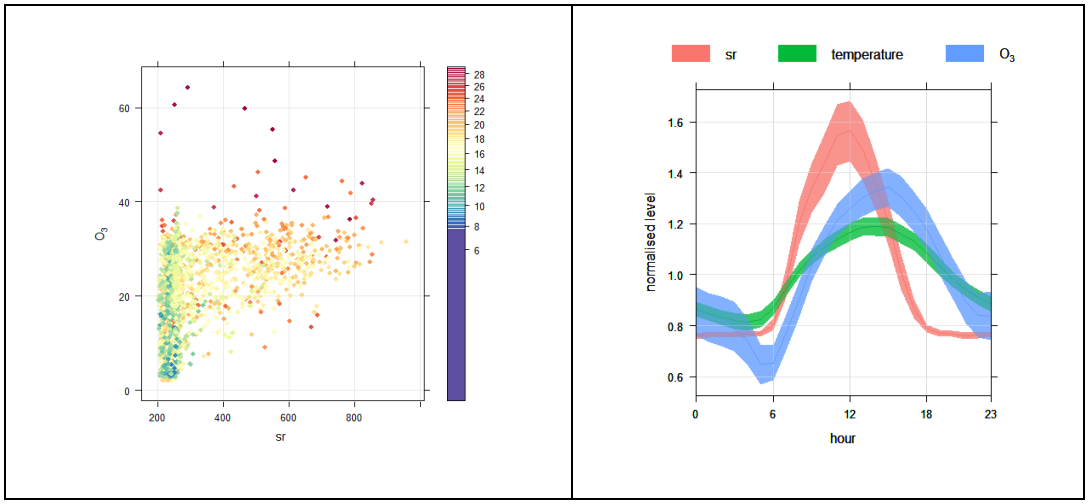


Figure 8.9. Scatter plot (left) of solar radiation vs. ozone coded by the levels of temperature, and diurnal cycle (right) of ozone, temperature and solar radiation for July, August and September 2009 at Kirkstall road Leeds.

8.3.3 Relative humidity

Humidity is the degree of dampness or the amount of water vapour in the atmosphere. At a given temperature, relative humidity is the ratio of the actual mass of water vapour in the air to the mass of vapour in saturated air (holding maximum water vapour without condensation). Relative humidity is expressed as percentage (%). Relative humidity is different from absolute humidity which is the mass of water vapour per cubic meter of total moist air. The limit to how much water vapour the air can hold varies with temperature, warm air can hold more vapours than cold air, therefore when unsaturated air is cooled, relative humidity increases due to its decreasing water holding capacity.

Figure 8.10 shows the frequency distribution of hourly mean relative humidity data (%) from Kirkstall road in Leeds from November 2007 to October 2009. The distribution is non-normal and left skewed (positive skewed), which is also confirmed by the fact that median (69) value is greater than the mean value (67). The minimum and maximum values of relative humidity data were 20 and 85 %, respectively. Figure 8.10 (right) shows the distribution of the data over different season (winter, autumn, spring and summer) by density lines. The distributions of different seasons have almost the same trend i.e. higher frequency/density at higher values of relative humidity (70 – 80 %) and vice versa, but the magnitude (density) is different for different season. Relative humidity is shown to be higher during winter and autumn and lower during summer and spring season. This shows the dependence of relative humidity on temperature i.e. as temperature rises in the summer it increases saturation point of the air which causes the relative humidity to decline.

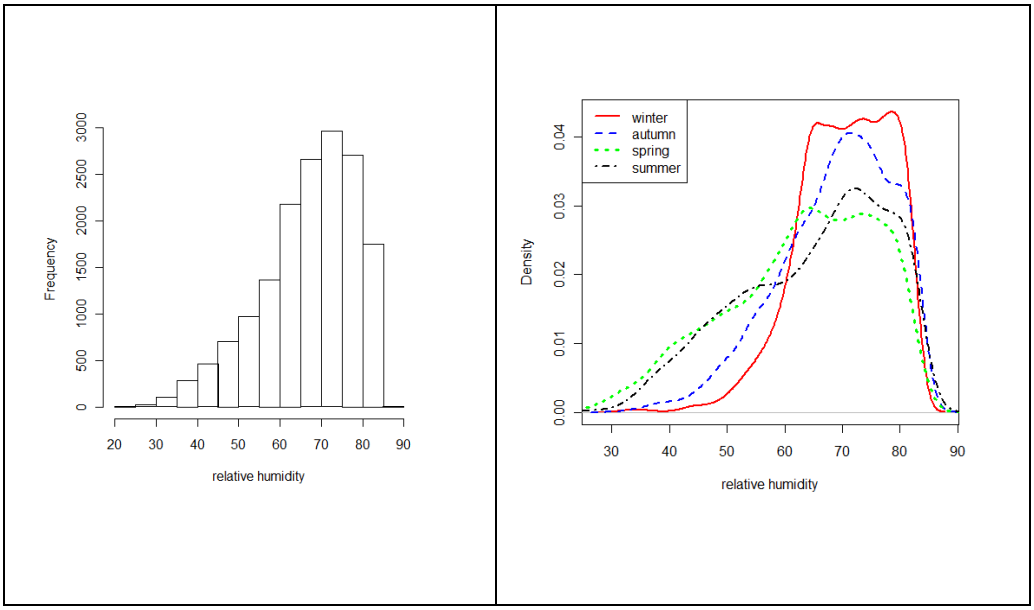


Figure 8.10. Frequency distribution of hourly mean relative humidity data (a) histogram of whole dataset from November 2007 to October 2009, (b) density lines of different seasons (winter –DJF, spring – MAM, summer – JJA, autumn – SON) at Kirkstall roadside monitoring site in Leeds.

8.3.3.1 Relative humidity and ozone

Figure 8.11(a) shows the scatter plot between ozone and relative humidity using hourly data for about 2 year period (November 2007 to October 2009) from Kirkstall site. Statistical analysis reveals negative correlation between ozone and relative humidity and the Spearman correlation coefficient value was '-0.59'. As shown by the linear regression model in Figure 8.11(a) that relative humidity can control up to 35% variation in ozone concentration. Scatter plot for various seasons is shown in Figure 8.11 (b). The correlation is negative for all seasons and the highest correlation coefficient was observed for summer months (June, July and August) and lowest for winter months. Among summer months August showed the highest correlation between ozone and relative humidity (-0.72) and February showed the weakest correlation coefficient (-0.42).

Seasonal and diurnal variations of relative humidity in relation to ozone are shown in Figure 8.12, using data from Kirkstall road in Leeds for about 2 years period (November 2007 to October 2009). As relative humidity and ozone are not on the same scale, therefore normalise levels of these variables are presented. The amount of relative humidity in the air is higher during winter months and lower during summer and spring months. Ozone concentration on the other hand is higher during summer and spring months and lower during winter months. On daily basis at about 06:00 hour in the morning the levels of relative humidity start decreasing whereas that of ozone start increasing. Relative humidity

and ozone reach their lowest and highest level at about 14:00 hour in the afternoon. Afterwards relative humidity level increase and ozone concentration decrease as atmosphere gets cooler in the evening.

The mechanism and reason of the negative correlation between relative humidity and ozone are not clear. The negative correlation might be causal or not. At first glance the correlation does not seem causal and it seems like temperature is the actual cause which is affecting relative humidity and ozone concentration at the same time. Temperature is negatively affecting relative humidity and positively ozone concentration and both of these variables seem closely related, which is nicely demonstrated in the above correlation analysis. In Figure 8.13 high solar radiation (coded by dark red colour) is linked with low relative humidity and high ozone concentration. If we assume that the correlation is causal in that case relative humidity might be either conducive to ozone dry deposition (a sink for ozone) or a hindrance to photochemical ozone formation.

There is no evidence in the literature that increasing relative humidity slows down ozone formation. Duenas et al. (2002) has reported that relative humidity plays an important role in air quality, as relative humidity may play a role in the overall reactivity of the atmospheric system, either by affecting chain termination reactions or in the production of wet aerosols, which in turn affect the flux of ultraviolet radiation. Furthermore, relative humidity is also considered to be a limiting factor in the disposition of NO_2 because high percentages of humidity favour the reaction of the NO_2 with particles of sodium chloride salt.

Grontoft et al., (2003) concluded from his laboratory experiment that at low air humidity the equilibrium surface deposition velocity of ozone was found to decrease as more adsorbed water prevented direct contact of the ozone molecules with the surface. At high air humidity the equilibrium surface deposition velocity was found to increase as the mass of water on the surface increased. Cox and Penkett (1972) studied sulphur dioxides and ozone in a contained environment and showed that deposition velocity was very sensitive to the humidity of the system. Their results showed that deposition velocity of sulphur dioxides and ozone increased with increasing humidity, which can have a significant negative effect on ozone concentration.

McClurkin and Maier (2010) conducted a laboratory study to investigate the effect of relative humidity on ozone half – life time. They reported that as humidity increased from 0 to 45%, half – life time decreased by about 54% and when relative humidity was increased from 45 to 87 % ozone half – life time decreased by about 35 %. Figure 8.13 (a) (from

McClurkin and Maier, 2010) shows how ozone half – life decreases with increasing relative humidity at different temperature.

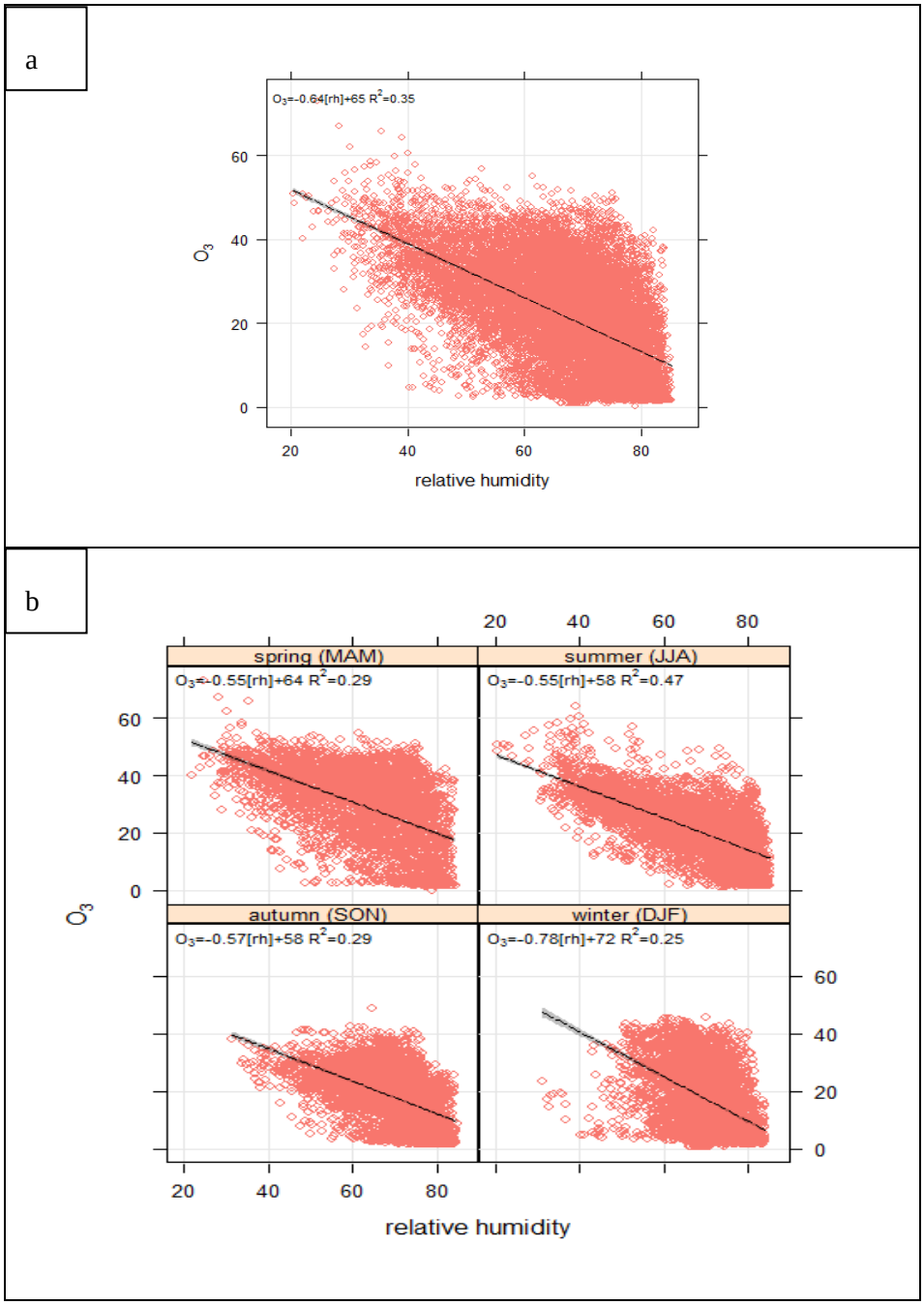


Figure 8.11. (a) Scatter plot of ozone and relative humidity for hourly mean data during November 2007 to October 2009 from Kirkstall road in Leeds, (b) scatter plot of ozone versus relative humidity for various seasons.

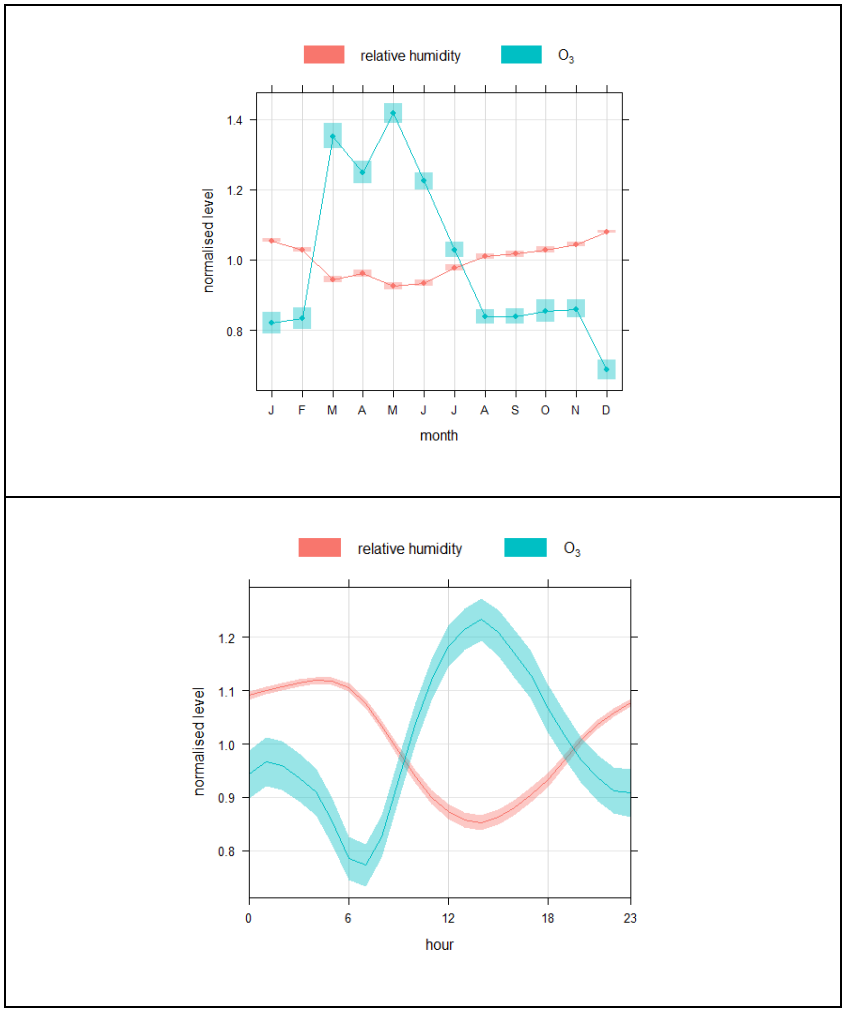


Figure 8.12. Seasonal (top) and diurnal (bottom) variation of relative humidity and ozone during November 2007 to October 2009 at Kirkstall road in Leeds.

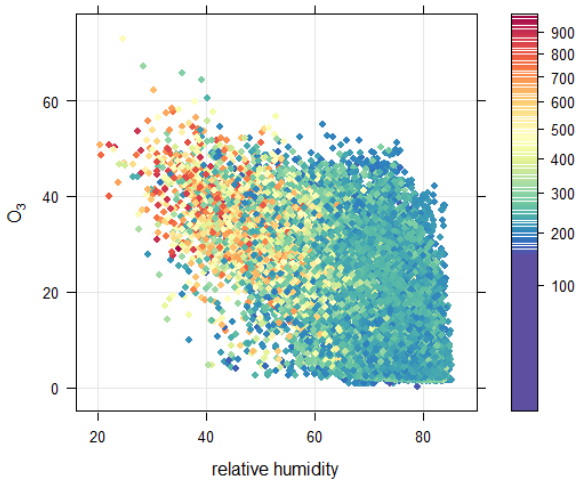


Figure 8.13. Scatter plot of ozone vs. relative humidity by the levels of solar radiation during November 2007 to October 2009 at Kirkstall road in Leeds.

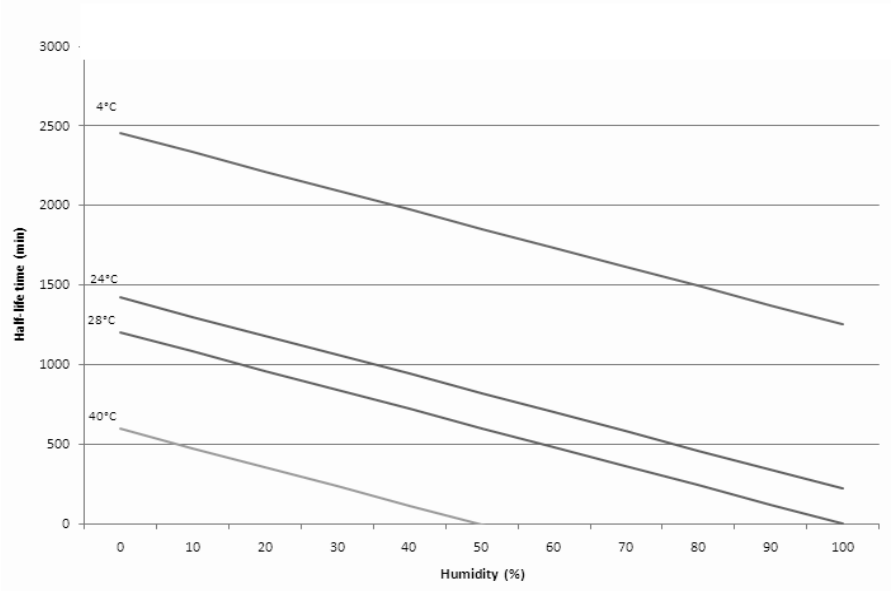


Figure 8.13 (a). Showing the effect of relative humidity (%) on ozone half – life time (minutes) (Figure source: McClurkin and Maier, 2010).

8.3.4 Wind speed

The wind speed hourly mean data (meter per second – m/s) are analysed to see how wind speed changes on daily and seasonal basis at Kirkstall road in Leeds. Frequency distribution of wind speed data (Figure, 8.14) shows that wind speed data are not normally distributed and the distribution is right skewed (positive skewed) for the whole dataset (left) as well as for different seasons (right). The highest frequency is observed when wind speed is less than 1 m/s. At the right tail of the distribution when wind speed is greater than 4 m/s, the frequency is very low. Figure 8.14 (bottom) shows how wind speed varies at different quantiles of the data. The quantiles used were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.99, and 0.9999. Moreover, minimum, median and maximum levels of the data are also shown. The lowest wind speed recorded was 0.003, median (0.79) and highest was 6.21, these are shown on the Figure (8.14 – bottom) as asterisk in green, blue and red colour, respectively. About 99.5 % data had a wind speed less than 4. Out of the 88 hours having wind speed greater than 4 m/s, 74 hours were in January, February and March. Figure 8.15 also demonstrates that wind speed is higher in these three months, particularly in March, which shows the highest wind speed. The lowest wind speed was observed in September.

On diurnal cycle the highest wind speed was observed from 13:00 to 15:00 hours (Figure 8.15). The diurnal cycles of different seasons show that peak wind speed in winter and autumn occurs an hour earlier than in summer and spring. The peak in occurrence of the wind speed in the afternoon probably results from the atmospheric instability which is caused by high temperature in the afternoon. Atmospheric lapse rate (temperature falling

with height due to surface heating) in the afternoon also facilitates mixing and downdrafts from the synoptically driven winds at a higher level (Hewston and Dorling, 2011). Since the vertical mixing and atmospheric instability are dependent on solar radiation it (Hewston and Dorling, 2011) follows that the afternoon peak wind speed should vary seasonally, which has been demonstrated in the diurnal cycle (Figure 8.15). It can also be observed from Figure 8.15 that on average higher wind speed can be observed for more hours during summer and spring compared to winter and autumn.

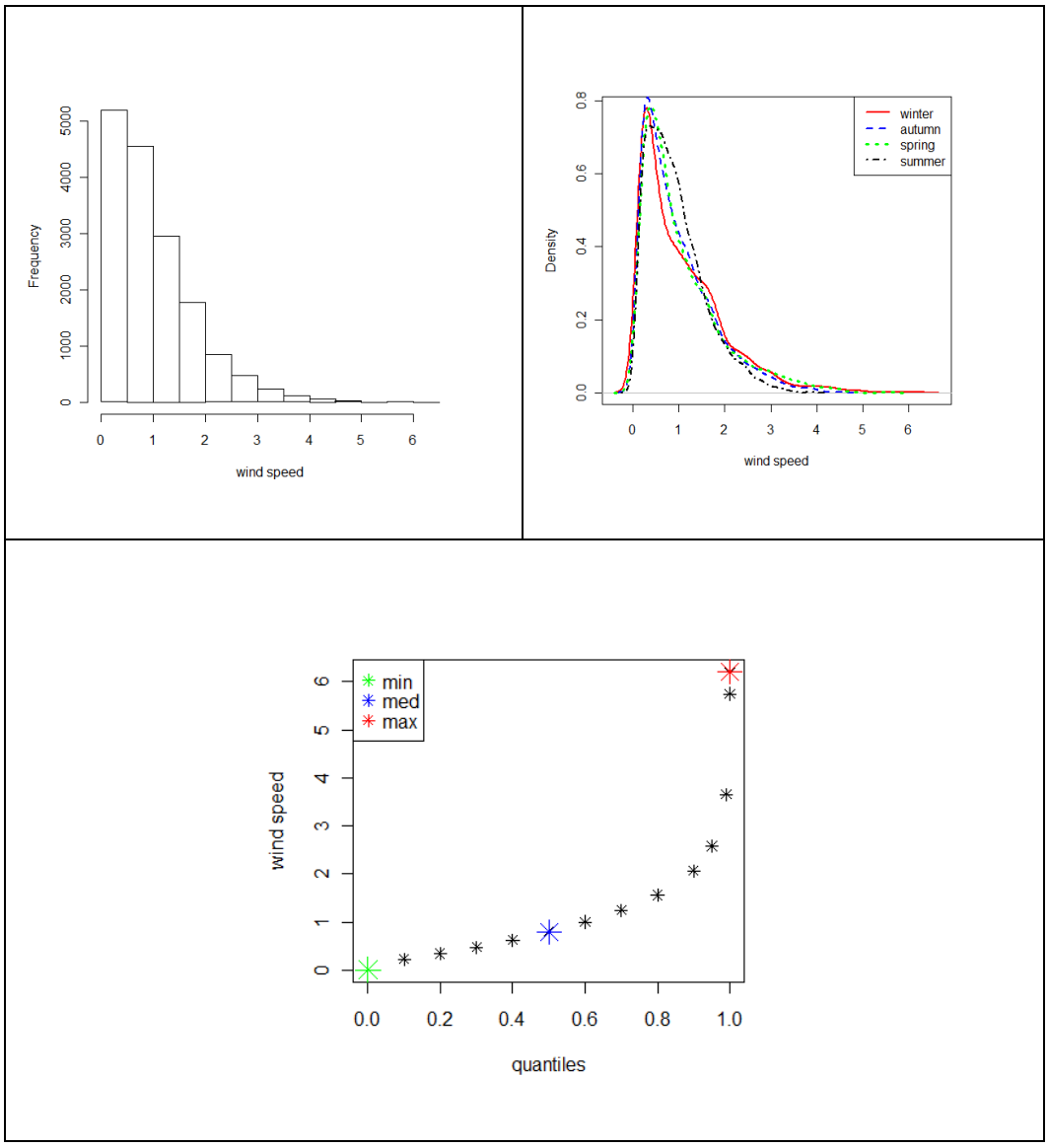


Figure 8.14. Distributions of wind speed data over a 2 years period (November 2007 to 2009) from Kirkstall road in Leeds, shown by a histogram (left) and density lines (right) conditioned by season.

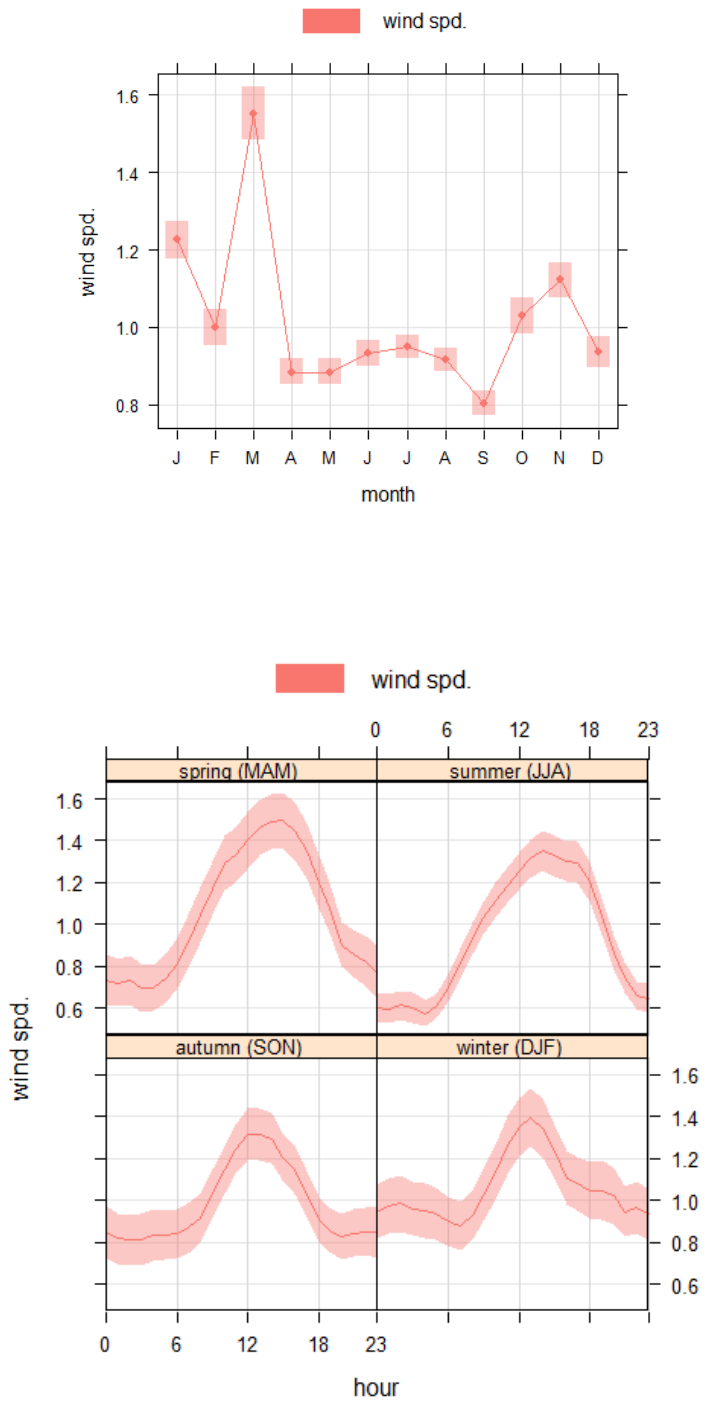


Figure 8.15. Showing the seasonal (top) and daily variation (bottom) of wind speed at Kirkstall road in Leeds from November 2007 to October 2009.

8.3.4.1 Wind speed and ozone

Wind speed plays a vital role in the dispersion of air pollutants and transportation of air pollutants from one place to another ranging from local to regional or global scale (e.g., Chipperfiled, 2006). To investigate the effect of wind speed on ozone concentration, hourly mean wind speed and ozone concentration were used for a period of about 2 years

(November 2007 to October 2009) at Kirkstall road in Leeds. The scatter plot (Figure 8.16) of ozone and wind speed with smooth line (left) and hexagonal binning techniques (right) shows positive association between ozone and wind speed. Spearman correlation coefficient between wind speed and ozone concentration for the whole dataset was 0.58 and showed considerable seasonal variation. Correlation coefficients were 0.68, 0.65, 0.48 and 0.45 for winter, autumn, spring and summer, respectively. The scatter plots for different seasons are shown in Figure 8.17, with smooth trend lines.

The dataset come from a roadside monitoring site, where the concentration of freshly emitted NOx is generally pretty high, particularly in winter and autumn months. When wind speed is high it disperses NOx and hence reduced ozone titration, alternatively in calm or low wind conditions NOx pollutants stay in the local area and react with ozone bringing its concentrations down. On the other hand in summer and spring months high solar radiation encourages convective mixing of the atmosphere and couples the ground layer with the higher altitude where wind speed is generally higher due to synoptic system. Therefore air pollutants can be dispersed even when observed wind speed is low at ground surface, which probably weaken the correlation between ozone concentration and wind speed. This effect is also shown in Figure 8.18, where the scatter plot shows the effect of wind speed in various seasons on ozone concentrations conditioned by solar radiation. In winter and autumn higher ozone concentration is linked with higher wind speed but in spring and summer higher ozone concentration does not correlate well with high wind speed. Particularly in summer peak ozone concentration is found when wind speed is less than 2 m/s. The effect of solar radiation (colour code shown on the right hand side) on ozone concentration is more prominent in summer and the effect is hardly observable in winter and autumn, where the effect of wind speed seems dominant.

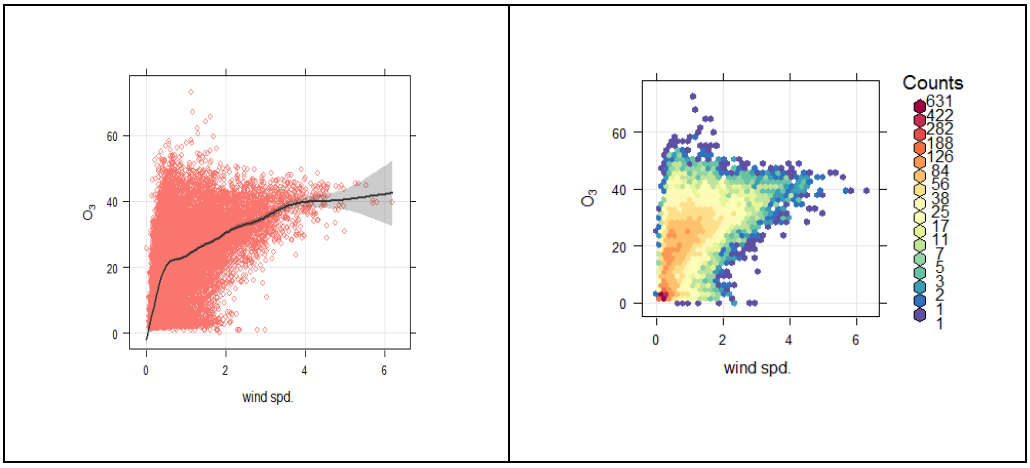


Figure 8.16. Ozone vs. wind speed from November 2007 to October 2009 at Kirkstall road in Leeds; scatter plot with smooth line (left) and scatter plot with hexagonal binning (hexbin) (right). Smooth line (black solid curve) with 95 % confidence intervals shows non-linear relationship between ozone and wind speed.

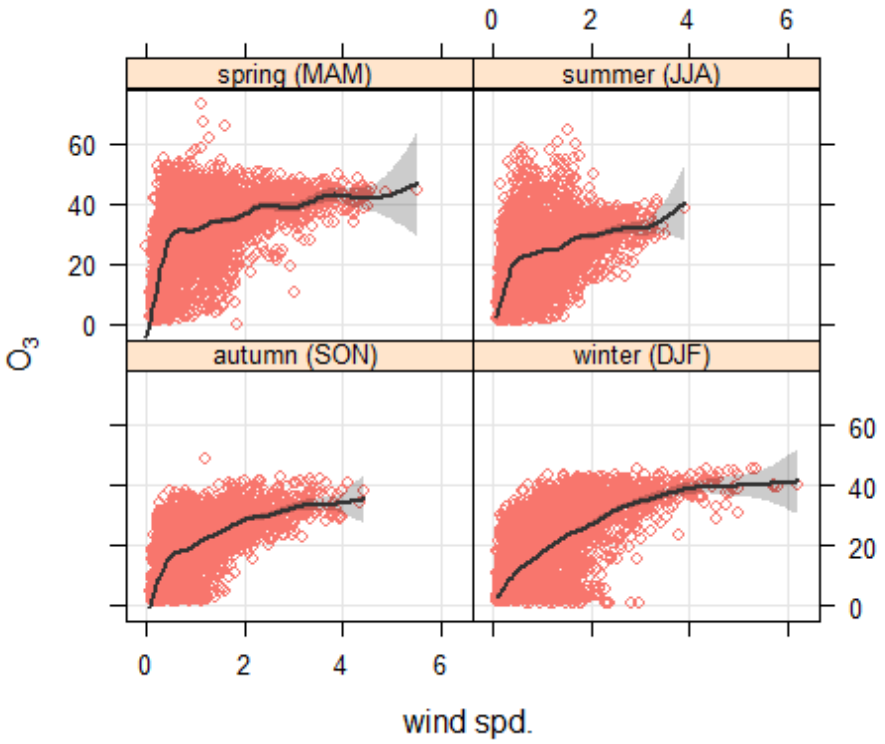


Figure 8.17. Scatter plots of ozone concentration and wind speed in different seasons, using 2 years data (November 2007 to October 2009) at Kirkstall road in Leeds. Smooth lines (black solid curves) with 95 % confidence intervals show non-linear relationship between ozone and wind speed.

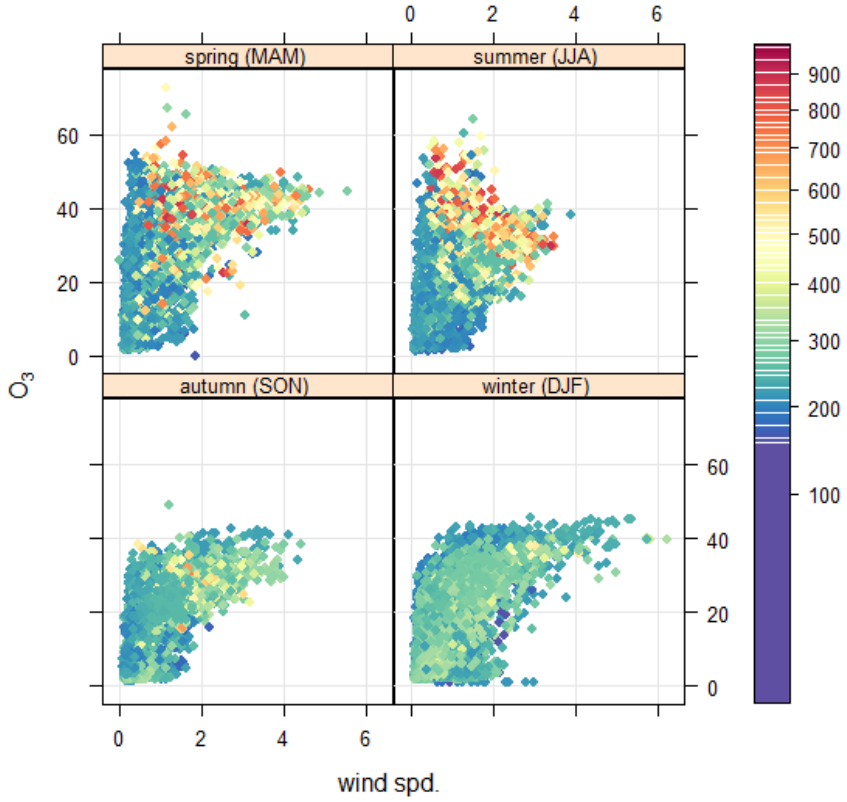


Figure 8.18. Scatter plot of wind speed and ozone conditioned by levels of solar radiation (sr) at Kirkstall road in Leeds over a period of about 2 years (November 2007 to October 2009).

8.3.5 Wind direction

Wind direction is reported by the direction from which it originates, for example, a wind blowing from the north to the south will be called north wind or northerly wind. Wind direction is normally measured in degrees from north ranging from 0 to 360, where 0 or 360 represents north and 90, 180 and 270 represent east, south and west direction, respectively. Hourly mean wind direction (Degrees) data are summarised by a wind rose in Figure 8.19, showing data for a 2 years period (November 2007 to October 2009) from Kirkstall road in Leeds. The data are shown as a percentage of time that the wind is blowing from a certain angle and wind speed range. Wind rose also characterises wind speed at the site and presents zero wind speed as calm. No calm was observed in the period under consideration therefore calm is zero and mean wind speed is 1 m/s. The wind is predominantly blowing from south-west (about 25%) and west (about 18%). Wind speed is low most of the time (0 – 2), particularly when blowing from south or southwest direction. Interestingly the number of hours when the wind was blowing from the north is zero, which according to the data means in the 2 years time the wind never blew from the north. Only 3 hours had wind direction

angle greater than 320°, which were 321, 321 and 345°. But when this was further investigated it appeared that the house located on the north side of the monitoring site might be sheltering the monitoring site from that side. Figure 8.20 shows the picture of the monitoring site along with the schematic diagram showing how winds might be blowing from north side passing over the top of the monitoring station and then propagate towards the road.

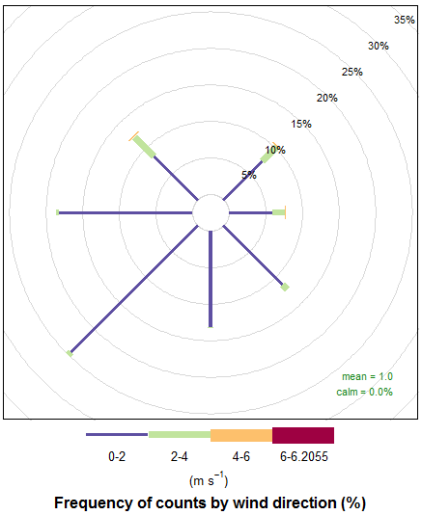


Figure 8.19. Wind rose showing wind direction and wind speed hourly mean data for about 2 years (November 2007 to October 2009) at Kirkstall road in Leeds.

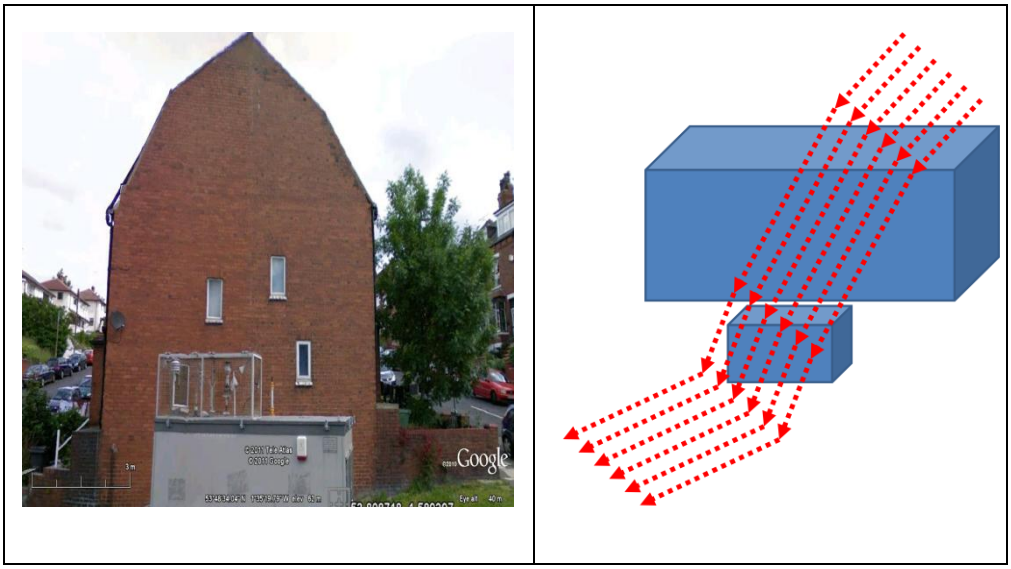


Figure 8.20. Picture of the monitoring site highlighting the house in the north of the station deflecting winds blowing from that direction (Figure source: The picture (left-side) is obtained from Google earth).

8.3.5.1 Wind direction and ozone

Polar plots are used to investigate emission sources of air pollutants as well as the dependence of pollutants on wind speed (Carslaw et al., 2006). The plots are constructed by averaging pollutant concentration by wind speed categories (0–1 m/s, 1–2 m/s, etc.) as well as wind direction (0–10, 10–20, etc.). The relationship of ozone with wind speed and wind direction is depicted in Figure 8.21 with the help of a bivariate polar plot. In polar plots the levels of different variables are shown as a continuous surface, which are calculated through using Generalized Additive Models smoothing techniques (Carslaw and Ropkins, 2012).

It can be observed that generally high wind speed correlates positively with high ozone concentration. Lowest ozone concentration is shown at the centre of the plot, which presents low wind speed. Highest ozone concentration (dark red colour) is observed roughly at 60, 120, and 315^{o} when the wind speed is about 5 m/s. The third quadrant (southwest) shows low levels of ozone, particularly at 45^{o} where ozone concentration seems low at all wind speed. Kirkstall Road (A65) runs northwest to southeast and the monitoring site is on the northeast side of the Kirkstall road between Woodside View and Woodside Terrace. NOx emitted by road traffic in the south and southwest direction is most probably the main cause for low ozone concentration in the third quadrant. Concentration of NOx (Figure 8.21 – right) is shown for comparison purposes and it can be observed that ozone and NOx levels have the opposite trends, due to NOx and ozone reactions which destroy ozone. NOx concentrations are highest at the centre of the polar plot characterised by low wind speed and as wind speed increases it disperses the locally produced NOx. NOx concentrations are comparatively higher in the southwest direction.

To show the effect of wind direction and wind speed on ozone concentration in different seasons, we used pollution rose (a type of wind rose), which is different from polar plot in sense that wind speeds are represented by different width ‘paddles’ and that it shows the proportion (expressed as a percentage) of time that the wind is blowing from a specific direction. The changes of wind speed and wind direction have been described in section 8.5; here the changes of ozone with these variables are briefly discussed. As expected highest ozone concentration is shown in spring (March, April and May) and lowest in autumn (September, October and November). In spring higher ozone concentration are shown to be linked with winds blowing from southeast, west and northwest, whereas in autumn higher ozone concentration is linked with the north east direction. In summer and winter the trend from various directions seems to be almost uniform.

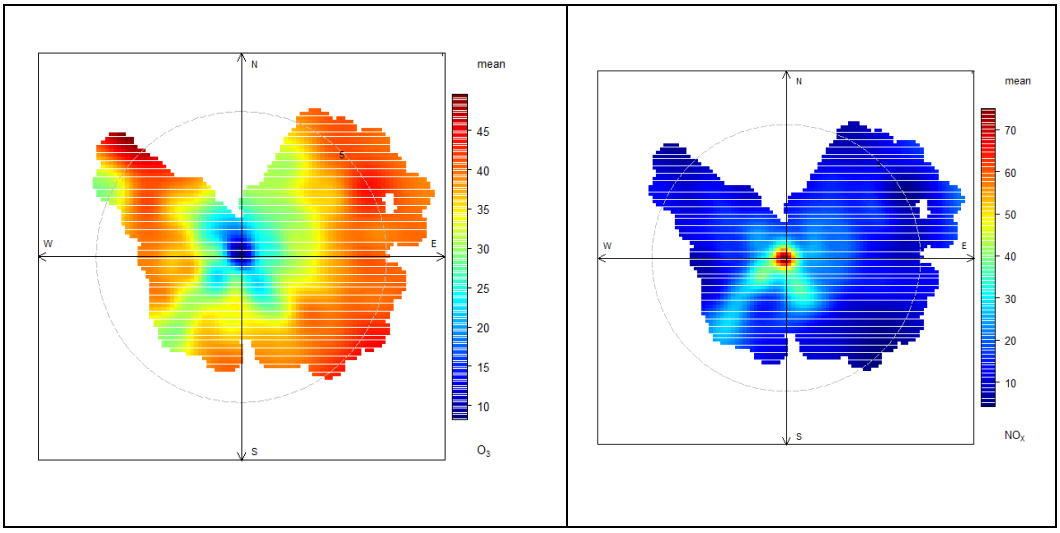


Figure 8.21. Bivariate polar plot showing ozone (left) and NOx (right) concentration from November 2007 to October 2009 at Kirkstall road Leeds.

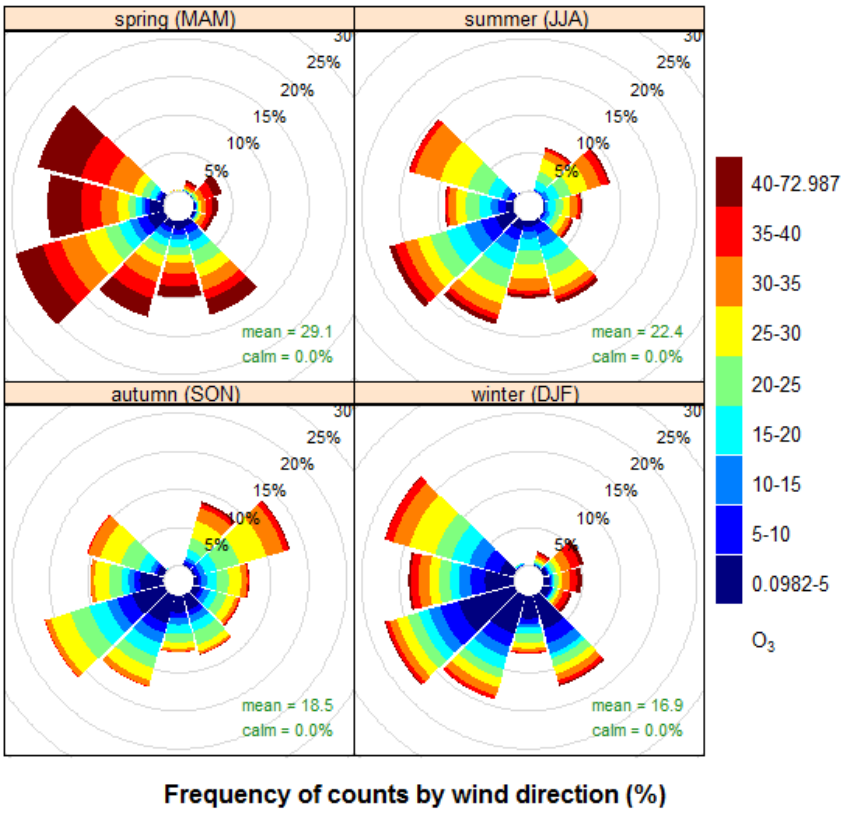


Figure 8.22. Bivariate polar plot showing differences in ozone concentration in different seasons affected by wind speed and wind direction using data from November 2007 to October 2009 at Kirkstall road in Leeds.

8.3.5.2 Correlation analysis of wind direction

Wind direction needs to be dealt with differently in statistical analysis, due to its directional or circular nature, which can be represented as a point on the circumference of a circle. Therefore normal arithmetic mean, correlation or regression method cannot be applied to study the effect of wind direction on ozone. Jammalamadaka and SenGupta (2001) refer to the relationship of ozone and wind direction as linear – circular relationship, as opposed to linear – linear (ozone and wind speed) and circular – circular (wind direction and 24 hour daily cycle). This linear-circular correlation coefficient has been defined as the multiple correlation between a linear variable x (e.g., ozone) and the sine and cosine of a circular variable α (e.g., wind direction), which is given as below.

$$r^2 = \frac{r_{xc}^2 + r_{xs}^2 - 2r_{xc}r_{xs}r_{cs}}{1 - r_{cs}^2} \qquad (8.1)$$

Where r_{xc}, r_{xs}, r_{cs} represent the correlation (x, cos α), correlation (x, sin α) and correlation (cos α, sin α), respectively. Wind direction (α) needs to be in radians (not in degrees). To convert degree into radian, simply multiply wind direction in degrees by π/180.

The correlation coefficient between ozone and wind direction estimated by Equation 8.1 was 0.23 for the whole dataset. The correlation coefficient for spring, summer, winter and autumn were 0.22, 0.20, 0.37 and 0.39, respectively, which show highest correlation between ozone and wind direction in autumn followed by winter.

If we want to know how wind direction is correlated with hour of the day, day of the year or month of the year, it would be an example of circular – circular correlation, where every hour, day or month behave like a degree of an angle. Therefore hour of the day, day of the year and month of the year would be multiplied by 2π/24, 2π/365 and 2π/12, respectively, in the same way as we multiply wind direction by 2π/360 to convert it into radians (Jammalamadaka and SenGupta, 2001). The formula for the circular-circular correlation coefficient (r_c) for n pairs of observations of two angular variables, α and β, with sample mean directions μ and ν is given below.

$$r_c = \frac{\sum_{i=1}^{n} \sin(\alpha i - \mu)\sin(\beta i - \nu)}{\sqrt{\sum_{i=1}^{n} sin^2(\alpha i - \mu) sin^2(\beta i - \nu)}} \qquad (8.2)$$

Where μ and ν are the means of α and β. The package CircStats (Agostinelli, 2009) was used to estimate the circular correlation coefficient of α and β. CircStats does not have code for linear – circular correlation, therefore we have to write our own code.

Circular – circular correlation coefficient measures the degree that two variables are related by a rotation, therefore correlation between wind direction and hour of the day (-0.002) or day of the year (0.16) was weak as wind direction would be expected to show rather a season fluctuation affected by large scale atmospheric circulation. On the other hand linear – circular correlation between ozone and day of the year (0.51) or hour of the day (0.17) was relatively stronger, which might indicate the daily and seasonal cycle of ozone linked with the amount of solar radiation. Daily and hourly mean data was used to perform correlation analysis of day of the year and hour of the day, respectively with wind direction and ozone from Kirkstall road site in Leeds during 2008. The strong correlation of ozone with day of the year can be use in ozone prediction, particularly at those monitoring site where meteorology or traffic data is not available.

8.3.6 Quantile regression model for meteorology and ozone

In this section the effect of meteorology on ozone concentration is investigated using the hourly data, which was collected at Kirkstall road for year 2008. As explained in section 8.1, temperature data are not reliable and therefore cannot be used in the model. Wind direction needs to be dealt with differently in statistical analysis, due to its directional or circular nature. Wind direction is given in degrees; therefore the wind direction was first multiplied by $\pi/180$ to convert it into radians and then sine and cosine of the wind direction are used instead as suggested by many researchers (e.g. Carslaw et al., 2007; Westmoreland et al., 2007); with sine (wd) positive from the east and cosine (wd) positive from the north. The outputs of the QRM model is visualised in Figure 8.23. Ozone concentration is also modelled at Marylebone site for 2008 using wind speed, wind direction and temperature as covariates, depicted in Figure 8.24.

As defined in other chapters, positive quantile regression coefficients indicate positive effect of the predictor on ground level ozone. In contrast negative coefficients indicate negative effect on ozone concentration. If confidence intervals of the coefficients overlap with zero line, regardless of the negative or positive sign, the effect is considered to be insignificant. Furthermore, if confidence intervals of a quantile regression coefficient overlap with the ordinary least square coefficients, it shows that the effect is not significantly different from the mean effect. Understandably larger coefficients show stronger effect and vice versa.

The effect of relative humidity on ozone concentration is negative and significant at all quantiles. Most of the quantile regression coefficients are not significantly different from the

mean effect estimated by OLS except at quantile 0.1, 0.2, and 0.4. The strength of the effect seems to decline at both ends of the distribution. The effect of solar radiation seems very weak and the coefficients range from 0.005 to -0.015 for quantile 0.1 and 0.9, respectively. The effect of solar radiation is significant at almost all quantiles, but the negative correlation coefficients are confusing. The effect is shown to be positive only at quantile 0.1 and negligible (not significant) at quantile 0.2. The effect of wind speed is significant at all quantiles at both monitoring sites (Marylebone and Kirkstall). Of all the variables wind speed seems to affect the concentration of ozone the most, as wind speed has the strongest regression coefficients. The effect of wind speed seems to decrease with increasing ozone concentrations at Kirkstall site (Figure 8.23), whereas it has the opposite trend at Marylebone site. In addition the correlation coefficients at Marylebone site are much stronger. The variations in the effect of wind speed on ozone concentrations in London and Leeds signify the importance of local site characteristics. The effect of wind direction is more complicated and again the effect is different in Figure 8.23 and 8.24. At Kirkstall site the effect is weaker and changes from positive at lower quantiles to negative at higher quantiles. The effect of wind direction observed at Marylebone is much stronger and significant at all quantiles. Marylebone site have much more traffic flow (about 80000 vehicles per day) than the Kirkstall road. Marylebone is characterised as a street canyon, where recirculation of air pollutants can play a significant role in the observed ozone concentration. Furthermore, the ozone titration by NOx is much stronger at the Marylebone site and wind speed might be diluting the freshly emitted NOx and hence reducing its scavenging effect leading to a positive effect on ozone concentration. The effect of temperature on ozone concentration at Marylebone site is visualised in Figure 8.24 (bottom panel). The effect of temperature on ozone concentration is positive and significant at all quantiles. The strength of regression coefficients increase at higher quantiles and reach the highest level at quantile 0.99. Ozone concentration is generally higher in summer most probably due to high temperature which encourages photochemical ozone formation, which probably explains why ozone shows stronger association with temperature in summer.

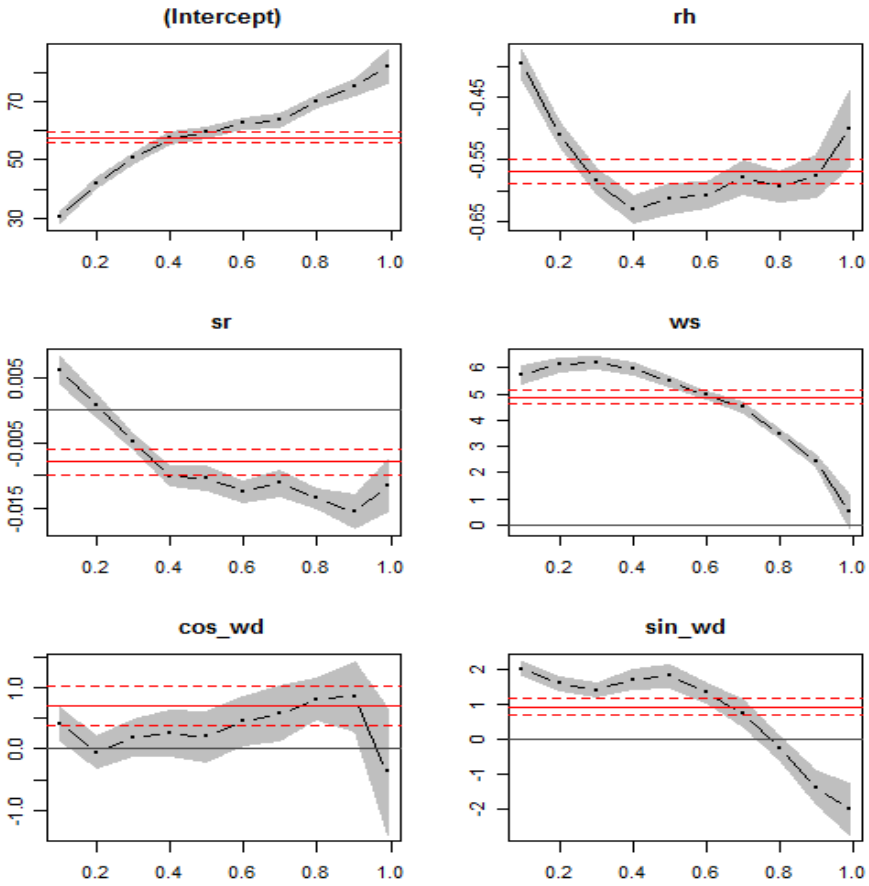


Figure 8.23. The output of quantile regression model, showing the effect of relative humidity (rh), solar radiation (sr), wind speed (ws) and wind direction (wd) (sine and cosine of wd) on hourly mean ozone concentrations at Kirkstall site for the year 2008. Quantile regression coefficients (dashed dark line) and ordinary least square regression coefficients (solid red line) are presented with their 95% confidence interval.

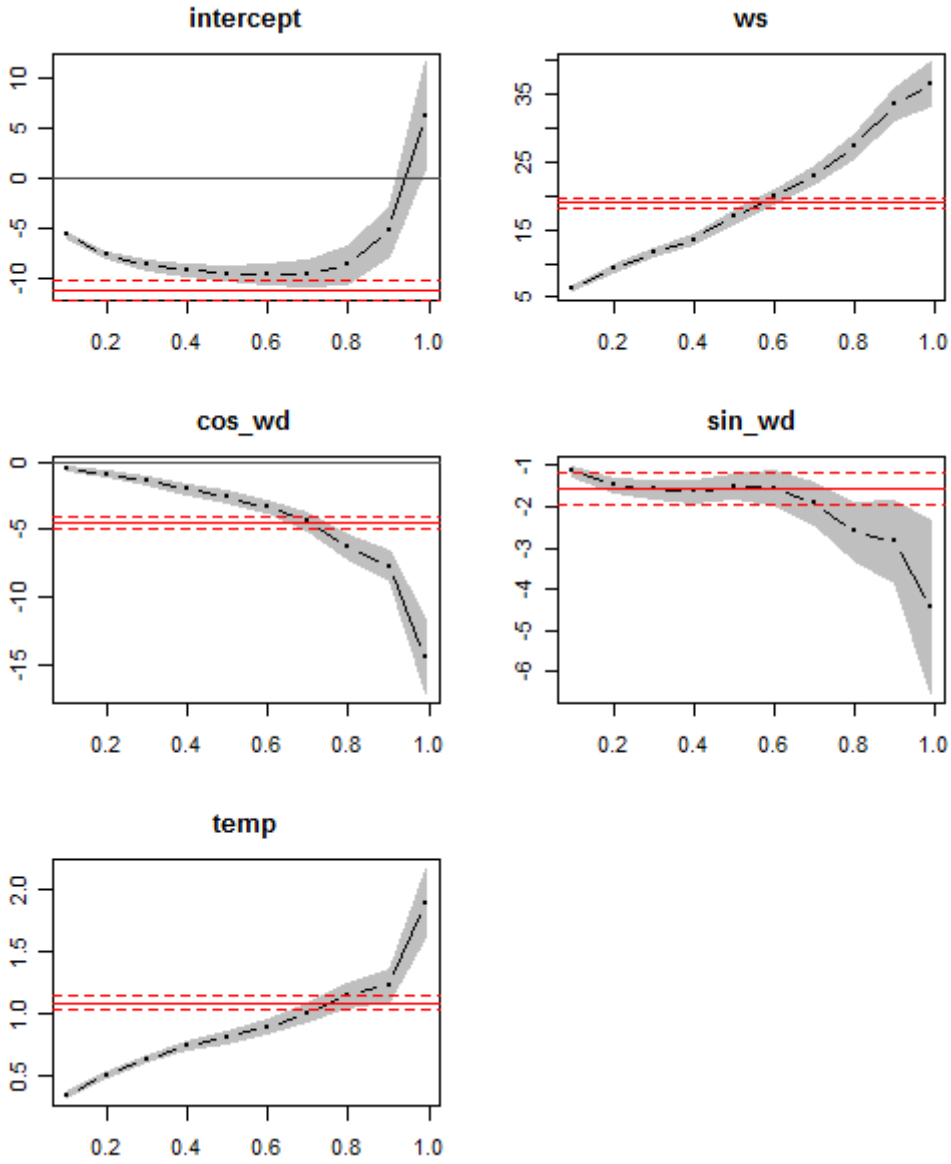


Figure 8.24. The output of quantile regression model, showing the effect of temperature, wind speed (ws) and wind direction (wd) on hourly mean ozone concentrations at Marylebone site for the year 2008. Quantile regression coefficients (dashed dark line) and ordinary least square regression coefficients (solid red line) are presented with their 95% confidence interval.

8.3.6.1 Assessment of the models

Several statistical metrics for assessment of the QRM and OLS models were calculated for both monitoring sites (Marylebone and Kirkstall monitoring sites). The values of FAC2, MB, MGE, NMB, NMGE, RMSE and R2 are given in Table 8.1. These metrics have been defined in chapter 4, section 4.7. Generally the models developed for Kirkstall monitoring site show slightly better performance, which is probably due to the site characteristics.

Marylebone site is relatively harder to model due to the street canyon effect and other complexities, for instance higher volume of traffic emitting various air pollutants, which are not taken account of in the model. In addition the models for Kirkstall site have wind speed, wind direction, relative humidity and solar radiation as independent variables, whereas the models for Marylebone site have temperature instead of solar radiation and relative humidity.

FAC2 value > 0.50 for both models shows satisfactory model performance, whereas the value of NMB is out of the range of -0.2 and +0.2 and is not so convincing as the values of NMB needs to be within this range. Furthermore, in agreement with other chapters QRM over performs OLS.

Table 8.1. Showing statistical metrics for the models (QRM and OLS) developed for Kirkstall and Marylebone site using data for year 2008. The testing data for both sites are for May 2009.

Metrics	Kirkstall Site		Marylebone site	
	QRM	OLS	QRM	OLS
FAC2	0.74	0.73	0.72	0.59
MB	-6.59	-8.78	-8.95	-14.82
MGE	8.67	11.42	12.36	19.42
NMB	-0.21	-0.28	-0.23	-0.37
NMGE	0.28	0.36	0.32	0.49
RMSE	10.79	13.99	15.32	25.20
R^2	0.74	0.34	0.69	0.33

8.4 Summary

In this chapter the effects of meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction) on ozone concentration have been investigated using data from Kirkstall and Marylebone monitoring site. Graphical presentation, correlation analysis, and QRM are applied in this chapter. Statistical analysis shows that the relationship between ozone and meteorology changes during different seasons considerably.

Generally temperature and wind speed demonstrate positive effect, whereas relative humidity demonstrates negative effect on ozone concentration. The effect of wind direction is more complicated and, being a circular variable, needs to be handled differently. The effect of meteorology varies at Marylebone and Kirkstall site due to some local factors (e.g., height of buildings, street canyon effect, and traffic volume), which can affect the flow of wind, recirculation of pollutants and the chemistry of ozone. Furthermore, as revealed by QRM, the effect of the meteorology varies at different ozone concentration. Sometimes the strength of effect changes but the nature (positive or negative) remains the same as in the case of wind speed, other times both strength and nature change as in the case of solar radiation. The model developed at Kirkstall site shows better performance, most probably due to local characteristics of the sites and that the Kirkstall model uses more independent variables i.e. relative humidity and solar radiation instead of temperature.

This chapter emphasises the importance of investigating the effect of meteorology on the whole ozone distribution, rather than just the mean value. It is shown that the effect of meteorology changes at different quantiles of the ozone concentration, which remains obscured in applying mean based and linear regression. Furthermore, it is shown that the association between meteorology and ozone changes in both space (between different monitoring sites) and time (during different seasons and even during different hours of the day). Therefore it is suggested that these factors are taken into account when analysing the association between ozone and meteorology. In particular both ozone and meteorology data are required to be collected at the same monitoring site, otherwise the outcome might be biased or erroneous.

As shown above the effect of meteorology on ozone concentration vary both in space and time. In the next chapter the spatial variability of ozone is further investigated and the effect of various spatial parameters on ozone concentration has been characterised, which will provide further insight into the spatial behaviour of ground level ozone.

CHAPTER 9: SPATIAL ANALYSIS OF OZONE VARIATIONS IN THE UK

9.1 Introduction

Atmospheric ozone concentration is affected by multiple factors. Other chemical species, including NOx, volatile organic compounds (VOCs), particulates (PM_{10}, $PM_{2.5}$), carbon monoxides (CO), sulphur dioxide (SO_2), (Cape, 2008; Munir et al., 2012), meteorological variables such as wind speed, wind direction, cloud cover, precipitation, solar radiation, temperature, relative humidity and air pressure (Duenas et al., 2002; Baur et al., 2004), sources of precursors emissions and climate change (The Royal Society, 2008) can all contribute to ozone concentration. These factors affect the horizontal and vertical transport and produce a range of sinks and sources via their chemistry (e.g., aqueous phase chemistry, photochemical ozone formation etc), dry and wet deposition, and precursor emissions from anthropogenic (e.g., NOx and VOCs) and natural (e.g., isoprene) sources (Andersson et al., 2006).

Comprehensive models that attempt to model the effect of all of these factors on ozone concentration typically require numerous hard-to-access inputs and are often highly computer intensive, limiting their more widespread use, especially in applications where ozone predictions need to be aggregated over large spatial and temporal ranges. One such application, the generation of national annual ozone maps, is fundamental to the process of ozone-related risk and damage assessment (Coyle et al., 2002). Therefore, the intention here is to investigate how well ozone concentration could be modelled with a much smaller but easier to access set of model inputs and whether such models, being more amenable, could provide a useful tool for policy makers wishing to compare multiple pollutant mitigation strategies.

Ozone concentration varies considerably throughout the UK. Spatial variations of ozone can be linked with several phenomena, including ozone titration by freshly emitted nitric oxides (NO), dry deposition (to ground surface, plants and other materials), vertical and horizontal movement, and photochemical ozone formation (e.g. PORG, 1998, Coyle et al., 2002). However, the balance of these different phenomena can be influenced by local factors: for instance, ozone titration by NOx is higher in urban areas (AQEG, 2009; Jenkin, 2008); dry deposition is lower to water surfaces (Entwistle et al., 1997); photochemical ozone formation rate is higher in sunny areas of the country (Jenkin, 2008); and higher altitudes exhibit higher average ozone concentration (Chevalier et al., 2007). Therefore, our approach

has focused on surrogates (or proxies) for the above parameters. The approach is not without presence because, e.g., Coyle et al. (2002) previously identified altitude of a monitoring site as a surrogate for wind speed, while else it has been well established that ozone concentration is higher near coasts due to less dry deposition of ozone on water surfaces (Entwistle et al., 1997).

Therefore, here we propose an ozone model for the UK using such spatial parameters, distance from the coast, easting & northing coordinates, altitude of the site, and NOx concentration. The metrics used for expressing ozone levels in this paper are ozone annual mean, AOT40 (Accumulated Ozone concentrations Over a Threshold of 40 ppb or 80 $\mu g/m^3$ and are estimated to assess the impact of ozone concentration on agricultural crops) and SOMO35 (Sum of Ozone Means Over 35 ppb or 70 $\mu g/m^3$ recommended by World Health Organisation for quantification of health impacts). On details on these metrics see Stedman and Kent (2008), UNECE (2004) and Coyle et al. (2002). The model is implemented as a generalised additive model (GAM) because the GAM is an advanced regression model that relaxes some of the restrictions imposed by linear regressions (e.g. linearity and normality assumptions). The model is simple to set up: The spatial parameters used in the model were all obtained from the UK AURN website (UK-AIR, 2012) or measured using commonly available mapping software, e.g. Google Earth or loa-package for R (Ropkins et al., 2012); and explained a considerable proportion of ozone variation. The model can therefore be readily applied to a location or region where NOx measurements or predictions are available to provide an estimate of associated ozone concentrations, and by inference the negative feedback associated with different NOx mitigation activities.

9.2 Methodology

The study is based on hourly ozone concentrations ($\mu g/m^3$) collected at 80 monitoring sites in the UK. Ozone concentration has been modelled using a generalised additive model (GAM). Data sources and the statistics applied have been described in the following sections.

9.2.1 Data source

Ozone and NOx data from 80 monitoring sites used in this chapter were obtained from the UK AURN on line archive (UK-AIR, 2012). The environment of the monitoring sites can be categorised into seven types using AURN definitions: rural background, rural background agriculture, rural background nature, suburban, urban background, urban industrial and urban traffic (UK-AIR, 2012: http://uk-air.defra.gov.uk/networks/site-types). These can be broadly grouped into three main categories (types) i.e. urban (54), suburban

(5) and rural (23) sites, as shown in Figure 4.1 (chapter 4). For more details regarding the monitoring sites see the UK-AIR website (UK-AIR, 2012), which provide a full description of the monitoring sites and the air pollutants measured.

In this chapter the variations of ozone along easting and northing have been investigated. Using British National grid reference, an easting is the distance (expressed in meters) along the horizontal axis and a northing is the distance along the vertical axis of the false origin (the UK southwest corner of the SV square). Easting and northing and altitude of the monitoring sites are given on the AURN website. Distance from the coast for each monitoring site was estimated using Google Earth version 6.1.0.5001 (Google Earth, 2011).

NOx concentration, which is used as independent variable in the GAM model, is not monitored at several ozone monitoring sites in the UK. In this case NOx measurements from the nearest site of the same (or similar) type were used as a surrogate. The sites where NOx data were not available are given below along with their associated surrogates (reported in brackets): Auchencorth Moss (Bush Estate), Bottesford (Market Harborough), Great Dun Fell (Eskdalemuir), Lerwick (Fort William), Lough Navar (Derry), Mace Head (Derry), Sibton (St Osyth), Strath Vaich (Fort William) and Weybourne (St Osyth).

Altitudes for most of the monitoring sites were available at the UK AURN website, however the altitude for Blackpool Marton, Norwich Lakenfield and Port Talbot Margam were not given at the AURN website. Therefore their altitudes were estimated using the Google Elevation API (application programming interface), in this case accessed via the R package 'loa' (Ropkins et al., 2012).

9.2.2 General Statistics

All statistical analysis was undertaken using the R programming language (R Development Core Team, 2012), base installation packages and specialist packages identified below.

Statistical metrics used to assess the performance of the model were: Factor of 2 (FAC2), Coefficient of Determination (R^2), Normalised Mean Bias (NMB), Root Mean Square Error (RMSE), Normalised Mean Gross Error (NMGE), which were calculated using the modStats function in R package openair version 2.13.2 (Carslaw and Ropkins, 2012). See chapter 4, section 4.7 for the description of these statistical metrics. Figures were plotted using a combination of in-house code, mgcv (Wood, 2011) and openair; and maps were drawn using the R package 'loa' (Ropkins et al., 2012).

In addition to annual mean other statistics used were AOT40, and SOMO35 and number of hours when ozone concentration was greater than 100 ($\mu g/m^3$). AOT40 are accumulated ozone concentrations over 40 ppb (80 $\mu g/m^3$) and are estimated to assess the impact of

ozone concentration on agricultural crops. The critical level of AOT40 for agricultural crops is 3000 ppb h (Coyle et al., 2002), which is accumulated during daylight hours for the three months (May, June, and July) when clear sky radiation is above 50 W/m^2 (Fuhrer, et al., 1997). Air quality strategy for England, Scotland and Wales (AQS, 2007) recommends the calculation of AOT40 over 12 hours (08:00 to 20:00) of the day; and when AOT40 values reach the critical level (3000 ppb h), it is considered that ozone concentration has exceeded the threshold level and is likely to cause damage to agricultural crops. To remove the effect of annual variations in ozone concentration, assessments of the critical level are based on the average AOT40 taken over the most recent 5 years (2007 to 2011) as suggested by Coyle et al., 2002. For further details on AOT40 see chapter 4, section 4.8, UNECE, 2004, and Coyle et al., 2002. SOMO35 stands for the Sum of Ozone Means Over 35 ppb (70 $\mu g/m^3$). For quantification of the health impacts the World Health Organisation recommends the use of the SOMO35 indicator. It is defined as the yearly sum of the daily maximum of 8-hour running average over 35 ppb. For each day the maximum of the running 8-hours mean ozone is selected and the values over 35 ppb are summed over the whole year. For more details on SOMO35 see chapter 4, section 4.8.

Annual mean ozone concentration ($\mu g/m^3$) is obtained by averaging the hourly concentration over the whole year. It is a useful metric for estimating long term trends in ozone concentrations and is therefore more dependent on NO concentrations, rather than on photochemical ozone formation (Stedman and Kent, 2008). Several other metrics are used in literature for expressing ozone concentration and ozone spatial and temporal trends vary according to the metric used. Generally peak ozone values, for instance maximum ozone concentrations over a threshold value such as 100 or 120 $\mu g/m^3$, maximum annual daily or annual ozone concentrations are more dependent on photochemical ozone formations and summer time ozone episodes, rather than on NOx concentrations (for details on annual average of the daily maximum of the running 8-h mean with a 70 $\mu g/m^3$ cut-off; annual average of the daily maximum of the running 8-h mean with a 100 $\mu g/m^3$ cut-off; or number of days with daily maximum of running 8-h mean exceeding 120 $\mu g/m^3$ see Stedman and Kent, 2008).

9.2.3 GAM

Multiple linear regressions are the most widely used methodologies for modelling the dependence of ozone concentration on several explanatory variables (e.g., Soja and Soja, 1999; Pont and Fanton, 2000; Tidblad et al., 2002; Pai et al., 2009). Linear regressions explicitly assume normality of the error term and linearity of the relationship between response variable (in this case ozone) and the covariates. As ozone data are not normally distributed and have non-linear association with predictors, several researchers (e.g., Baur et

al. 2004; Gardner and Dorling, 1999) have proposed that linear regression models may be ill proposed for ozone data analysis. GAM relaxes these restrictions and can handle the non-linearity in the association of dependent and independent variables (Wood, 2006, Koenker, 2005).

In this PhD project QRM is applied for modelling ground level ozone concentration using several predictors, including traffic related air pollutants, meteorological parameters and traffic characteristics (see Chapter 6, 7, and 8). However, in this chapter GAM is employed because of several reasons: (a) The spatial or geographical parameters used as predictors in this Chapter have only one value for each site, for example, altitude of the monitoring site or distance of the site from the coast. To fully appreciate the capability of the QRM model, generally more than 1 quantile will be used. However, that is not possible as the variable has only one value, therefore QRM might not be appropriate here; (b) GAMS use curves or surfaces rather than a series of regression model to take account for non-linear behaviour, and that the approach is more amenable to use with variables that interact differently depending on their own values rather than the predictors value. So, the approach is more appropriate for modelling latitude and longitude related effects, and (c) the GAM method is better suited for predictive use.

9.2.4 GAM Model Development

Firstly a GAM model was developed to study only the effect of site type (urban or rural) on ozone concentration. As site type (RB, RBA, RBN, SUB, UB, UI, and UT) is a qualitative or categorical parameter, therefore it needs to be handled differently. GAM model can handle a categorical variable as shown below. The model developed is shown below and the results are described in section 9.3.4:

$$\text{Ozone} = f(\text{as.numeric}(\text{site-type})) + \varepsilon \quad \ldots\ldots\ldots (9.1)$$

A GAM model was also developed for annual mean ozone concentration using the spatial variables easting and northing (m), altitude (m), distance from coast (km) and NOx concentrations ($\mu g/m^3$) as independent variables and annual mean ozone concentrations ($\mu g/m^3$) as dependent variable. Various models formulas were investigated, and the following, in which the effect of easting and northing has been fitted as an interactive term was selected on the basis of performance:

$$\text{ozone} = f(\text{easting, northing}) + f(\text{altitude}) + f(\text{distance from coast}) + f(\text{NOx}) + \varepsilon \quad \ldots.(9.2)$$

In Equation (9.1) the ‘f’ term (also expressed as ‘s’ sometimes) is the smooth function of the covariates and ε is the residual or error term. For smoothing term the degree of smoothing was automatically assigned by the generalized cross validation (GCV) method described by

Wood and Augustin (2002). For more details regarding the smooth function and GAMs, readers are referred to Wood (2011) and Wood (2006). Several metrics were calculated for assessing the model performance, which are described in chapter 4, section 4.7.

9.3 Results and discussions

In this section data analysis and the results of the model are described. Firstly in section 9.3.1 to 9.3.7 the associations of ozone with spatial variables are analyse applying graphical presentation and correlatin analysis. In section 9.3.8 the results and performance of the GAM model are analysed. In section 9.3.9 the spatial variability of ozone expressed in AOT40 (ppb hr or $\mu g/m^3$ hr), SOMO35 (ppb hr or $\mu g/m^3$ hr) and annual mean ozone concentration (ppb or $\mu g/m^3$) are compared.

9.3.1 Spatial variations of ozone

Ozone concentrations demonstrate considerable spatial variations across the UK. Ozone concentration at a given location in the UK can be influenced by a combination of global, regional and local-scale effects (Jenkin, 2008). The observed trend in ozone concentration therefore is determined from the net effect of these three factors. The relative contributions of each factor vary both spatially and temporally in the UK. In the UK the following four local factors play a vital role in controlling ozone concentrations:

1. Altitude: Upland tends to have higher ozone concentrations due to topographical effect and demonstrates relatively less diurnl variations (Chevalier et al., 2007; Coyle et al., 2001);
2. Proximity to coast: Sites near the coast show generally higher ozone concentrations and less diurnal variations **(**Entwistle et al., 1997);
3. Southeast factor: The southeast region of the UK tend to have higher photochemical ozone formation (Jenkin, 2008) and high rate of ozone depletion by NOx (Coyle et al., 2002);
4. Urban Influence: Rural areas tend to have higher ozone level due to less NOx scavenging effect (Jenkin, 2008; AQEG, 2009).

The effects of these four factors on ozone concentrations are investiagted in this chapter in detail. Hourly ozone data from 80 ozone monitoring sites were obtained for the most recent five years (2007 to 2011). Annual mean and five years mean ozone concentrations were calculated for each site. The five year mean was calculated to account for the yearly variation and have a more persistent value for each site for further spatial analysis. The five year mean ozone concentrations at various monitoring sites in the UK have been visualised

in Figure 9.1. Ozone monitoring sites can be divided in to four main categories according to the 5 years mean ozone concentrations (µg/m^3). These categories are low (16 – 30, blue colour), moderate (30 – 45, green colour), high (45 – 60, yellow colour) and very high (60 – 74, red colour). The spatial variability of annual ozone and their comparison with AOT40 and SOMO35 are described in section 9.3.9. In the following section, variability of annual ozone with respect to various spatial characteristics are discussed.

9.3.2 Urban and rural comparison

Ozone concentrations are generally higher at rural monitoring sites than suburban and urban monitoring sites, as shown in Figure 9.2, where annual mean ozone concentration (µg/m^3) for year 2007 to 2011and 5years mean are visualised. Out of top 20 sites having the highest 5 year mean ozone concentration, 17 are rural and 2 suburban sites and only one urban. There are 31 monitoring sites that have 5 year mean ozone concentrations less than 42; out of these only one is rural (Glazebury) and two suburban (Mold and Manchester South), the rest are all urban sites. This clearly shows that ozone concentrations are relatively higher at rural sites. Figure 9.2 shows that at ozone concentrations 40 to 50 µg/m^3, there is a mixed area where both rural and urban sites can be found. This is due to the fact that apart from urban and rural effects there are other factors (e.g. altitude, proximity to coast and other local factors) that have influence on ozone concentration. Due to these factors each category (rural, urban and suburban) has a degree of scatter in their values. The five year average ozone concentrations (µg/m^3) at rural sites range from 41 to 73; suburban range 42 to 68; and urban range from 16 to 51. The five year mean ozone concentrations (µg/m^3) for rural, suburban and urban are 55, 49 and 40, respectively, which means that according to our analysis ozone concentrations in rural areas are 15 µg/m^3 (27%) higher than urban areas and 6 µg/m^3 (12%) higher than suburban areas.

There are 7 very high sites (where ozone concentrations range 60 – 75 µg/m^3) and 5 low sites (where ozone concentrations range 45 – 60 µg/m^3), the rest are roughly half moderate and half high (Figure 9.1). Out of the 5 low sites, 3 sites are situated in London and 2 in Manchester and they are all urban background sites, except London Marylebone, which is an urban traffic (formally called roadside or kerb) site. The low 5 sites are London Marylebone, London Hillingdon, London Bloomsbury, Manchester Piccadilly and Salford Eccles. Among the low sites, London Marylebone has the lowest yearly and 5 years mean ozone concentration (16.5µg/m^3). The seven very high sites are all rural sites, except Lerwick. Lerwick is a suburban site according to DEFRA (UK-AIR, 2012) classification but Scottish air quality, 2012 has classified Lerwick as a rural site. The writer personally is more inclined towards Scottish air quality classification due the nature of the surrounding area and in fact due to the high ozone concentration measured at the site. However, this

project follows classification of DEFRA, therefore Lerwick will be treated as suburban site. The other six very high sites are Mace Head, Strath Vaich, Aston Hill, Weybourne, Narberth and Yarner Wood. The highest five years mean was recorded at Mace Head (73), followed by Strath Vaich (68) and Lerwick (67).

Rural monitoring sites are located more than 20 km away from urban agglomerations (large urban areas) and more than 5 km away from other built-up areas, industrial installations or motorways or major roads, so that the air sampled is representative of air quality in a surrounding area of at least 1000 km^2 (UK-AIR, 2012). Due to these characteristics rural sites are generally characterised by low traffic flow and hence low emission of NOx. It is shown (chapter 6) that NO/NO_2 ratios are generally higher in urban areas and lower in rural areas. The amount of NOx and the ratio of NO_2/NO are considered important for the higher ozone concentrations in the rural areas. On the other hand in urban areas fresh NO emitted mainly by road traffic react with ozone molecules and reduces ozone levels, particularly in urban traffic areas (roadside or kerb sites). The urban effect on ozone concentration is known as urban decrement or urban influence (AQEG, 2009).

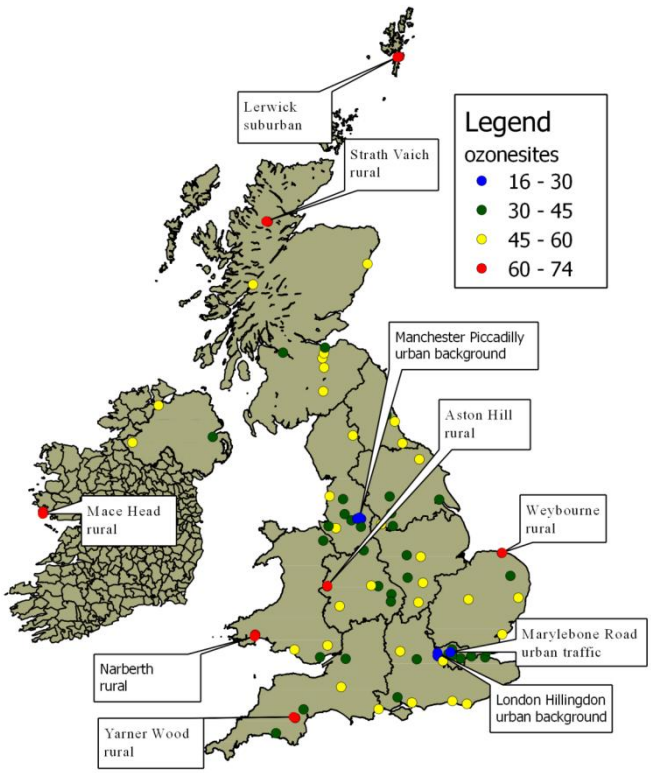


Figure 9.1. Ozone monitoring sites colour coded according to 5 year mean ozone concentrations in ($\mu g/m^3$) (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

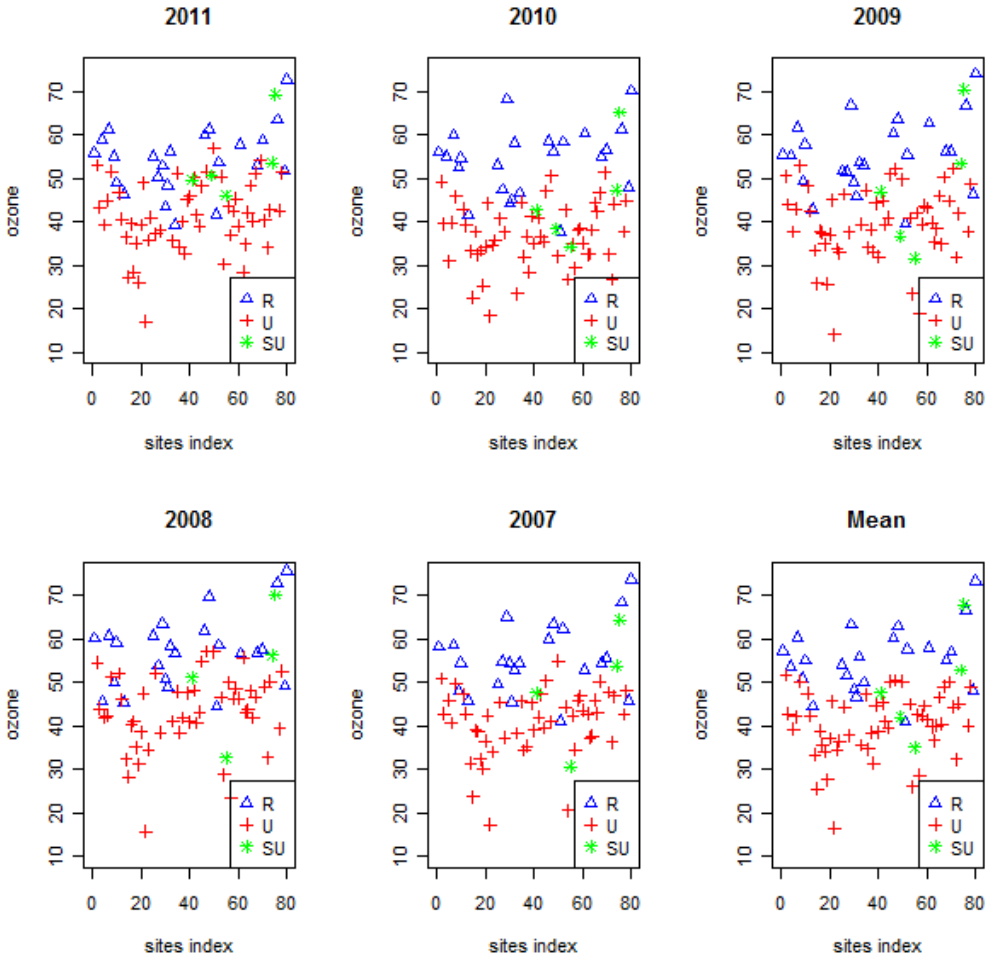


Figure 9.2. Mean ozone concentration (µg/m^3) characterised by site type (rural - R, urban – U and suburban - SU) for year 2007 to 2011 and 5 years mean. Rural sites are expressed by blue triangles, urban by red summation sign and suburban by green asterisk.

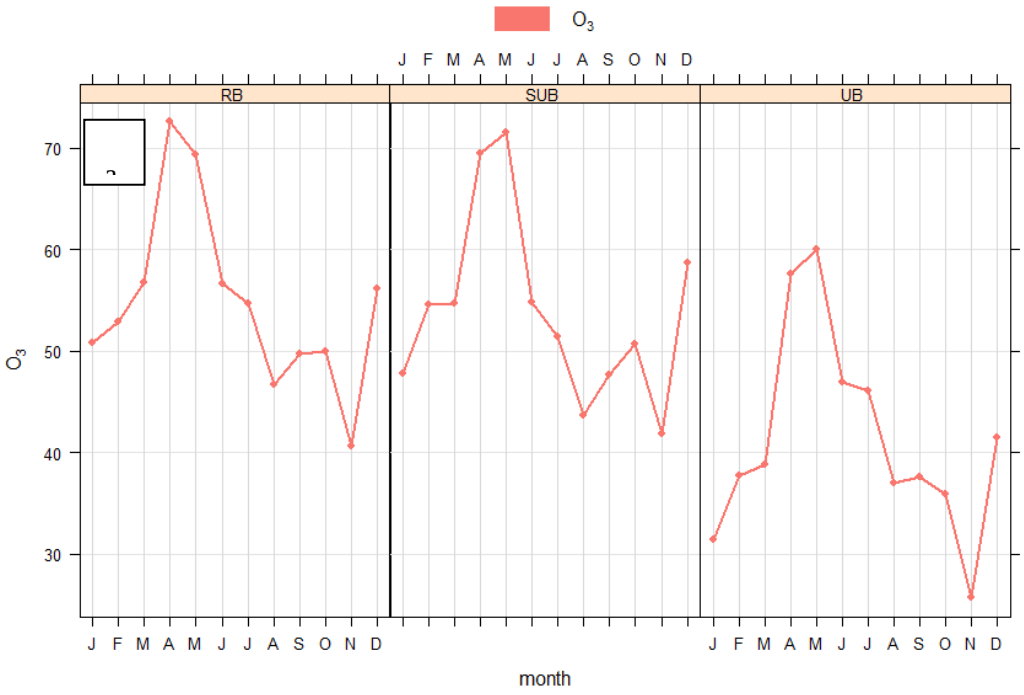
9.3.3 Urban influence on monthly, weekly and diurnal cycle of ozone

Ozone concentrations vary spatially in the UK and have different seasonal, weekly, and diurnal cycle in rural, urban and suburban areas. The hourly ozone data (µg/m^3) from 80 monitoring sites are visualised in Figure 9.3 (a, b, and c). Figure 9.3 demonstrates that ozone concentrations are considerably lower at urban sites than both rural and suburban sites. The seasonal cycles (Figure 9.3a) of ozone at rural, suburban and urban sites, although generally show the same pattern i.e. high in April and May and low in November, ozone concentrations are much lower at urban sites. In every single month ozone concentration is higher at rural than urban sites. Table 9.1 shows the percent urban decrement in ozone concentrations at urban sites, which was calculated as shown below.

% Urban Decrement = [(rural ozone – urban ozone)/rural ozone]*100.

Urban decrement is considered to be due to the fresh NO emitted mainly by road traffic. The monthly urban decrement ranges from 13 to 38 % for May and January, respectively (see Table 9.1 for more details). Table 9.1 (a) shows that urban decrement is higher in winter and lower in summer months, probably due to the fact that in winter months atmosphere is relatively stagnant as compared to summer months due to high temperature in summer. When the atmosphere is turbulent and the air gets mixed up quickly, NOx scavenging effect is reduced due to dispersion. Furthermore, in summer ozone advection from the surrounding rural areas may reduce the urban decrement.

On weekly and daily basis ozone cycles show considerable difference at rural and urban locations. Figure 9.3 (b and c) visualise the weekly and diurnal cycle of ozone at rural, suburban and urban sites and clearly demonstrates how ozone concentrations differ at these sites. The differences between rural and urban locations on weekly and daily basis are also given in Table 9.1 b & c. On weekly basis the lowest difference between rural and urban sites was observed on Sunday (18%) followed by Saturday (23 %) and highest on Friday (about 28%), which is understandable due to low traffic activities on the weekend. On daily basis lowest difference between urban and rural site was observed at 00:00 to 04:00 am and highest during 06:00 to 10:00 am. The lowest difference was 10 – 11 µg/m^{3}and highest was 15 - 17 µg/m^3. The lowest and highest differences in ozone concentration between urban and rural sites correspond well with the traffic flow, which is generally lower on weekend and higher on weekdays. In the morning and afternoon peak hours the difference is greater, most probably caused by high level of NO emitted by road traffic in these hours.



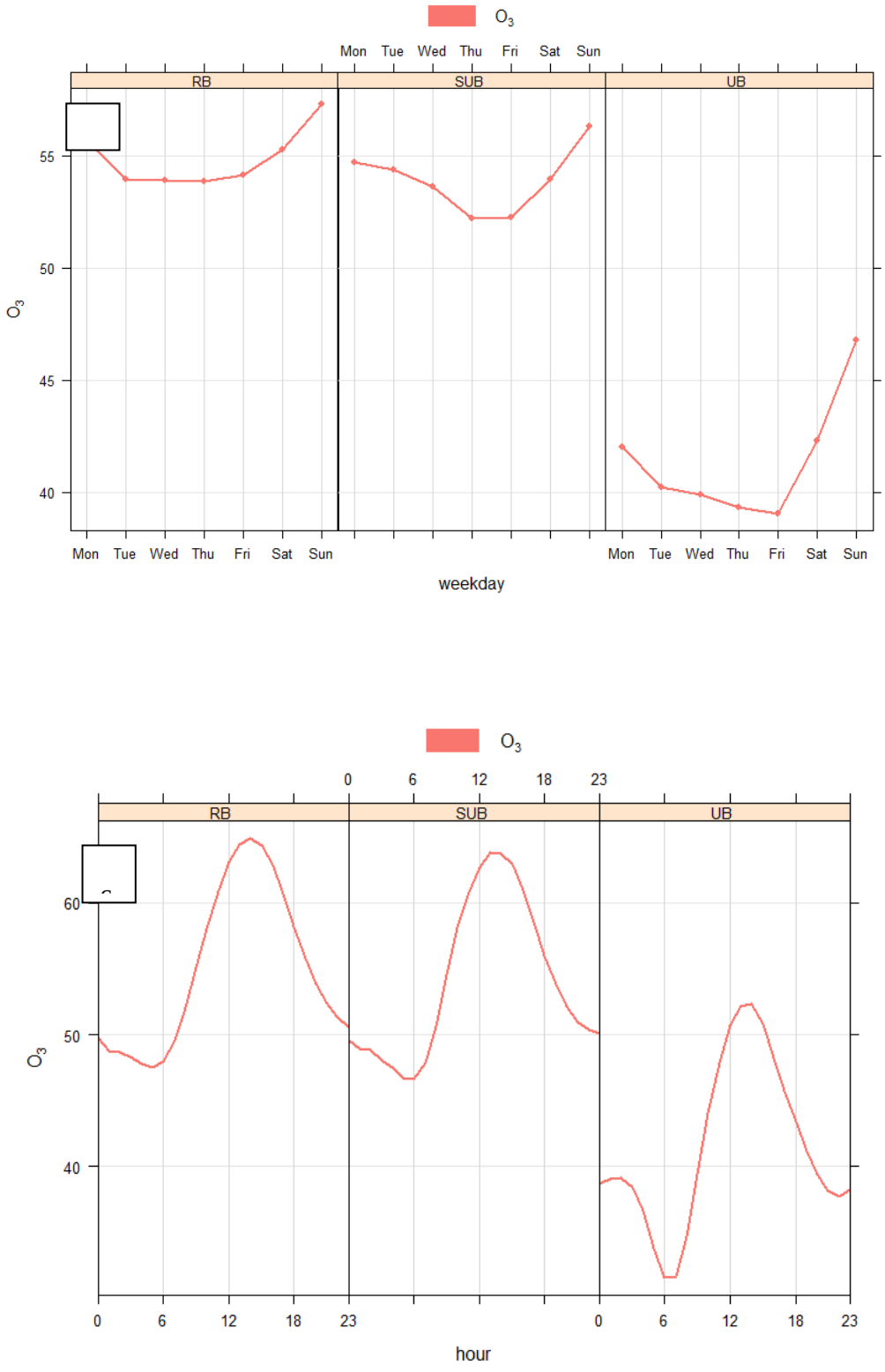


Figure 9.3. Ozone concentrations (µg/m^3) at RB (rural), SUB (suburban) and UB (urban) sites: (a) seasonal (b) weekly and (c) diurnal cycle of ozone using data for 2011 for all 80 sites.

Table 9.1. Ozone concentrations ($\mu g/m^3$) for 2011 at rural (RB) and urban (UB) sites and their differences and percent differences; for (a) Monthly, (b) weekly and (c) daily.

(a) Monthly

Month	RB O_3 ($\mu g/m^3$)	UB O_3 ($\mu g/m^3$)	Urban Decrement ($\mu g/m^3$)	% Urban Decrement
January	50.84	31.39	19.46	38.27
February	52.93	37.69	15.24	28.79
March	56.75	38.79	17.97	31.66
April	72.61	57.62	14.99	20.64
May	69.35	60.05	9.30	13.41
June	56.69	46.88	9.82	17.32
July	54.74	46.09	8.65	15.80
August	46.70	37.02	9.67	20.72
September	49.77	37.62	12.16	24.43
October	49.94	35.92	14.02	28.07
November	40.64	25.65	14.99	36.87
December	56.13	41.50	14.63	26.07

(b) Weekly

Weekday	RB O_3 ($\mu g/m^3$)	UB O_3 ($\mu g/m^3$)	Urban Decrement ($\mu g/m^3$)	% Urban Decrement
Monday	55.68	41.99	13.69	24.59
Tuesday	53.93	40.20	13.72	25.45
Wednesday	53.89	39.90	13.99	25.96
Thursday	53.85	39.34	14.51	26.95
Friday	54.11	39.02	15.09	27.89
Saturday	55.24	42.29	12.95	23.45
Sunday	57.27	46.78	10.49	18.32

(c) Daily

Hour of the day	RB O_3 ($\mu g/m^3$)	UB O_3 ($\mu g/m^3$)	Urban Decrement ($\mu g/m^3$)	%Urban Decrement
0	49.76	38.74	11.02	22.15
1	48.77	39.04	9.73	19.96
2	48.69	39.14	9.55	19.61
3	48.28	38.44	9.84	20.39
4	47.78	36.62	11.15	23.35
5	47.46	33.83	13.63	28.72
6	47.98	31.58	16.39	34.17
7	49.57	31.67	17.90	36.11
8	52.01	34.67	17.34	33.35
9	55.06	39.38	15.69	28.49
10	58.03	44.02	14.01	24.15
11	60.86	47.87	12.98	21.34
12	63.07	50.72	12.36	19.59
13	64.42	52.18	12.24	19.00
14	64.88	52.29	12.60	19.41
15	64.33	50.83	13.50	20.99
16	62.90	48.26	14.64	23.27
17	60.69	45.72	14.97	24.66
18	58.23	43.41	14.82	25.45
19	55.82	41.21	14.61	26.17
20	53.83	39.37	14.46	26.87
21	52.42	38.14	14.29	27.25
22	51.33	37.73	13.61	26.51
23	50.57	38.24	12.34	24.40

9.3.4 Investigating urban influence using GAM

The differences in ozone concentration at urban, rural and suburban site are described with the help of GAM (defined in chapter 4), using ozone as dependent and site type as independent variable. There are seven types of monitoring sites, which are rural background (RB), rural background agriculture (RBA), rural background nature (RBN), suburban background (SUB), urban background (UB), urban industrial (UI) and urban traffic (UT). Site type shows whether a monitoring site is a rural, urban or suburban. It can be observed in Figure 9.4 that site types from 1 to 3, which are RB, RBA, and RBN have positive effect; whereas site types from 5 to 7 (UB, UI, and UT) have negative effect on ozone concentration. The suburban which has been assigned number 4 shows a weaker negative effect than urban sites. The highest negative effect on ozone concentration is demonstrated by number 7 that represent urban traffic (roadside) monitoring sites. London Marylebone is one of the urban traffic site and has recorded the lowest mean ozone concentration, most probably due to high road traffic flow (80, 000 vehicles/hour) (UK-AIR, 2012), which emit large amount of NOx. The negative effects of NOx on ozone concentration are well established (e.g. Jenkin, 2004; Jenkin, 2008).

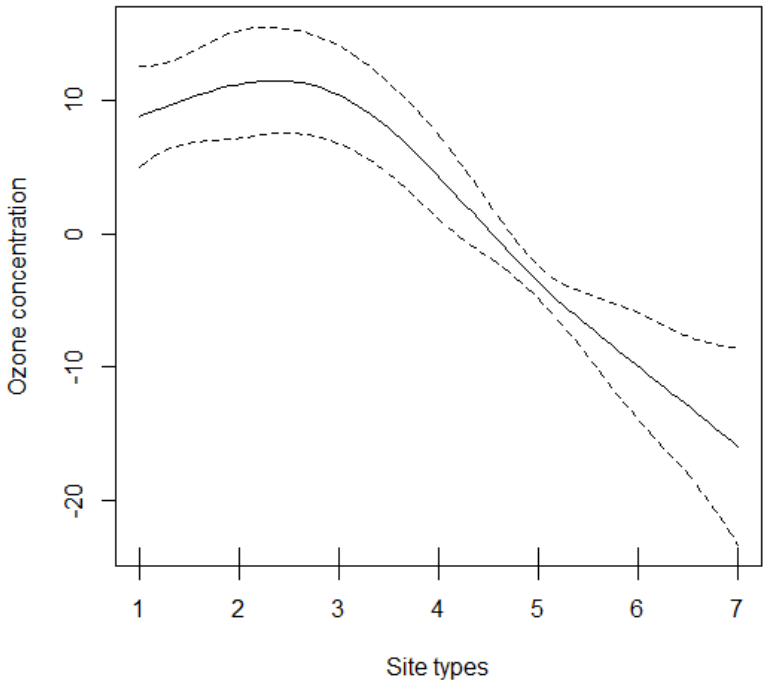


Figure 9.4. The outputs of GAM using dummy variable for monitoring site type (RB, RBA, RBN, SUB, UB, UI and UT), using 5 years mean ozone (µg/m^3) data (2007 to 2011) from eighty monitoring sites.

9.3.5 Northsouth and eastwest variations in ozone concentrations

Ozone concentrations vary spatially in the UK (Coyle et al., 2002) and as described in the preceding sections, the main factor responsible for this variation is the rural-urban factor. In Figure 9.1 the green and blue points (characterising low ozone concentrations) can be mostly seen in the large cities of England (e.g. London, Birmingham, Nottingham, Manchester and Leeds). In the northern part of England (beyond Yorkshire and Humberside), which have relatively high altitude the number of low (low ozone concentration) and moderate (ozone concentration) sites are negligible. Further north (Scotland) although have very few monitoring sites, these are mostly red or yellow indicating relatively high annual ozone concentrations, such as Lerwick and Strath Vaich. Furthermore, the numbers of sites with high ozone concentrations are also dominant in the southern part of England, which also has some low ozone sites. In other words, the southern part contain majority of both low and very high sites. Several factors, including altitude, the amount of NOx emissions, and meteorological variables, especially temperature and solar radiations influence ozone concentrations in the UK (e.g., Jenkin, 2008, Jenkin et al., 2002, Coyle et al., 2002). The southern part is relative sunnier and more urbanised, the former contribute positively and the latter contribute negatively to the observed ozone concentration, therefore those sites which are in the rural area demonstrate high level of ozone, however those sites situated in urban areas demonstrate low ozone levels due to the scavenging effect of NOx.

The five years mean ozone concentration was plotted against the northing and easting coordinates (Figure 9.5), which shows a positive trend in ozone concentrations towards north and negative towards east. The southeast part of the UK is relatively sunnier and is affected by ozone precursors (NOx and VOCs) believed to be transported from the northwest Europe. Both of these properties are conducive to photochemical ozone formation. On the other hand this part contains the largest urban area (e.g. London); where ozone concentrations are lower due to NO titration. Therefore, the northsouth or eastwest relationship is confounded by a couple of factors, which are urban influence, local meteorology and altitude.

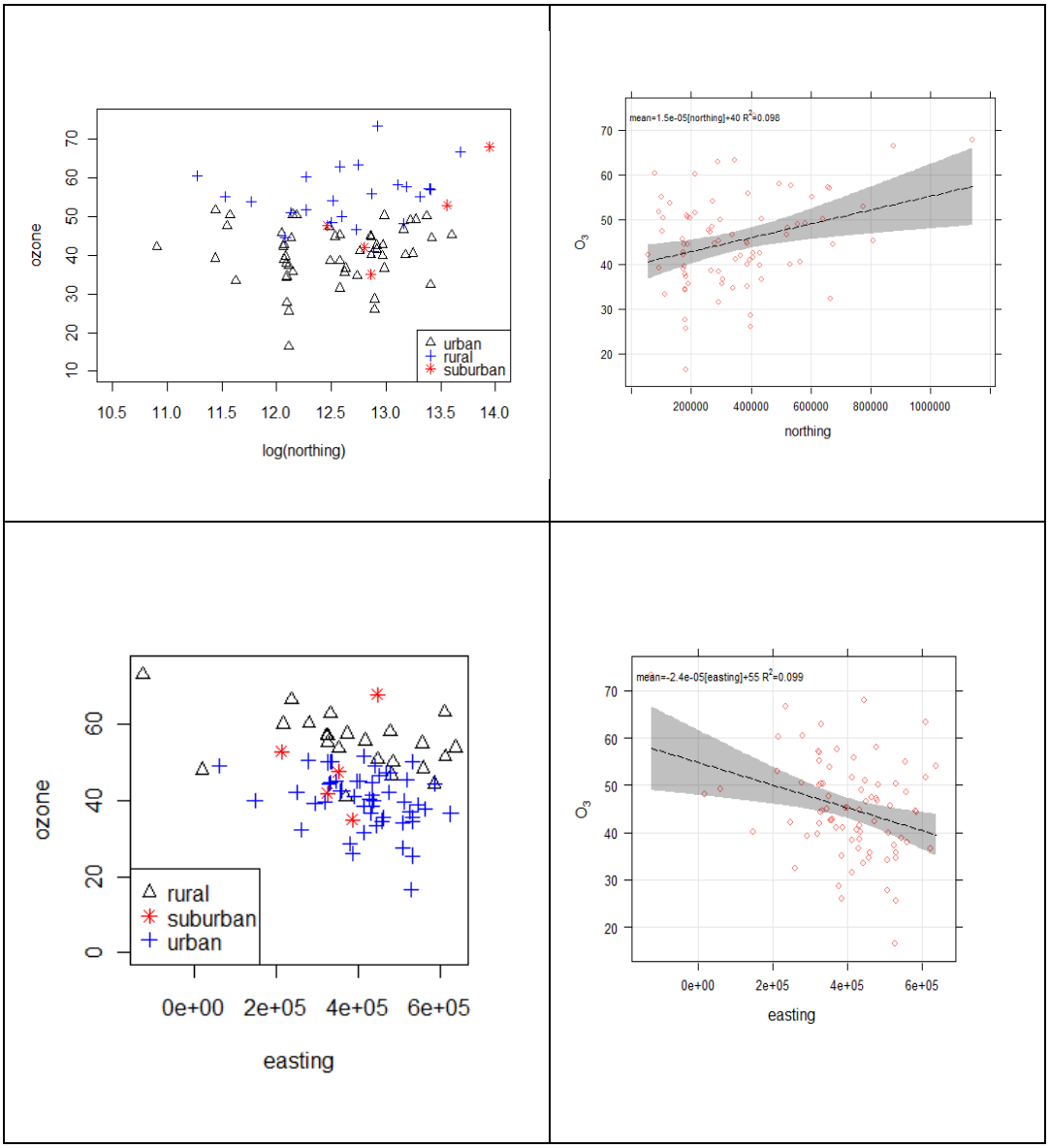


Figure 9.5. Five years mean ozone concentrations (µg/m^3) from 80 rural, urban and suburban monitoring sites, plotted against the northing and easting (in meters) of the monitoring sites.

Alternatively 8 hour running means of ozone concentrations were calculated for year 2011 and a subset of ozone concentrations above 100 µg/m^{3}was taken. That is all those hours were selected when ozone concentration was greater than 100µg/m^3, and the number of hours were counted for each site. The counts of hours (the number of hours when ozone concentration was greater than 100) are shown in Figure 9.6. In spite of some scatter (Lerwick, Strath Vaich and Mace Head), the counts clearly decreased going towards northwest. In other words there is a decreasing trend in ozone concentration towards northwest. Correlation was negative between counts and northing and positive between

counts and easting. The northing factor was considerably stronger than the easting factor. When the sites were divided into rural and urban sites, the value of correlation coefficient between counts and northing became stronger. Scatter plots of counts against northing are shown in Figure 9.7, where rural, urban, all sites (rural and urban) and rural without 2 sites (Weybourne and Strath Vaich) are shown in panel top – left, top – right, bottom – left, and bottom – right, respectively.

This shows that different metrics (measuring units, e.g. annual mean, number of hours over a certain threshold) have different spatial variation in the UK. For instance, annual mean ozone concentrations showed an increasing northing trends, whereas counts over the threshold of 100µg/m^3, showed a decreasing northing trend. This is further elaborated in latter sections, using AOT40, SOMO35 and annual mean ozone concentrations in section 9.3.9.

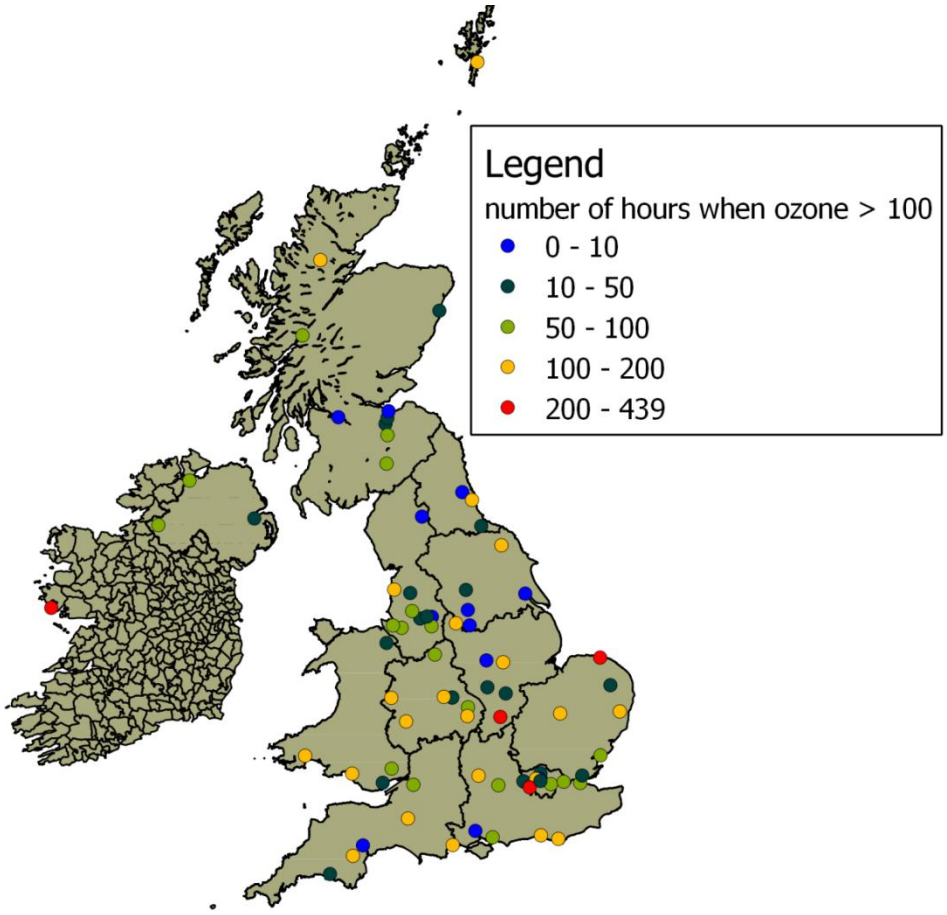


Figure 9.6. UK map with ozone sites colour coded by counts (the number of hours when ozone concentration was greater than 100 µg/m^3), using ozone data for 2011 from 80 monitoring sites (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

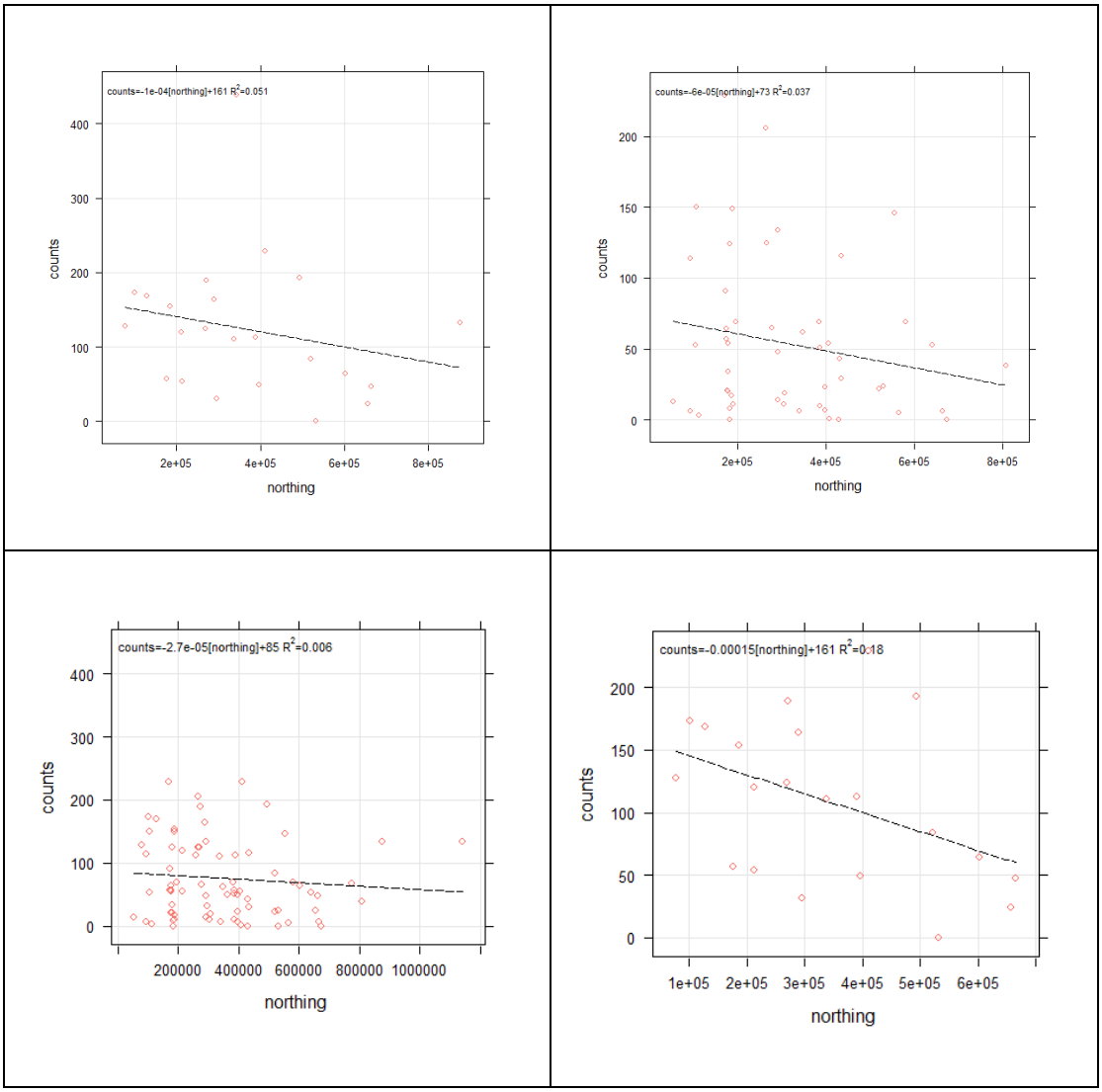


Figure 9.7. Scatter plot of counts (the number of hours when ozone concentration was greater than100 µg/m^3) and northing at rural (top-left), urban (top-right), both urban & rural (bottom-left), and rural without 2 sites (Weybourne and Strath Vaich) (bottom-right).

9.3.6 Variation in ozone concentrations with altitude

In this section the effect of altitude (meters above seas level, m asl) on average annual ground level ozone concentration is investigated. The sites having the highest altitude is Great Dun Fell (GDF), which has 847 m asl elevation, followed by Ladybower (420 m asl) and Aston Hill (370 m asl). The sites that have the lowest elevations are Hull Freetown (4 m asl) and Wicken Fen (5 m asl). The mean and median altitudes are 87 and 43 m asl, respectively. The mean value is twice the value of median probably caused by the high altitude of GDF and Ladybower.

Atmospheric turbulence is considerably enhanced in mountainous and hilly areas which affect pollutants circulation (Chevalier et al., 2007). Ozone concentrations near the ground

surface are reduced by dry deposition and NOx titration, therefore background ozone levels increase with height. The ozone gradient is very steep up to 1000 m (around 30 ppb/km) and gentler but still meaningful above (around 3 ppb per kilometre) (Chevalier et al., 2007).

In Figure 9.8, the five years mean ozone concentrations are plotted against the altitude of the monitoring sites. There seems to be a clear positive correlation between the two variables. The Spearman's rank correlation coefficient was 0.37 for the whole dataset, but when the sites were divided to rural and urban, the Spearman's rank correlation increased slightly to 0.43 for rural sites and decreased drastically to 0.12 for urban sites. Probably the reason for the weaker correlation at urban sites is the fact that most of the urban monitoring sites are located in flat areas; the maximum altitude in urban areas is 175 m asl (Leamington Spa). Within 175 m altitude the difference in ozone concentration would be obviously not much, which is causing poor correlation with altitude. The correlation for rural sites might have been even stronger in the absence of two sites (Mace Head - MH and Weybourne – WB), which are clear outliers as their altitude is 15 and 16 m asl and the five year mean ozone concentrations ($\mu g/m^3$) was 73 and 66, respectively. The most probable reason that makes ozone concentration higher at MH and WB in spite of their low altitudes is that both of these sites can be classified as coastal sites. Dry deposition of ozone, which is particularly important at night times and markedly decreases ozone concentrations (Coyle et al., 2002) do not occur over open water surfaces as much as on land surface or vegetation (Entwistle et al., 1997). Therefore during on-shore wind flow coastal sites observe higher ozone concentrations than the sites further inland. Roughly daily mean ozone concentrations with on-shore winds flow are 5 to 7 $\mu g/m^3$ higher at the coasts than at inland sites **(**Entwistle et al., 1997). When the two sites were removed from the data, the relationship was markedly improved (as shown in Figure 9.8, bottom-right) and the Spearman's rank correlation increased to 0.69. This also shows how different factors interfere in the relationship of ozone with other variables. Furthermore, altitude affects the diurnal cycle of ozone in the UK. Figure 9.9 demonstrates the diurnal cycle of ozone at four monitoring sites, which are selected on the basis of their altitudes, i.e. 2 of these sites have highest and 2 have lowest altitude. The sites are Great Dun Fell (GDF), Ladybower (LB), High Muffles (HM), and Wicken Fen (WF) and their altitudes are 847, 420, 267 and 5 m asl, respectively. Generally ozone concentrations are higher during day times particularly during the afternoon due to enhanced photochemical ozone formation and lower during night times probably due to dry depositions plus NOx scavenging effect. Figure 9.9 shows that the sites with greater altitudes have less differences in night and day ozone concentrations and vice versa. Night time ozone depletion depends on local topography and meteorology. Sites situated on hill face little night time ozone depletion, whereas low lying sites experience more night time ozone depletion (Entwistle et al., 1997; Coyle et al., 2001). On hill sites as the lower layers

of the troposphere cools, the cold air flows down-slope and is replaced by relatively ozone rich air from above; whereas at low lying sites due to a phenomenon called inversion a very stable boundary layer is produced, stopping replenishing of ozone from top layers. Inversion refers to the atmospheric phenomenon when the normal vertical temperature gradient is inverted such that the air is colder near the surface of the Earth and warmer above. Great Dun Fell, having the highest altitude had highest and lowest ozone concentrations of 55 and 52 µg/m^3, respectively during the diurnal cycle showing an amplitude of 3 units; whereas the Wicken Fen site, having the lowest altitude had highest and lowest ozone concentration of 61and 31 µg/m^3, respectively showing an amplitude of 31 units. This shows how much the diurnal cycle of ozone, most probably due to differences in night time dry deposition is affected by the altitude of the site. It can also be observed that various sites do not show much difference in ozone concentration during the afternoon hours and that major differences in ozone concentration occur during the night time hours which leads to differences in diurnal cycles at various sites.

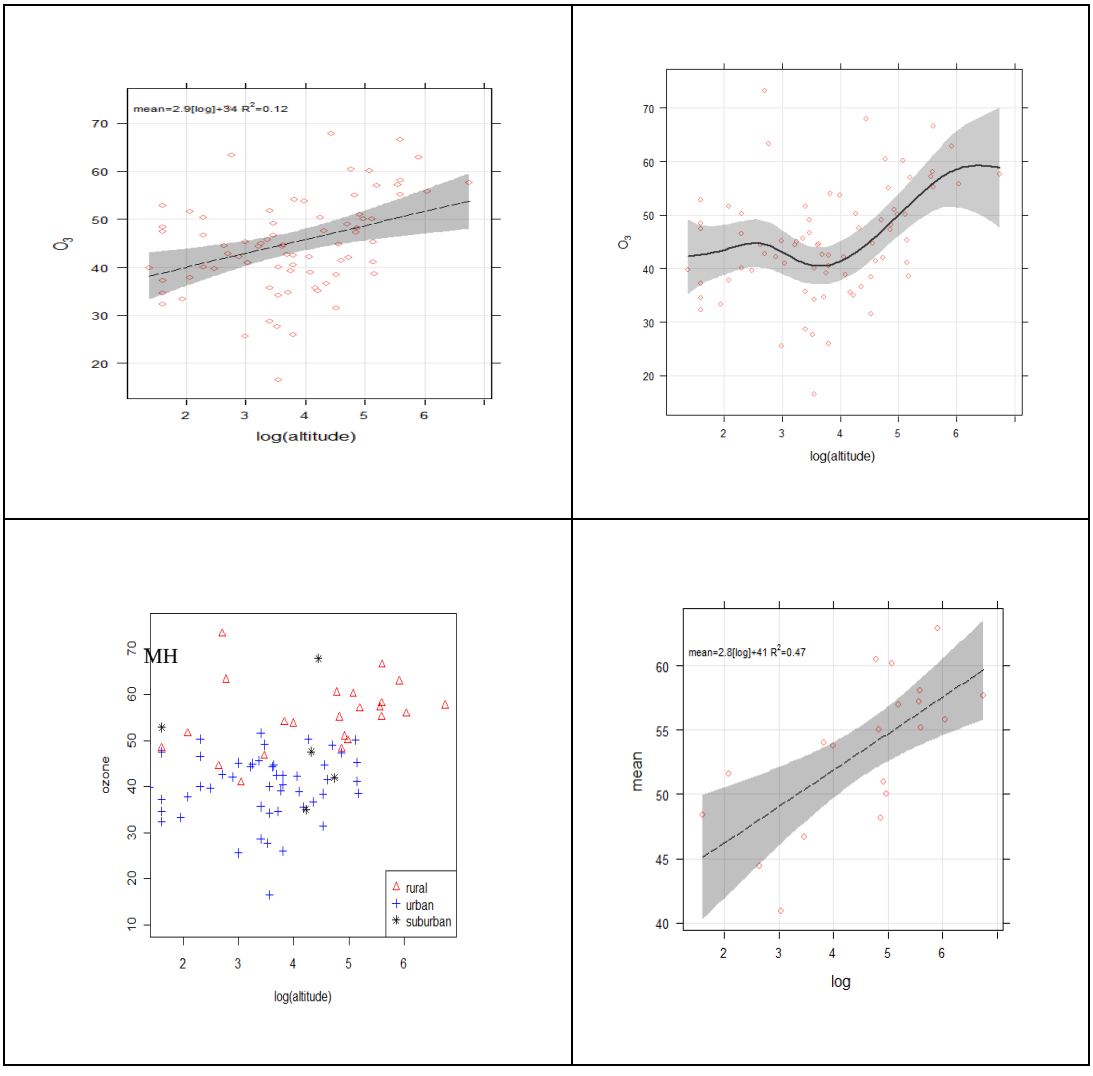


Figure 9.8. Five years mean ozone concentrations (µg/m^3) plotted against altitudes of the sites, top plot shows all sites with linear line and smooth line and the bottom left plot is coded by the type of site (rural, urban and suburban), whereas the bottom-right plot shows only the rural sites (without Mace Head - MH and Weybourne – WB, the two coastal sites).

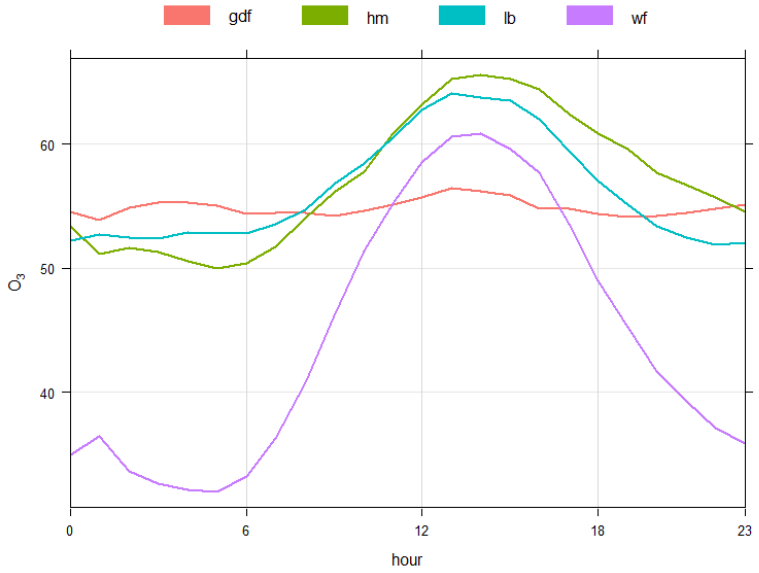


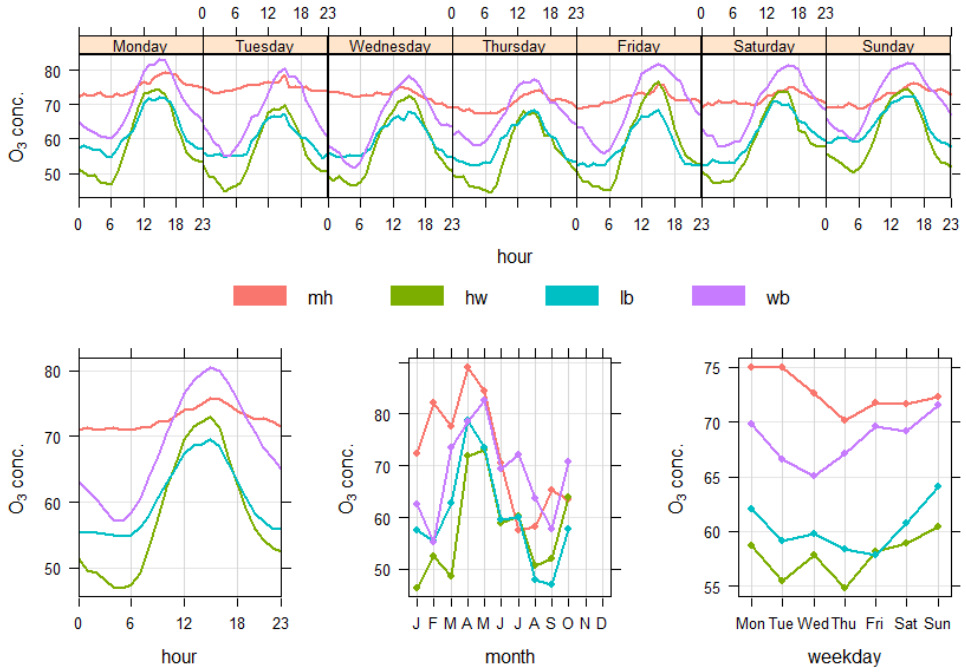
Figure 9.9. Diurnal cycles of ozone (µg/m^3) at Great Dun Fell (gdf), High Muffles (hm), Ladybower (lb) and Wicken Fen (wf) for year 2011.

9.3.7 Coastal effect on ozone concentrations

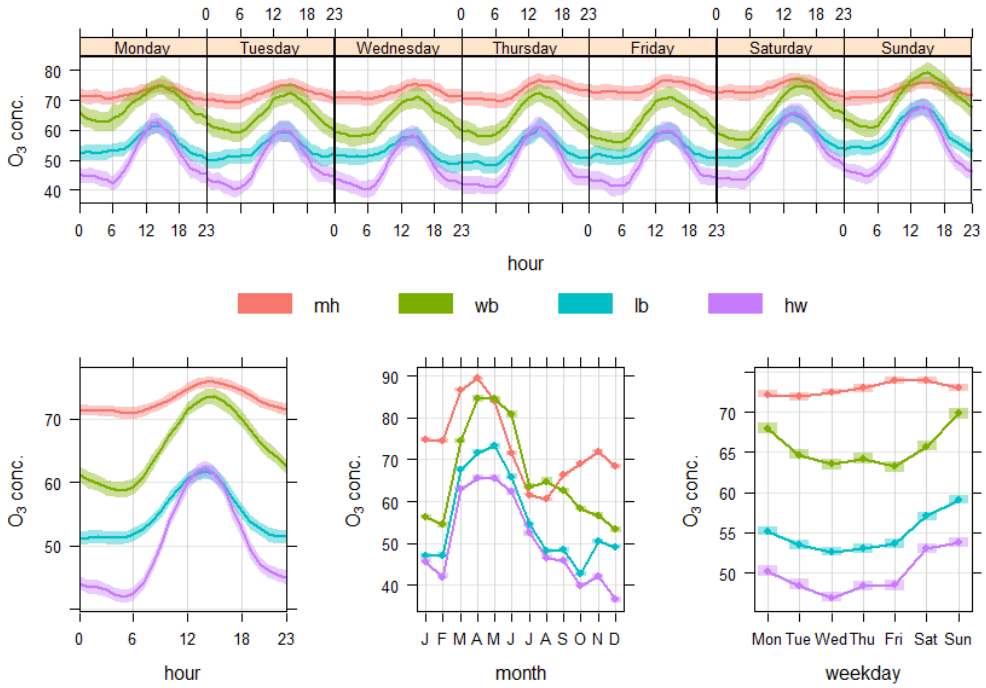
It is shown by Entwistle et al. (1997) that the deposition rates of ozone are different to water surfaces and ground surface or vegetations, which leads to different ozone concentrations at inland and coastal sites. Ozone deposition rate is greater to land surfaces, especially to vegetation than to water surface. The relatively less deposition of ozone to water surface may lead to vertical gradients in the boundary layer over the open sea relatively smaller than on land. This results in high ozone concentrations on seas surface. Therefore with on-shore winds, coastal sites experience higher concentrations of ozone than sites further inland; while with off-shore flow the differences between the coasts and inland is smaller.

Figure 9.10 (a and b) show the time variations of ozone concentrations at four monitoring sites (mh – Mace Head, wb – Weybourne, lb – Ladybower, and hw – Harwell). Mace Head is the only true coastal site and is located about 100 meters off the sea shore in a rural background area of Ireland. Weybourne can also be considered as a coastal monitoring site and is less than a kilometer away from the sea-side, located on the north coast of Norfolk in eastern England in a rural background location. Ladybower and Harwell are two inland monitoring sites situated in east-Midland and southeast of the UK, respectively (UK-AIR, 2012). It can be observed (Figure 9.10) that mean ozone concentration for year 2011 and

four years mean ozone concentrations (2007 to 2010) are greater at Mace Head and Weybourne. The diurnal cycle of ozone shows much less day and night differences at Mace Head than the other sites. Standard deviation was 16 for Mace Head and about 21 for the other sites. Mean ozone concentrations were 72, 68, 56 and 55 for Mace Head, Weybourne, Ladybower and Harwell, respectively. It should be noted that apart from proximity to coast other characteristics may vary at these sites that might affect ozone concentration. These may include altitude or urban effect. To avoid these confounding factors all sites included in this example are rural sites and their altitudes are 15, 16, 420, 137 for Mace Head, Weybourne, Ladybower and Harwell, where the coastal sites have less altitude and theoretically they should have less ozone concentration and larger amplitude (day-night variations) but observations at these sites show the opposite trend i.e. higher ozone concentrations and smaller amplitude at the coastal sites. This indicates that coastal effect is contributing to the observed concentrations rendering ozone levels higher and day – night differences lower.



(a) 2011



(b) 2007 to 2010

Figure 9.10. Time variations of ozone concentration at mh (Mace Head), wb (Weybourne), lb (Ladybower) and hw (Harwell) (a - top) for year 2011 and (b – bottom) mean for year 2007 to 2010.

To further investigate the effect of distance from the coast on ozone concentration, distance from the coast of all ozone monitoring sites was measured in kilometre (km) using Google-Earth and correlation analysis was performed. Spearman correlation coefficient was negative between distance from the coast and mean ozone concentrations, which means the closer the site to the coast, the larger the ozone concentrations and vice versa. Spearman correlation coefficient was -0.39 between 5 years mean ozone concentration and distance from the coast. Figure 9.11 shows the scatter plot between mean ozone concentrations and the distance from the coast. When the monitoring sites were divided into urban and rural sites, the Spearman correlation coefficient increased for urban sites (-0.48) and decreased for rural sites (-0.28). The higher negative correlation for urban sites is most probably due to NOx scavenging effect in urban areas that destroy ozone molecules.

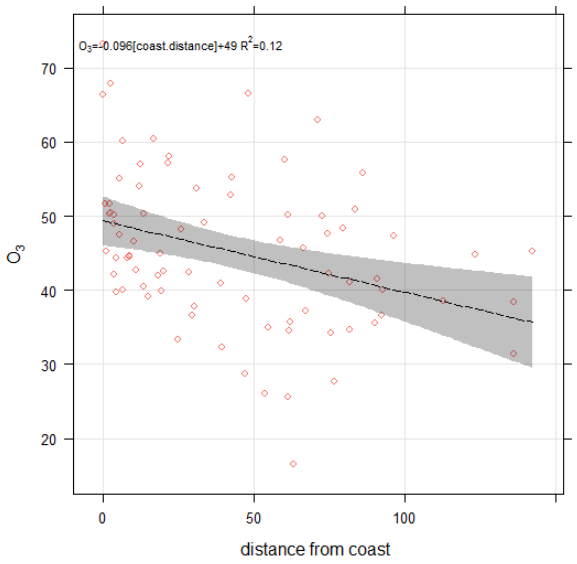


Figure 9.11. Scatter plot of 5 years mean ozone (µg/m^3) and distance from the coast (km) of all sites, showing a Spearman correlation coefficients of -0.39.

9.3.8 Out puts of GAM

Results of the spatial GAM model developed in section 9.2.4 are discussed in this section. Outputs of the model (Equation 9.2) are visualised in Figure 9.12. The significance value (p-value) is less than 0.05 for all covariates showing a significant effect, except altitude. However, the p-value for altitude was close to 0.05 and when altitude was removed from the model, GCV value increased from 16 to 23 and the adjusted R^2 decreased from 0.92 to 0.85, suggesting its inclusion was beneficial. In addition, compared with Equation 9.2: the substitute of northing and easting with latitude and longitude did not have a significant effect on the performance of the model; the use of separate easting and northing terms, i.e. f (easting) + f (northing), had a slight but significant effect on the goodness of fit (R^2 - value); and the performance of model did not improve significantly when NOx was substituted with its two components (NO_2 and NO).

The effects of easting and northing on ozone concentrations are depicted in Figure 9.12 (top-panel central element), along with the confidence intervals (shown to either side). Annual mean ozone concentration increases towards north and decreases towards east across the UK. This trend was consistent with the previously reported by Coyle et al. (2002); who contributed this to enhanced depletion of ozone in large urban areas in the southeast of the UK, e.g., London. However, here it should be noted that this trend was reversed when only high ozone concentration was considered. For example, if either hourly maximum ozone concentrations or hourly ozone concentrations over 100 µg/m^3 were analysed, ozone concentrations increased towards southeast (as discussed above). Jenkin

(2008), who observed a similar (reversed) high ozone trend, attributed this to the relatively sunnier climate of the south and an additional ozone precursors (NOx and VOCs) burden from northwest Europe. Both of these factors could contribute to higher level of photochemical ozone formation, and increase episodic ozone levels in spring and summer seasons. The current observations would then suggest that episodic ozone, which mostly occurs in spring and summer afternoon, does not have a major influence on annual mean ozone concentration. In contrast, annual average ozone concentration seems to be driven by the altitude of the site and the degree of urbanisation, which provide a continuous sink for ozone, particularly during night hours and winter seasons when atmospheric conditions are unfavourable for photochemical reactions.

Altitudes of the monitoring sites show a positive effect on ozone concentration and mean ozone concentration seems to increase with increasing altitude (Figure 9.12, bottom-middle). Previously both Coyle et al. (2002) and Chevalier et al. (2007) reported similar trends, citing possible reasons including: greater dry deposition and NOx titration of ozone near ground surfaces; greater atmospheric turbulence in mountainous and hilly areas, increasing dispersion rates and reducing the effective mixing time for reactive species; and reduced night times ozone depletion in higher mountain regions. The correlation between ozone and altitude was stronger for the rural monitoring stations by comparison to urban monitoring sites. The weaker correlation at urban sites is most likely the result of several factors: (1) Rural sites were spread across a much wider range of altitudes providing a wide range of measurements to test a correlation across; (2) Urban sites tended to be at lower altitudes so local ozone concentrations were lower and signal-to-noise ratios were reduced; and (3) Although at least partially accounted for by the NOx term in the model, the urban decrement may also act as a confounder.

Ozone concentration declines with distance from the coast, negatively correlated with the distance from the coast within a range of 0 to 60 km (Figure 9.12, bottom - left). Entwistle et al. (1997) reported that ozone deposition was less to water surface than to ground surface or plants leaves. Therefore coastal sites show higher ozone concentrations during periods when winds are blowing on-shore by comparison to inland monitoring sites. During off-shore wind this difference is reduced (Entwistle et al., 1997). Beyond about 60 km from the coast ozone concentration appears to increase with distance from the coast but confidence intervals are large and sample size small making this portion of the smoothing term more debatable. Here, the negative correlation was stronger for urban sites, by comparison to rural sites, most likely as a result of the gas phase titration of ozone by freshly produced NOx in urban areas.

The effect of NOx on ozone concentration is shown in Figure 9.12 (bottom - right). The negative correlation between NOx on ozone concentration is well established (e.g. Jenkin, 2004; Jenkin, 2008). Due to higher level of NOx and its scavenging effect, ozone concentration is considerably lower in urban areas where NOx concentrations are typically high. The five year mean ozone concentration for rural, suburban and urban sites was 55, 49 and 40, respectively. This means that ozone concentrations in rural areas are 15µg/m^3 (27%) higher than urban areas and 6 µg/m^3 (11%) higher than suburban areas. According to UK-AIR (2012) rural monitoring sites are characterised by low NOx concentrations due to the fact that they are located more than 20 km away from large urban areas and more than 5 km away from other built-up areas, industrial installations, motorways or major roads and associated NOx sources. By comparison, in urban areas sources such as road traffic emit large amounts of NOx and act as a sink for ozone.

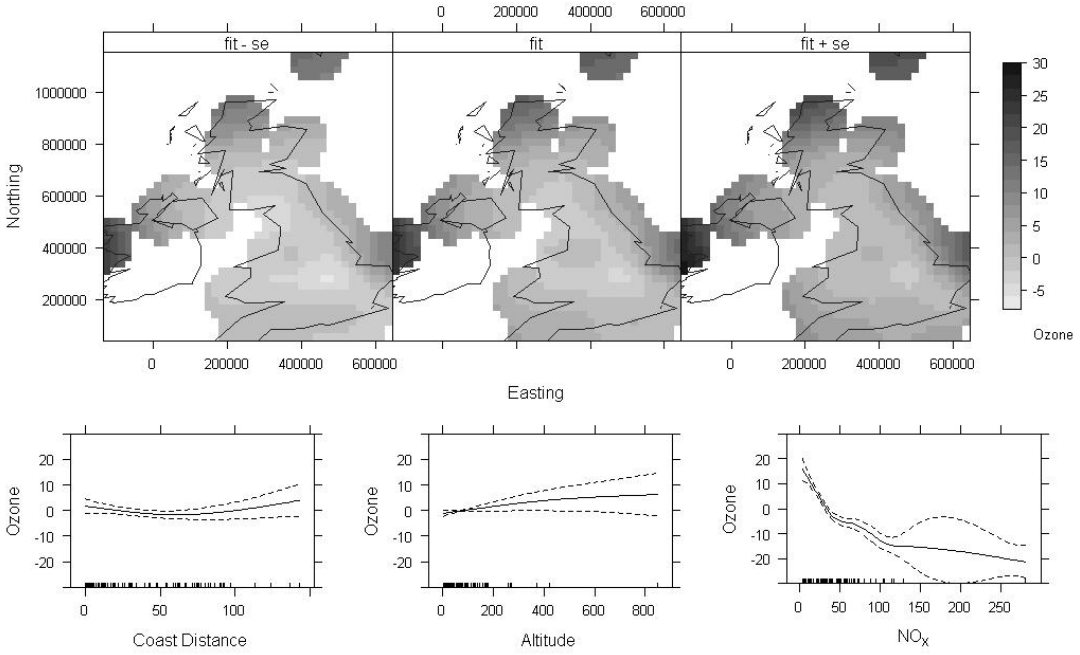


Figure 9.12. Model (Equation 9.2) outputs using mean ozone concentration for year 2010 as response variable and easting, northing, altitude, distance from coast and NOx concentration as explanatory variables for 80 ozone monitoring sites. For the interactive easting/northing term (top) the response surface is shown in three parts, with the model fit as the centre panel and the associated lower and upper (95%) confidence intervals to the left and right, respectively. For the three single component terms the fit line and confidence intervals are shown as a solid line and dashed lines, respectively. The vertical lines adjacent to the lower x-axis show the presence of data.

9.3.8.1 Assessing performance of the models

The statistical metrics used to evaluate the models performance are described in chapter 4, section 4.7 and their values are presented in Table 9.2. Derwent et al., (2010) recommend that an air quality model is considered acceptable if more than half of the predicted pollutant (in this case ozone) concentration lies within a factor of 2 of the observed concentration and faulty if not. The FAC2 presented in Table 9.2 has a value of 1, indicating that 100% predicted values lie within a factor of 2. It is further recommended (Derwent et al., 2010) that air quality models are considered acceptable if NMB values lie within the range between -0.2 and +0.2 and faulty if not. The NMB value for this model (0.00) lies within the described range.

Table 9.2. Statistical metrics for evaluating the performance of the model.

Metrics	Base Model 5 years mean (2007 – 2011)	Test Cases			
		Temporal[1]		Spatial[2]	
		Training 2010	Testing 2011	Training 2010	Testing 2010
FAC2	1	1	1	1	1
MB	0.00	0.00	-1.50	0.00	-0.01
MGE	2.12	2.50	3.70	2.64	3.03
NMB	0.00	0.00	-0.03	0.00	0.00
NMGE	0.05	0.06	0.08	0.06	0.07
RMSE	2.96	3.60	4.91	3.80	3.90
R^2	0.93	0.92	0.86	0.88	0.83

[1]Temporal model was developed for 2010 and tested for 2011using all 80 sites

[2]Spatial model was developed for 2010 using data from 68 sites and tested for the same year for 12 sites, not part of the training data.

To further evaluate the performances of the models, predicted and observed ozone concentrations are compared. Both temporal and spatial predictions of ozone are considered. For temporal (future) ozone prediction the model was developed for year 2010 and validated for year 2011. For spatial prediction the dataset for 2010 was divided into two subsets i.e. training data (used for model development) and testing data (used for model validation). The training data has 68 and testing data has 12 monitoring sites. The 12 sites (Figure 9.14) were systematically chosen to make sure representation from various geographical types (e.g. urban, rural, sites from England, Scotland and N Ireland etc.).

Figure 9.13 compares observed and predicted ozone concentration with the help of a scatter plot, which is very useful to consider for model evaluation (Carslaw, 2011). In the scatter plot it is much easier to see where the data lie and to get a feeling about bias, etc. Relatively more points lie below the 1:1 line (middle line in Figure 9.13) and there seems to be a slight negative bias. The dashed lines show the within factor of two (FAC2) region and it is perhaps worth noting that all points lie well within this region (FAC2 = 1). R^2 and NMB were 0.86 and -0.03, respectively, for predicted and observed ozone concentrations. The values of other metrics are presented in Table 9.2 (column 4).

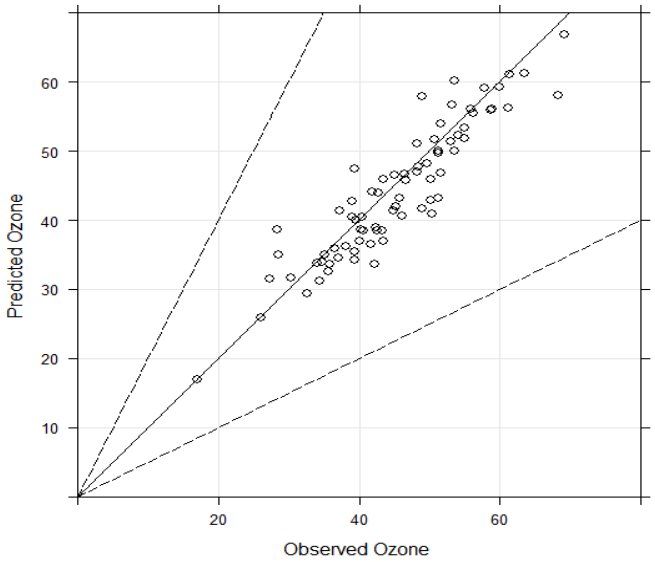


Figure 9.13. Comparison of observed 2011 ozone concentrations and predicted concentrations based on the 2010 model and 2011 NOx measurements. The middle solid line is 1:1, and the above and below dashed lines are 0.5:1 and 2:1, respectively. So, the area between the two dashed lines is the factor of two (FAC2) regions.

9.3.8.2 Spatial prediction

The 12 ozone monitoring sites used for spatial model validation are shown in Figure 9.14. The predicted and observed values correlate well. The highest difference between observed and predicted ozone concentration for urban sites was estimated for Newcastle Centre (7.63 µg/m^3) and for rural sites it was for High Muffles (5.88 µg/m^3), whereas Reading New Town showed the least difference between observed and predicted ozone concentration (0.11 µg/m^3). For five sites the model slightly over-estimated and for seven sites under-estimated ozone concentrations. Several other statistics were estimated to check the performance of the model. NMB, R^2 and FAC2 metrics were 0.00, 0.83 and 1, respectively (other metrics are presented in Table 9.2, column 6). The score and Figure 9.14 of these statistics indicate good model performance.

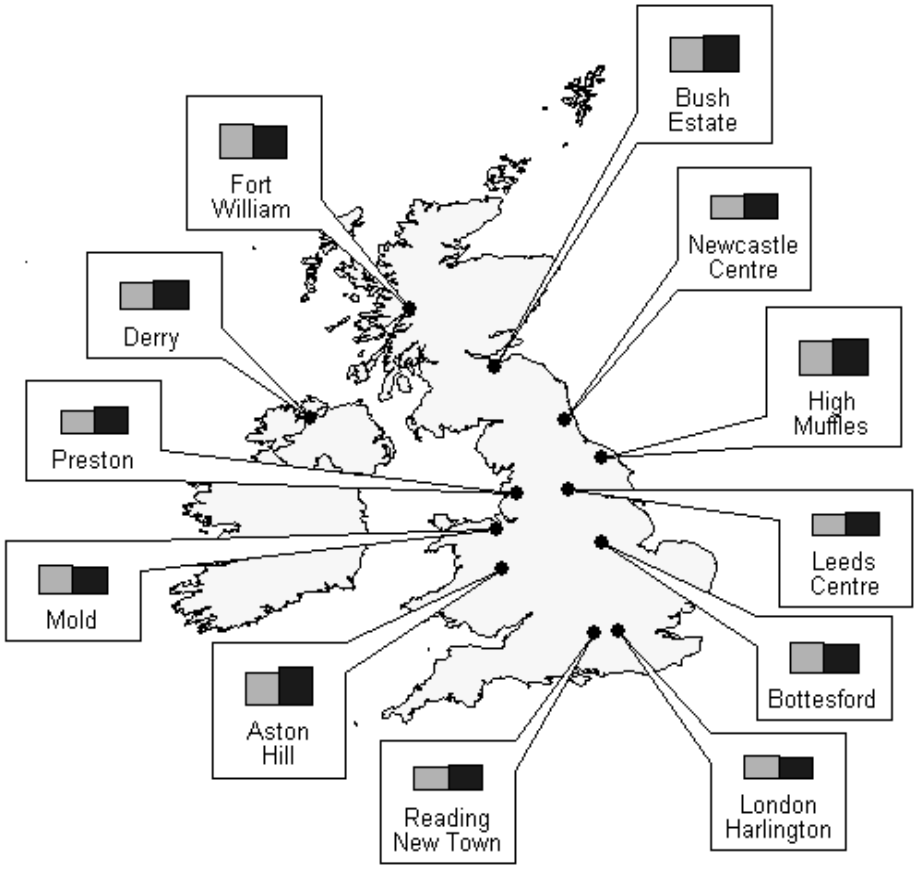


Figure 9.14. Comparison of observed and predicted ozone concentration (µg/m^3), grey columns show predicted ozone and dark black columns show observed ozone. The difference in predicted and observed concentrations (µg/m^3) were 1.13 (Aston Hill), -3.02 (Bottesford), 2.51 (Bush Estate), -1.27 (Derry), -6.38 (Fort William), 5.88 (High Muffles), -1.45 (Leeds Centre), -1.70 (London Harlington), -6.98 (Mold), 7.63 (New Castle), -0.76 (Preston) and 0.11 (Reading New Town).

9.3.8.3 Model use for scenario testing

This section demonstrates the use of the model as a scenario testing tool. NOx emission reduction strategies can potentially have a significant effect on ozone concentration, and tools that helps to investigate this negative feedback quickly and robustly can help develop more reliable strategies for the management of future ozone level. The main impacts of a changing urban ozone decrement will not be on the rural sites and agricultural crops where traditionally most concerned has been focused with ozone damage but in the urban areas where the largest populations spend the majority of their time, on urban green spaces where

increasing values have been placed and the older and more sensitive building materials that make up some of our oldest urban institutions.

Recently Carslaw et al. (2011) presented new NOx predictions for the year 2020. Scenario 3 in this work was based on a revised road traffic emission factors derived from vehicle emission remote sensing data. See Carslaw et al. (2011) for more details of various emission scenarios and the revised road traffic emission factors. NOx concentrations for 2010, NOx predictions for 2020 and associated differences for the scenario 3 case for this study are presented here in the first three columns of Table 9.3. On average NOx concentrations are projected to be about 46% lower in year 2020 by comparison to 2010. The lowest and highest percent difference was recorded for Aberdeen (25%) and London Marylebone (64%). Compared to 2010, five sites have greater than 50 % reductions in NOx projections for 2020, whereas only one site (London Bloomsbury, 53%) is expected to suffer the same amount of increment in ozone concentration, followed by London Marylebone (46 %). Using these NOx projections in the proposed model (Equation 9.2), associated ozone trends were estimated (column five to seven in Table 9.3). On average ozone concentrations are projected to be about 26 % higher in year 2020, and the estimated range was about 7 % (London N. Kensington) to 53 % (London Bloomsbury).

Several authors have previously expressed concerns regarding the potential negative feedback effect on ozone levels from current NOx mitigation strategies (e.g. Williams, 2007; AQEG, 2009). There is clear evidence that annual mean ozone levels in urban areas are increasing, mainly because of a reduction in the levels of NOx (or more specifically NO) and the associated reduction in the NOx titration effect. In 2007 it was estimated that if the trend then observed continued, the urban annual mean would approach that of rural ozone sometime around 2020 (Williams, 2007). More recently less pronounced trends have been observed and AQEG (2009) predict that ozone concentration in 2020 will be still lower in urban areas than in rural areas. Ozone projection presented in Table 9.2 suggests about 26 % increase in urban ozone by 2020. As the urban decrement was estimated to currently be of the order of 27%, this would suggest a small 2020 decrement of the order of 1%. However, here it should be recognised that the current model assumes that for any given site ozone trends will be governed by NOx levels because all other model inputs (location, altitude and distance to coast) are fixed, or, put more simply, background ozone levels are effectively static. Elsewhere, several authors (e.g. Derwent et al., 2007; Carslaw, 2005, and Jenkin, 2008) have reported that average background ozone concentration in rural areas is increasing about half a unit ($\mu g/m^3$) per year, driven by emissions and processing of ozone precursors on a global scale. If this trend is assumed to be on-going, a half a unit per year background ozone would equate to an additional increase to ozone at all sites of 5 $\mu g/m^3$ (9

%) by 2020, although it is unclear how this additional background contribution would be distributed across the UK and this is an aspect of the approach that we would seek to refine in future research.

Table 9.3. NOx ($\mu g/m^3$) and ozone concentrations ($\mu g/m^3$) for year 2010 (observed) and 2020 (estimated) and the differences between the two years.

Site Name	NOx[1] ($\mu g/m^3$)			Ozone[2] ($\mu g/m^3$)		
	2010	2020	Difference abs (%)	2010	2020	Difference abs (%)
Aberdeen	40	30	-10 (25.00)	44.15	47.78	+3.63 (8.22)
Belfast centre	67	35	-32 (47.76)	37.72	42.48	+4.77 (12.64)
Cardiff centre	50	35	-15 (30.00)	35.57	42.07	+6.51 (18.29)
Derry	32	15	-17 (53.13)	44.91	54.20	+9.29 (20.69)
Glasgow centre	103	45	-58 (56.31)	26.81	35.31	+8.50 (31.71)
L. Bloomsbury	105	50	-55 (52.38)	22.58	34.58	+11.99 (53.11)
L. Kensington	58	40	-18 (31.03)	34.41	36.77	+2.36 (6.85)
L. Marylebone	280	100	-180 (64.28)	18.36	26.97	+8.61(46.90)
Man. Piccadilly	95	40	-55 (57.89)	26.74	37.38	+10.63 (39.76)
South. Centre	65	40	-25 (38.46)	33.27	38.93	+5.67 (17.03)
Average	89.5	43	-46.5 (45.62)	32.45	39.65	+7.20 (26.48)

[1]NOx data for 2010 (observed) come from the UK AURN and for 2020 (estimated) from Carslaw et al., 2011.

[2]Ozone data for 2010 (observed) is from the UK AURN and for 2020 is estimated using the model proposed in this chapter.

9.3.9 Comparison of different metrics (AOT40, SOMO35, and Annual Mean)

In this section different standards (guidelines or critical values) used for ozone measurement are compared and their spatial variation is analysed. The standards considered in this section are AOT40, SOMO35, and Annual Mean. These standards are

briefly described in the methodology section of this chapter. More details can be found in the Chapter – 4 (Methodology) and in the references cited.

9.3.9.1 Spatial comparison of various metrics

Figure 9.15 (a, b and c) depict the values of AOT40, SOMO35 and Annual Mean ozone concentration (µg/m^3) calculated for 5 years (2007 to 2011) for 80 ozone monitoring sites. It is worth mentioning that AOT40 values were calculated for ozone concentration measured in µg/m^3, therefore to consider exceedences of the critical level for the protection of agricultural crops, the value 6000 µg/m^3 hr rather than 3000 ppb hr was considered. Values of these metrics in individual year, names of the monitoring sites and site type are given in Appendices 1 (Annual Mean), 2 (AOT40) and 3 (SOMO35).

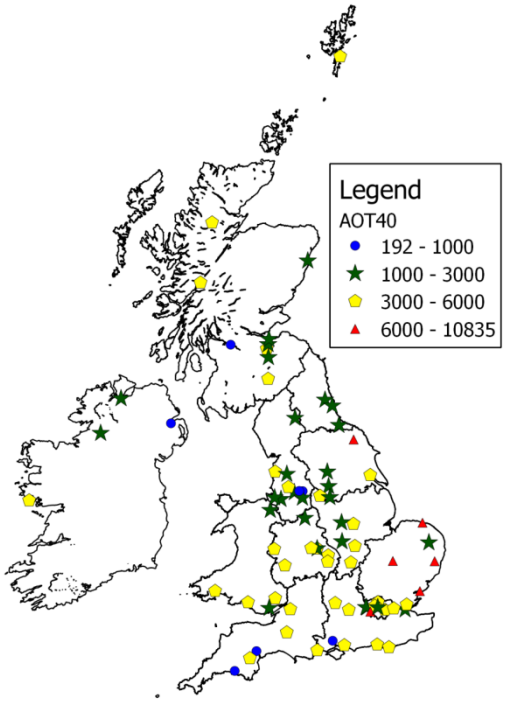
In Figure 9.15 (a) six monitoring sites, depicted as red triangles exceeded the critical level of 6000 µg/m^3 hr. These sites are High Muffles (6365 µg/m^3 hr), London Teddington (7469 µg/m^3 hr), Sibton (6415 µg/m^3 hr), ST Osyth (6381 µg/m^3 hr), Weybourne (10835 µg/m^3 hr) and Wicken Fen (6525 µg/m^3 hr). Five of these 6 monitoring sites are rural monitoring site. London Teddington is the only urban background site, which has exceeded the critical level. This again confirms the fact that rural monitoring sites have relatively high ozone concentrations and result in high AOT40 values. Secondly these sites are situated in the southeast of England, which is generally sunnier and is exposed to ozone precursors transported from the Western European countries. These precursors in the presence of solar radiation react and make ozone molecules by photochemical ozone formation. In individual years 2008 had the highest number of exceedences. Out of 80 monitoring sites 41 exceeded the critical levels of AOT0 (6000 µg/m^3 hr hr). In 2008 the average AOT0 value (6381 µg/m^3 hr) of all 80 sites was greater than the critical level. The average AOT0 values for other years in descending order were 3444, 2453, 2379 and 2309 for year 2009, 2007, 2011 and 2010, respectively. AOT40 values for 2009 and 2008 are significantly greater than the other years and in turn the AOT40 values in 2008 were significantly greater than those calculated for 2009. The numbers of exceedences were 14, 3, 2, and 2 in year 2009, 2010, 2007 and 2011, respectively. Based on five years average, majority of the sites have AOT40 values in the range of 3000 to 6000 µg/m^3 hr (Figure 9.15, a), which might indicate a potential threat in the future in case average ozone concentrations increase further (as suggested above). Most of these sites (3000 to 6000 µg/m^3 hr) are situated in the southern part of the UK, which could indicate higher ozone concentrations in this part but also because the numbers of sites are much more in this part of the country compared to the north. In the highlands of Scotland there are fewer monitoring sites, which are mostly in the yellow range (3000 to 6000 µg/m^3 hr). Although it is rather harder to decide which factor

has more dominant effect in the yellow range, i.e. high altitude (of Scotland) or southern part (of England due to high emission of precursors and being sunnier), however in the red range (AOT40 values > 6000 µg/m^3 hr) it is clear that southeast part due to high photochemical ozone formation has significantly higher ozone concentrations and hence AOT40 exceedences.

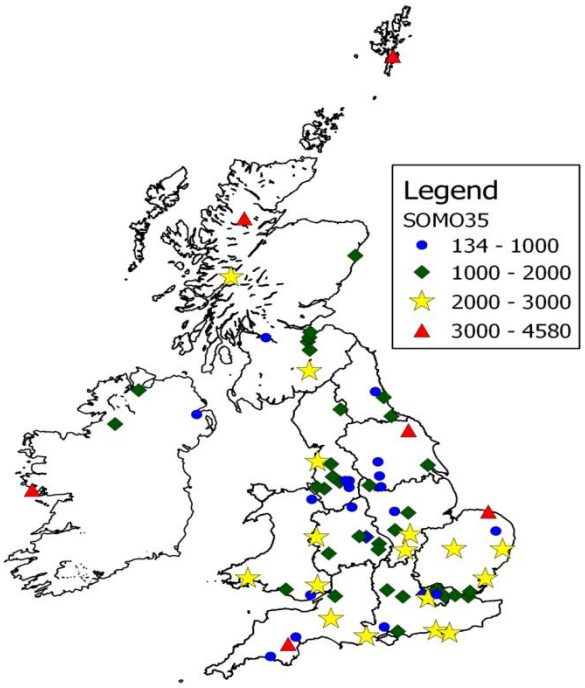
The values of SOMO35 µg/m^3 hr are depicted in Figure 9.15 b and present a different picture from the AOT40 values. There are 2 major differences in calculating AOT40 and SOMO35: firstly and more importantly AOT40 are calculated only for 3 months (May to July) and for 12 hours a day (08:00 to 20:00), whereas SOMO35 are calculated for the whole years and 24 hours a day; secondly AOT40 has a cut off value of 40 ppb (80 µg/m^3), whereas SOMO35 uses a cut off value of 35 ppb (60 µg/m^3). This indicates that AOT40 values are more related to peak values of summer times due to photochemical ozone formation. Probably this is the reason why SOMO35 present show a different pattern. There are 6 red sites (3000 to 4580 µg/m^3 hr hr), which are Lerwick, Strath Vaich, Mace Head, High Muffles, Weybourne and Yarner Wood having SOMO35 values of 3046, 3477, 4580, 3193, and 3014, respectively. There are only two sites in common i.e. High Muffles and Weybourne which are red in both AOT40 and SOMO35. These sites are all rural sites and majority of them can be considered as coastal site, such as Mace Head, Weybourne, and Lerwick. High muffles and Yarner Wood are not typical coastal sites but still not too far from the coast. Strath Vaich is one of those sites which are located in a hilly, remote area having very less NOx concentrations, which face very less titration of ozone by NOx. Yellow, green and blue ranges rather present a uniform picture throughout the UK. In individual years 2008 observed the highest average value of SOMO35 (2201(µg/m^3 hr), followed by 2009 (1571 µg/m^3 hr), 2007 (1539 µg/m^3 hr), 2011 (1533 µg/m^3 hr) and 2010 (1174 µg/m^3 hr).

Figure 9.15 (c) depicts 5 years average ozone concentrations, which were calculated for 2007 to 2011 for 80 ozone monitoring sites. There are 7 monitoring sites having ozone concentrations greater than 60 µg/m^3. The names and ozone concentrations (µg/m^3) of these sites are Lerwick (68), Strath Vaich (66), Mace Head (73), Weybourne (66), Aston Hill (63), Narberth (60), and Yarner Wood (60). These are all rural monitoring sites and 5 of them are the same which were red in SOMO35 and 1 was red in AOT40, which means annual mean ozone concentrations correlates well with SOMO35 rather than with AOT40. Correlation coefficients between annual-mean vs AOT40, annual-mean vs SOMO35 and SOMO35 vs AOT40 were 0.62, 0.86, and 0.86, respectively. Annual mean ozone concentrations for year 2007 to 2011 were 45, 48, 45, 42 and 46, respectively, again showing highest concentration for 2008 followed by 2011.

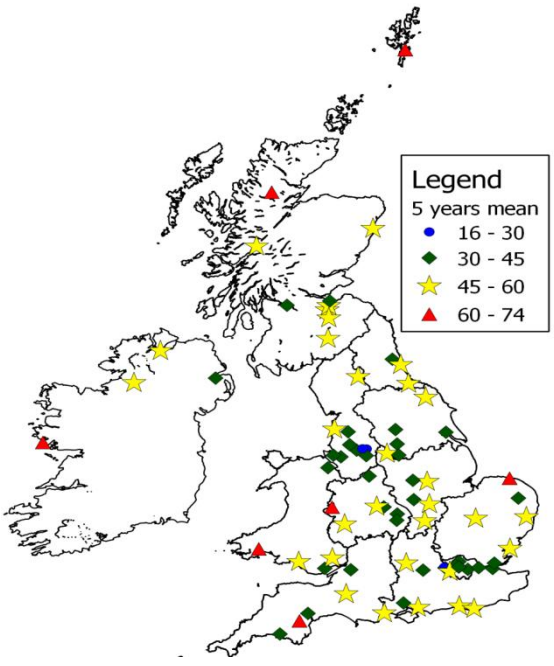
These metrics are calculated for the same data but still they show different spatial variations, probably because these are affected differently by various factors (e.g., NOx, spatial characteristics and Meteorological variables). Steadman and Kent (2008) have compared several ozone metrics and stated that annual mean ozone is strongly influenced by the magnitude of local NOx emissions, whereas SOMO35 are influenced by the magnitude of local NOx emissions and by photochemical episodes. Due to a cut off value of 40 ppb (80 µg/m^3) AOT40 metric is affected by both local NOx emissions and photochemical ozone episodes, therefore has stronger correlation with SOMO35 than annual mean.



(a) AOT40



(b) SOMO35



(c) Annual Mean

Figure 9.15. Spatial comparison of AOT40, SOMO35 and Annual Mean ozone concentrations. The metrics shown are 5 years average (2007 to 2011) for 80 ozone monitroing sites. The names of monitoring sites, values of metrics for each year and some other characteristics are shown in tables (Appendix A, B, and C) (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

9.4 Summary

Ozone concentration and its spatial variation is controlled by a number of factors, including meteorological parameters, several chemical species, sources of precursors emissions (e.g., road traffic characteristics) and climate change. In addition, geographical parameters affect ozone concentrations in various ways. In this chapter the aims was to analyse the spatial variability of ozone in the UK and for the first time develop a model with the help of spatial parameters (altitude of the sites, easting and northing, distance to coast, and rural – urban factor), which are easy to obtain and the model explains considerable proportion of variation in ozone. Rural – urban factors can be replaced with NOx concentration, which slightly improves the model performance and could provide a useful tool for policy makers wishing to link ozone trends with NOx emission strategies.

In this chapter spatial variations of ozone and the association of ozone concentration with spatial characteristics (easting, northing, altitude, distance to coast and site types) and NOx concentration are described. The association has been investigated with help of exploratory data analysis techniques and a GAM. A GAM model using these inputs exhibits characteristics consistent with established ozone behaviour in the UK. Background average ozone level has a pronounced northeasterly component. Ozone concentration is negatively correlated with the distance from the coast within a range of 0 to 60 km, a trend associated with relatively less dry deposition of ozone molecules on water surfaces. Furthermore, there is a positive association between the altitude of monitoring sites and ozone level, most likely due to local topographical effects. NOx, which is mainly derived from road traffic and other combustion sources in urban areas and is negatively correlated with ozone, appears to provide a good surrogate/marker for the site type (urban or rural). Several statistical metrics (e.g., FAC2, NMB, R^2, and RMSE) are estimated for the model and the scores of the metrics place confidence in the model performance. The model was validated both temporally and spatially and the predicted ozone showed strong correlation with observed ozone concentration. The use of the model as an impact assessment tool was demonstrated, and based on 2020 NOx projections it was estimated that the ozone in urban areas would increase by 26% over the same period.

The spatial variability of average annual ozone concentration is compared with health related ozone metrics (SOMO35) and the metrics set up for the protection of agricultural crops (AOT40). These metrics have different spatial and temporal trends in the UK, due to the fact that their levels are controlled by different factors, for instance annual mean ozone concentrations are controlled by local NOx emissions, whereas the levels of AOT40 and SOMO35 are controlled both by both local NOx emissions and photochemical ozone episodes during the summer.

This chapter investigates the spatial variability of ozone in the UK, the next chapter (Temporal trends in ozone concentrations in the UK) describes temporal variability of ozone, especially its historic trends to investigate how ozone concentration has changed over the last 20 years and what are the potential causes.

CHAPTER 10: TEMPORAL TRENDS IN GROUND LEVEL OZONE IN THE UK

10.1 Introduction

Temporal trend is a relationship between time and pollutant concentration and is one of the most important and common tasks in the study of air pollution. Trends are calculated to have a general idea as to how the concentrations of air pollutants might have changed over time; or to establish statistically whether a pollutant has significantly increased or decreased i.e. whether the trend is positive or negative and whether significant or not (Carslaw and Ropkins, 2012). There is a high interest in quantifying surface ozone concentrations and associated trends, as they serve to quantify the impacts of the anthropogenic precursor reductions and to assess the effects of emission control strategies set by national and international organisations (Sicard et al., 2009; Monteiro et al., 2012).

Ozone trends have been extensively investigated over the last decade or so and the factors believed to be responsible for ozone trends are discussed by several authors, such as Cape (2008), Jenkin (2008), Carslaw (2005), Derwent et al. (2007), and Derwent et al. (2010). The main factors controlling ozone trends include: the reductions in the emissions of anthropogenic volatile organic compounds (VOC) and nitrogen oxides (NOx) which act as precursors for ozone formation; reduction in local nitric oxide (NO) emissions that acts as a sink for ozone; changes in hemispheric baseline ozone concentration, and changes in ozone Strato-Tropospheric Exchange (STE) (e.g., Cape, 2008; Jenkin, 2008). Ozone trends at both rural and urban locations in the UK are influenced by trends in global, regional and local-scale effects (Jenkin, 2008). Average positive trends in ozone concentrations have been reported by many authors (Carslaw, 2005; Derwent et al., 2007; Jenkin, 2008; and AQEG, 2009). The gradual increase in average ozone concentration might have been caused by the hemispheric baseline ozone concentration resulting from global scale effects, which influences the baseline levels of ozone brought into the UK from the Atlantic Ocean (Derwent et al., 2007 and Jenkin, 2008). In contrast a significant decreasing (negative) trend in the annual maximum ozone concentration has been reported, which was contributed to the reductions in the emissions of anthropogenic volatile organic compounds (VOC) and nitrogen oxides (NOx) in the EU since the early 1990s (Jenkin, 2008; Derwent et al., 2010; Cape, 2008). Furthermore, Jenkin (2008) reported that the negative trends in the maximum ozone concentration at the urban sites are consistently slower than at the rural sites and contributed this to the progressive reduction in NOx emissions that has a local increasing impact on ozone concentrations through reducing ozone scavenging. This effect operates in

the opposite sense to the decreasing impact of VOC and NOx emission reductions on regional-scale ozone formation. The former has a positive whereas the latter has a negative impact on ozone concentrations.

Carslaw et al. (2011) analysed NOx trends at various roadside and urban monitoring sites in the UK and reported that NOx trends have stabilised during the last 6 years (2004 to 2009) or so. In this paper we intend to investigate how ozone trends have responded to the NOx trends during this period and beyond (2004 to 2011). Furthermore, a comparison is made between rural and urban trends in a view to investigate the decreasing urban decrements (the difference in urban and rural ozone levels caused by gas phase titration of ozone by locally produced NOx) and discus its reasons. In addition to traditional mean trends, this study determines trends at several ozone measuring metrics (minimum, first quartile, median, 3rd quartile and maximum). The spatial variations in ozone trends are investigated, in contrast to several authors (Derwent et al., 2007; Carslaw, 2005) who analysed trends only at one monitoring site. Furthermore, changepoint analysis is carried out, which helps identify the points where trends in ozone concentrations have changed significantly. Changepoint analysis provides further insight into the temporal trends of ozone concentration.

10.2 Methodology

In this paper temporal trends in ground level ozone concentrations are investigated using ground level ozone data from 15 rural and 5 urban monitoring sites (Figure 10.1), 1993 to 2011. The monitoring sites were chosen on the basis of data availability over the 19 years period. Ozone trends during the last 8 years (2004 to 2011) have also been investigated for the same monitoring sites separately to investigate how ozone trends have changed most recently in response to stabilising NOx trends reported by Carslaw et al. (2011). The sites are part of the UK AURN (automatic urban and rural network) established by DEFRA (Department of Environment, Food and Rural Affairs). The details about the UK AURN network can be found at the UK-AIR website (UK-AIR, 2012).

Ozone trends are estimated for minimum (percentile 0), first quartile (percentile 25), median (percentile 50), mean, third quartile (percentile 75) and maximum (percentile 100). In addition to quantile regression, this study employs TheilSen function (Carslaw and Ropkins, 2012), timePlot (Carslaw and Ropkins, 2012) and changepoint analysis (Killick and Eckley, 2011) to quantify ozone trends. Statistical analysis was carried out in the statistical software R programming language (R Development Core Team, 2012) and some specialised packages: Quantreg (Koenker, 2012), openair (Carslaw and Ropkins, 2012) and changepoint (Killick and Eckley, 2011). The package changepoint (Killick and Eckley, 2011) includes functions for detecting changes in mean and variance under various distributional and

distribution-free assumptions, which are suitable for non-normal ozone distribution (Munir et al., 2011).

Seasonal-trend decomposition using Loess (STL) was applied to account for the meteorological effect. Smoot-trend function has also been applied to fit a smooth non-linear line to the trend, along with 95 % confidence intervals. The smooth line is essentially determined by using Generalised Additive Model (GAM) (Hastie and Tibshirani, 1990). To estimate trend GAM actually models the relationship between ozone concentration and time, i.e, ozone = f (time) + ε, where f is the smooth term, time is the time period over which the ozone concentration is averaged (month or year) and ε is the error term. The amount of smoothness in the trend is optimised in a way that it is neither too smooth (therefore missing important features) nor too variable (perhaps fitting noise rather than real effects). Readers are referred to Wood (2006) for details on GAM and to Carslaw et al. (2007) on its applicability to air quality data analysis or estimating trends in air pollutant concentrations.

Figure 10.1. Showing 15 rural and 5 urban ozone monitoring sites, which are part of the UK Automatic Urban and Rural Network (AURN) and are used for estimating the ozone temporal trends in this study (Figure source: Figure developed by the author, information obtained from UK-AIR, 2012).

10.3 Results and discussions

Firstly ozone trends for both rural and urban monitoring sites for the period of 1993 to 2011 have been discussed (section 10.3.1), followed by trends for 2004 to 2011 (section 10.3.2),

ozone time variation in historic perspective (10.3.3), changepoint analysis (10.3.4) and measures undertaken to reduce pollutant emissions (10.4).

10.3.1 Ozone trends (1993 to 2011)

Ozone trends at Leeds centre and Ladybower monitoring sites are illustrated in Figure 10.2, as an example, the remaining results are shown in Table 10.1. In Figure 10.2 (top-panel) ozone trends are presented for 6 quantiles (Minimum – q0, first quartile – q0.25, median – q0.5, 3rd quartile – q0.75, q0.99 and maximum – q1) presented from bottom to top in ascending order. A clear negative trend can be observed at quantile 1 (maximum) at both Leeds Centre and Ladybower monitoring sites. For other quantiles the trend is positive and significant at most of the quantiles. At quantile 0 the trend is zero for all sites and therefore is not shown in Table 10.1. The ozone trends for the three middle quantiles (q0.25, q0.5, and q0.75) show a clear positive trend up to year 2004 – 2005 followed by a stable period or a period with little change. This has been further investigated in later sections. To quantify the extent of the trends, TheilSen function was used. Maximum trends at Leeds Centre and Ladybower were -2 and -3.53 μgm^{-3}/ year, respectively, which shows significant reduction in ozone concentration over the 19 years period at both rural and urban site (reason for the negative trends are discussed later), however the negative trend (absolute value) is greater at the Ladybower site, suggesting less reduction at rural site. Median trends at Leeds Centre and Ladybower were 0.87 (significant) and 0.17 (non-significant) μgm^{-3}/year, respectively. Furthermore, the mean ozone trend (Table 10.1) at Leeds Centre and Ladybower were -0.5 (Sig) and 0.13 (non-sig) μgm^{-3}/ year, respectively. Again both median and mean trends suggest either less reduction or more increment in ozone concentration over the study period, which implies a reduction in urban decrement. Highest ozone trends at maximum ozone levels in rural areas was estimated at Lullington Heath (-5 μgm^{-3}/ year) and in urban areas at Cardiff Centre (-3.5 μgm^{-3}/ year). Average maximum trends at rural and urban monitoring sites were -2.46 and -2.27 μgm^{-3}/ year, respectively, rural sites showing slightly higher reduction during the study period. In spite of considerable inter-site variation, the trends are positive at middle quantiles (0.25 to 0.75) at both rural and urban monitoring sites, however at rural monitoring sites trends are mostly non-significant, except Glazebury, whereas at urban monitoring sites the trends are predominantly significantly, except Belfast. Similarly mean ozone trends are proportionately more significant at urban monitoring sites. Urban sites show greater positive trends at the middle quantiles and lower negative trends at maximum ozone concentrations than rural monitoring sites, which might suggest that in urban areas average ozone concentration are increasing at higher rates than the rural areas.

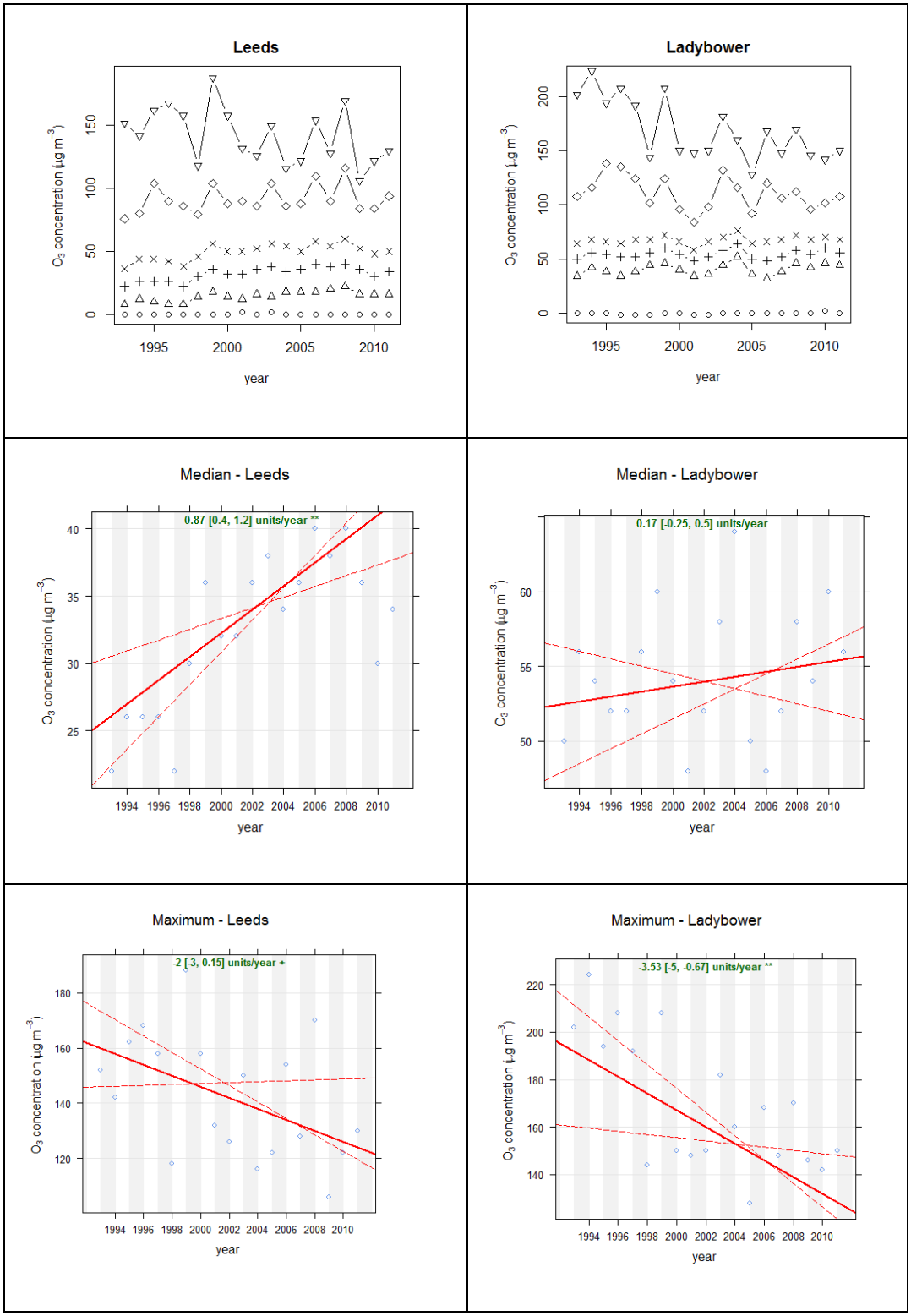


Figure 10.2. Ozone trend (µgm^{-3}/year) at Ladybower (right – panel) and Leeds Centre (left – panel) 1993 to 2011: trend lines at minimum, first quartile, median, third quartile, percentile 99, and maximum (top – panel); ozone trend at median (middle- panel); and maximum (bottom-panel) at both Ladybower and Leeds Centre.

Table 10.1. Ozone trends (µgm^{-3}/year) for years 1993 to 2011 at both urban and rural monitoring sites at selected quantiles.

Site name	Mean	Quantile 0.25	Quantile 0.5 (median)	Quantile 0.75	Quantile 0.99	Maximum
Rural Monitoring Sites						
Strath Vaich	-0.16	-0.29	-0.2	0	-0.09	-0.75
Mace Head	0.2	0.2	0	0.15	0	-0.11
Sibton	0.19	0.44	0.18	0	-1.37*	-3.6*
Yarner Wood	0.05	0.33	0	0.22	-0.67	-2.67*
Aston Hill	0.06	0.22	0	0	-1.23*	-2.85*
Ladybower	0.13	0.33	0.17	0.2	-1.14*	-3.53*
High Muffles	0.05	0.18	0	0	-0.44	-2.77*
Bottesford	0.44*	0.57	0.37	0.27	-0.44	-2.66*
Bush Estate	0.16	0.22	0	0.17	0	-1
Eskdalemuir	0.1	0.2	0	0.15	-0.35	-2 *
Glazebury	0.46*	0.86*	0.8*	0.5*	-0.37	-1.5
Great Dun Fell	-0.52*	-0.41	-0.4	-0.32	-2*	-4.78*
Harwell	0.02	0.4	0.2	0	-1.87	-3.23*
Lough Navar	-0.01	0	0	0	0.08	-0.4
Lulling. Heath	-0.35*	0	0	0	-2.59*	-5*
Average	0.05	0.22	0.07	0.09	-0.83	-2.46
Urban Monitoring Sites						
Belfast centre	0.24*	0.33	0.33	0.29	0.18	-1
Cardiff centre	0.47*	0.71*	0.77*	0.67*	-0.7*	-3.5*
Leeds centre	0.5*	0.57*	0.87*	0.86*	0.55	-2*
L. Bloomsbury	0.41*	0	0.71*	0.75*	0	-3.33*
Newcastle Centre	0.32	0.54*	0.62*	0.59	0.52	-1.5
Average	0.39	0.43	0.66	0.63	0.11	-2.27

Table 10.1 shows details of the ozone trends at various monitoring sites for 19 years (1993 to 2011). It can be observed in the table that annual maximum ozone trends are negative for both urban and rural sites. Urban sites, however, have experienced relative less reduction than rural sites. For the same period median and mean trends are positive for both rural and urban areas, but trends are substantially greater at urban sites. Therefore the trends for the study period show that average ozone concentration (median and mean) in urban areas are increasing at greater rate than in rural areas, which indicates that the ozone urban decrement (the amount by which ozone concentration is lower in urban areas than in rural areas, caused by gas phase titration of ozone by NOx) has decreased over the period.

Ozone trends at both rural and urban locations in the UK are influenced by trends in global (hemispheric), regional and local-scale effects (Jenkin, 2008). Jenkin (2008) investigated ozone trends for urban (1993 to 2006) and rural (1990 to 2006) areas and estimated average annual trend of 0.79 (μgm^{-3}/year) and 0.28 (μgm^{-3}/year), respectively, which is relatively higher than the trends reported here, probably indicating stabilising of the trend during the last 5 years. Jenkin reported a significant decreasing trend in the annual maximum ozone concentration and contributed it to reductions in the emissions of anthropogenic VOC and NOx in the EU since the early 1990s. Derwent et al. (2010) and Cape (2008) have given the same reasons for peak ozone reduction in the UK. Furthermore, Jenkin (2008) reported that the rates of change in the maximum ozone concentration at the urban sites are consistently more positive than at the rural sites and contributed this to the progressive reduction in NOx emissions that has a local increasing impact on ozone concentrations through reducing ozone scavenging effect. This effect operates in the opposite sense to the decreasing impact of VOC and NOx emission reductions on regional-scale ozone formation. The former has a positive whereas the latter has a negative impact on ozone concentrations.

Mean and median ozone trends are positive for the period (1993 – 2011) for most of the ozone monitoring sites. Average positive trends have been reported by many authors (Carslaw, 2005; Derwent et al., 2007; Jenkin, 2008; and AQEG, 2009). This gradual increase in average ozone concentration might have been caused by the hemispheric baseline ozone concentration resulting from global-scale effects, which influences the baseline levels of ozone brought into the UK from the Atlantic Ocean (Derwent et al., 2007 and Jenkin, 2008). Furthermore, the average trends both mean and median were greater at urban than rural sites. This again points to the fact that ozone urban decrement is decreasing with time and is most probably caused by reduction in NOx levels in urban areas. NOx is invariably negatively correlated with ozone and therefore any reduction in NOx concentration may result in ozone concentration to increase. NOx is an ozone scavenger and

reduces ozone concentration by gas phase titration and keep ozone levels lower in urban areas (urban decrement).

The annual minimum hourly-mean ozone concentration shows no trend because the concentration is essentially zero in each of the years. Likewise, low quantiles (up to 0.1 quantile) show very little trend as these correspond to conditions where the NOx concentration is sufficiently high that there is enough NO effectively to remove all ozone, so that even decreasing emissions does not lead to a notable increase in ozone concentration.

Cape (2008) has suggested several factors responsible for the observed ozone trends, including changes in anthropogenic emissions of precursors (both regional and global); effects of biomass burning (both regional and global); changes in stratosphere-troposphere exchange; changes in geographical emission patterns; and changes in air-mass transport patterns. Therefore it is very difficult to be categorical about the causes of long-term trends at a particular site. For example, at Mace Head the long-term trends have been attributed to hemispheric changes in methane, changes in patterns of transport of polluted air from continental Europe, and large biomass burning emissions from Siberia and North America (Derwent et al., 2007).

According to a recent report by European Environmental Agency (EEA, 2012) in the summer of 2011, the occurrence of the exceedances of the information threshold (a one-hour average ozone concentration of 180 $\mu g/m^3$) and the long term objective (maximum daily eight-hour mean concentration of 120 $\mu g/m^3$) for the protection of human health was the lowest since comprehensive Europe-wide data reporting commenced in 1997. This was principally due to unusually low temperatures and increased rainfall during the summer months. However, the number of exceedances of EU ground-level ozone concentration standards for protecting human health (Directive 2008/50/EC) remained at serious levels during summer 2011. Decreased anthropogenic emissions of some ozone precursors (carbon monoxide (CO), NOx and some VOCs) in the past two decades did not manifest significant reductions in the number of such exceedances. The ozone pollution problem therefore requires further mitigation efforts.

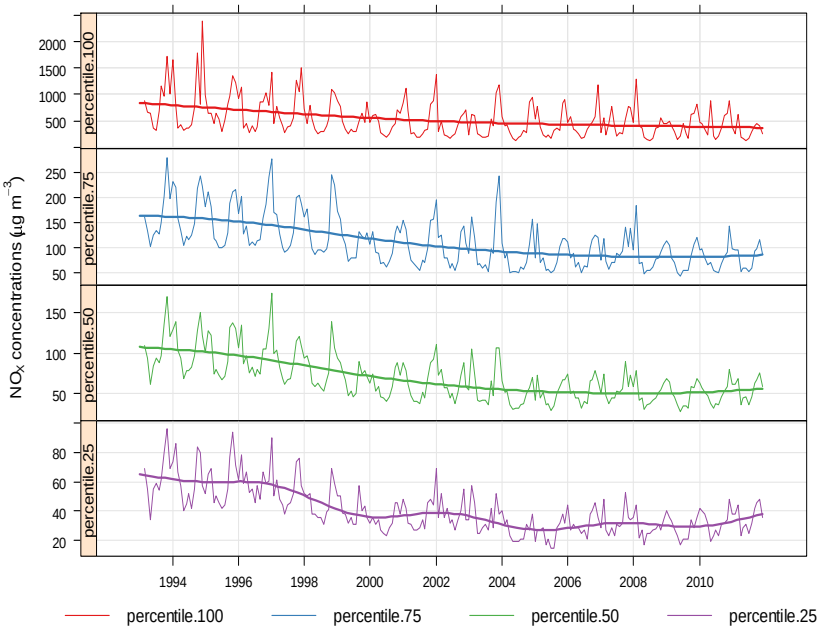
In response to the question why have episodic peak ozone levels not declined enough to meet WHO (2006) air quality guidelines for protecting human health, Derwnet et al. (2011) have responded that whilst NOx and VOC precursor emissions have declined by about 50–60%, episodic ozone levels have only declined by 30%. This is an indication of the importance of non-linearities inherent in the relationship of ozone with NOx and VOC. This is an important scientific issue which should have been taken into account in the design and formulation of the United Nations Economic Commission for Europe (UNECE) Protocols

and EU air quality policies. The underlying reason therefore for not meeting the WHO air quality guideline is that the policy-makers have not set a high enough ambition level for the agreed reductions in European NOx and VOC emissions. VOC and NOx emission reductions needed to be reduced by about 70% by 2010 rather than the 50–60% achieved, for the WHO air quality guideline to have been achieved in the UK and Europe (Derwent et al., 2011).

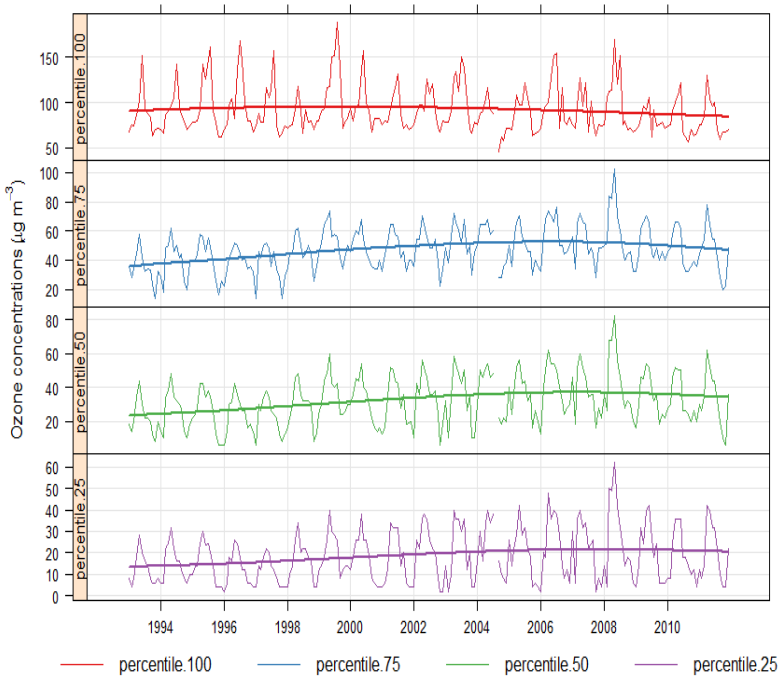
10.3.2 Ozone trends 2004 to 2011

Carslaw et al. (2011) analysed the trends in nitrogen oxides (NOx) concentration in the UK and reported that the decline in NOx concentration was substantially greater for 1996 to 2004 than 2004 to 2009. Carslaw et al. (2011) estimated NOx mean trends -17.8 μgm^{-3}/ year and -1.5 μgm^{-3}/ year for the period of 1996 to 2004 and 2004 to 2009, respectively at urban traffic (roadside) sites. They have reported that at urban centres and background sites the initial decrease was less striking compared with the roadside sites, however, the more stable trend in recent years was apparent in both cases. In this chapter the NOx trends at mean and various percentiles are briefly analysed first at Leeds Centre and then compared with ozone trends. The mean, median, q0.25, q0.75 and maximum trends in NOx concentrations at Leeds Centre from 1993 to 2011 are visualised in Figure 10.3 (a), where clearly the difference in trends before and after 2004 can be observed, which agree with Carslaw et al. (2011). The mean NOx trend was -5.67 (-7.43, -4.25; highly significant) and 0.17 (-1.71, 2.21; insignificant) for before and after 2004, respectively. Ozone trends using different percentiles are also shown in Figure 10.3 (b) at Leeds Centre, where the difference in ozone trends before and after 2004 can be observed. Furthermore, mean trends of NOx and ozone are visualised in Figure 10.3 (c) and that of NO and NO_2 in Figure 10.3 (d). It can be observed that the negative trends in NOx and NO have been stabilised after 2004 or so. Likewise, ozone positive trend after 2004 has been stabilised as well, however the trends are different at various percentiles, higher percentiles showing slightly greater negative trends than the lower percentiles, which is probably because higher ozone concentrations (e.g., maximum) are affected by different factors (e.g., summer time photochemical ozone formation), see chapter 9 and the references therein for more details, especially Stedman and Kent, 2008. In contrast to NOx and NO, the trend in NO_2 concentrations is rather different and shows positive trend after 2004 or so. In view of this analysis and the findings of Carslaw et al., 2011, the trend in ozone concentration for the period 2004 to 2011 is given further consideration in this section. The aim is to investigate how ozone trend has responded to the trend in NOx concentration at various rural and urban monitoring sites.

(a) NO_X


NOx concentrations (µg m-3)
percentile.100
percentile.75
percentile.50
percentile.25
1994
1996
1998
2000
2002
2004
2006
2008
2010

(b) Ozone


Ozone concentrations (µg m-3)
percentile.100
percentile.75
percentile.50
percentile.25
1994
1996
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2010

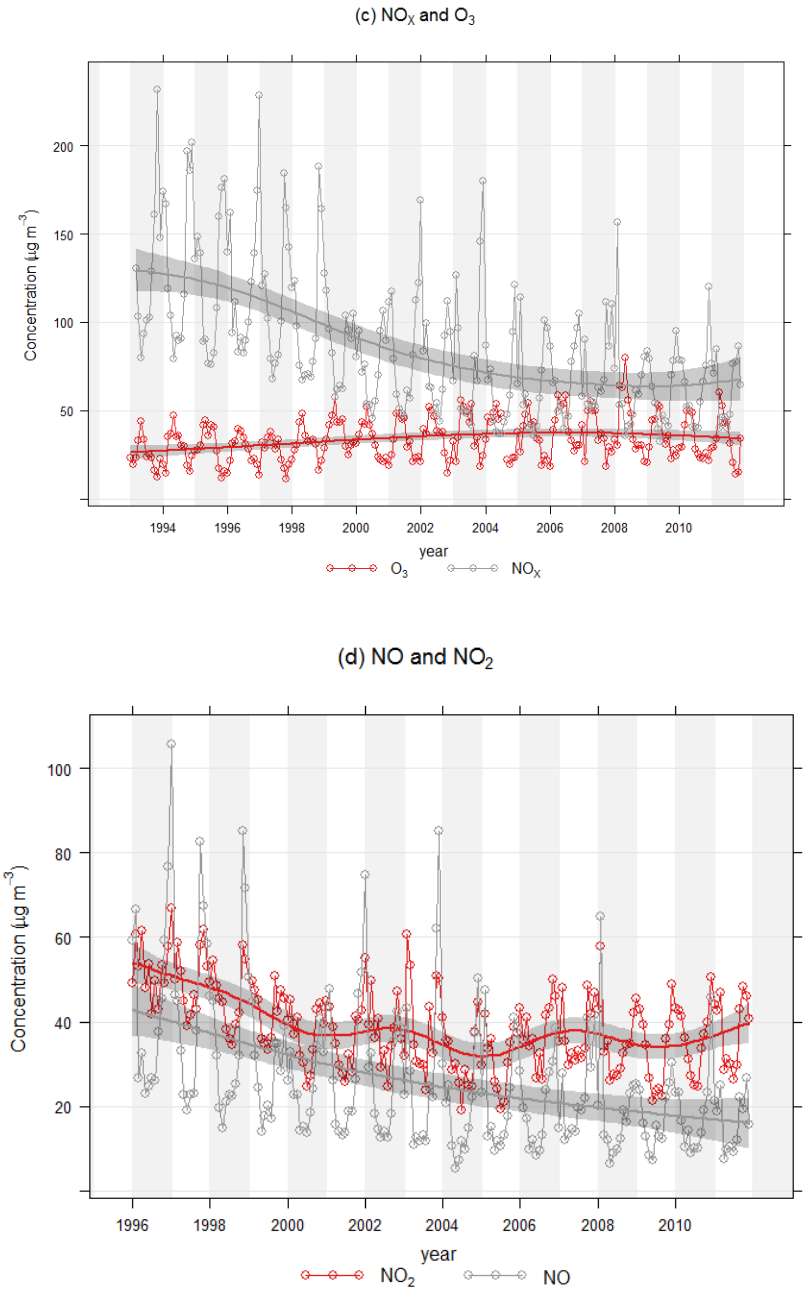


Figure 10.3. NOx (a) and ozone (b) trends at various percentiles, mean NOx and ozone trends (c), and mean NO_2 and NO trends (d) at Leeds Centre monitoring site from 1993 to 2011.

Figure 10.4 shows the mean ozone trend at Leeds Centre monitoring site during 1993 to 2011, which shows a clear difference in ozone trend before and after 2004. The ozone trend was +0.99 (0.39, 1.71; highly significant) and -1 (-2.31, 0.37; insignificant) for before and after 2004, respectively, which shows that ozone trends have responded to stabilising NOx trends and the positive ozone trend has slowed down or in fact turned negative. The ozone trends for other urban sites are given in Table 10.2, which also show negative trends from 2004 to 2011 at all urban sites except London Bloomsbury. The trend is significant only for

Newcastle Centre. Deseasonalised trends given in Table 10.2, are also negative (except London Bloomsbury) and significant for three (Leeds, Cardiff, and Belfast) out of five sites.

The negative mean ozone trends at urban sites after 2004 may be due to the fact that during this period NOx (especially nitrogen dioxide - NO_2) concentrations have not decreased (Figure 10.3 - d); NO_2 concentration rather seems to have increased during the last few years. It is well established that both nitric oxide (NO) and NO_2 are negatively correlated with ozone (e.g. Jenkin, 2004) and therefore an increase in NO_2 concentration will result in ozone concentration to decrease. The increasing proportions of NO_2 in the UK urban areas and roadside location have been reported by several researchers (e.g. Carslaw et al., 2007). Carslaw et al., (2007) has shown that directly emitted (primary) NO_2 has increased as a fraction of total NO_X from road transport sources. These increases appear to be mostly due to certain after-treatment devices, such as oxidation catalysts and particle filters fitted to diesel vehicles.

It can be observed in Table 10.2 that ozone trends are negative at most of the rural monitoring sites from 2004 to 2011. Average non-deseasonalised trend for the period was -0.80, which is nearly a unit per year (μgm^{-3}/ year). When deseasonalised, the trend decreased to -0.45, which is about half of the non-deseasonalised trend, which shows the importance of the meteorology in the observed ozone trends. Bush Estate and Eskdalemuir experienced no negative deseasonalised or non-deseasonalised trend, whereas Ladybower did not show deseasonalised trend only. The rest of the sites all had negative ozone trend. The trend was significant for approximately half of the sites. Lullington Heath experienced the highest deseasonalised (-2.12) and non-deseasonalised (-2.1) negative trend from 2004 to 2011. The spatial variations in ozone trends are probably due to local meteorological and topographical characteristics, such as altitude, proximity to sea, which are described in details in chapter 9. The specific behaviour of each monitoring site is also linked with the meteorological patterns that determine the origin of the emissions which influence the area (Monteiro et al., 2012).

Ozone trends at various quantiles (q0.25 (first quartile), q0.5 (median), q0.75 (3^{rd} quartile) and q1 (maximum)) at different monitoring sites both rural and urban are shown in Table 10.3. Majority of the trends are negative, in contrast to Table 10.1, where most the trends were positive, particularly at the middle quantiles. Average maximum trends (μgm^{-3}/year) were -3.02 and -2.02 at urban and rural sites, respectively, whereas median trends (μgm^{-3}/year) were 0.09 and -0.47 at urban and rural sites, respectively. Highest (absolute value) maximum trends (μgm^{-3}/year) in urban areas was estimated for Cardiff Centre (-6) followed by Newcastle (-4.09) and in rural areas for Lullington Heath (-9) followed by Great Dun Fell (-6.6). Majority of the trends at both urban and rural sites were insignificant, except

Cardiff Centre, Lullington Heath and Great Dun Fell, where only maximum trends were significant. This indicate that although ozone trends during the last 8 years have stabilised, most probably due to the emission control policies, the reductions are insignificant.

When ozone trend for the urban sites was categorised by season, only spring season (March, April and May) had positive trend (Figure 10.5-a) and the rest of the three seasons i.e. Summer (June, July, and August), Autumn (September, October and November) and Winter (December, January and February) had negative trend. The negative trend was only significant in summer, which was -1 μgm^{-3}/year. Rural sites had a similar pattern in ozone trend i.e. positive in spring (insignificant) and negative in other three season. Again only summer had negative significant trend of -1.14 μgm^{-3}/year (Figure 10.5-b). As explained in chapter 6, during winter due to the lack of solar radiation no photochemical ozone formation takes place and the level of ozone precursor increase in the atmosphere. In spring when the meteorological conditions improve in terms of solar radiations and temperature these trigger the photochemical ozone formation and as a result the levels of precursors decline. Therefore later in the year (summer) in spite of the presence of favourable meteorological conditions photochemical ozone formation is constrained by the level of precursors.

Deseasonalised trends for both urban and rural sites are shown in Table 10.4, where it can be observed that the trends at both rural and urban sites are negative and highly significant in summer and significant in winter season and non-significant during spring and autumn. Here it should be noted that non-deseasonalised trends in spring were positive and have turned negative after being adjusted for the seasonal effect. Which confirms that the positive trends in spring (shown in Figure 10.5) are due to seasonal effect, as explained above.

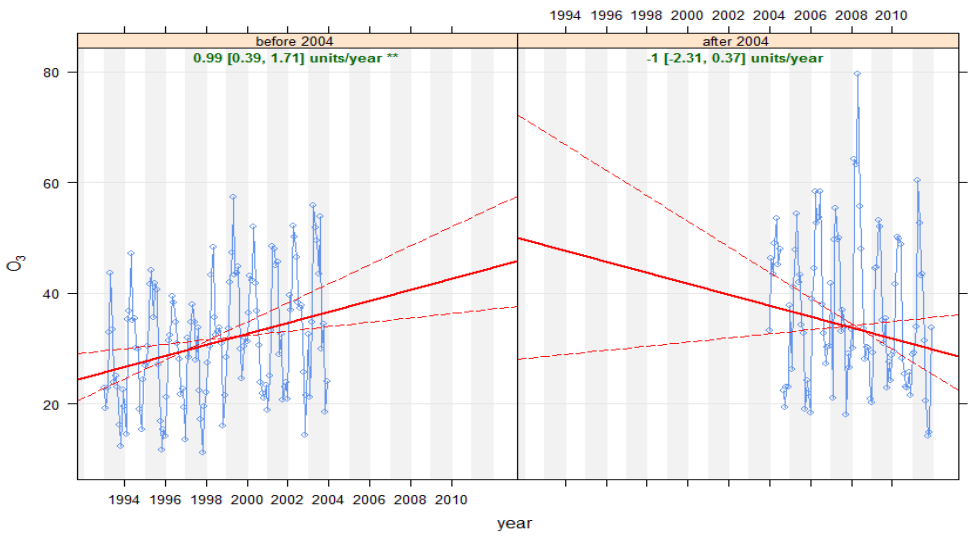


Figure 10.4. Mean ozone trends before and after 2004 at Leeds Centre monitoring site.

Table 10.2. Mean ozone trends 2004 – 2011 at both urban and rural sites.

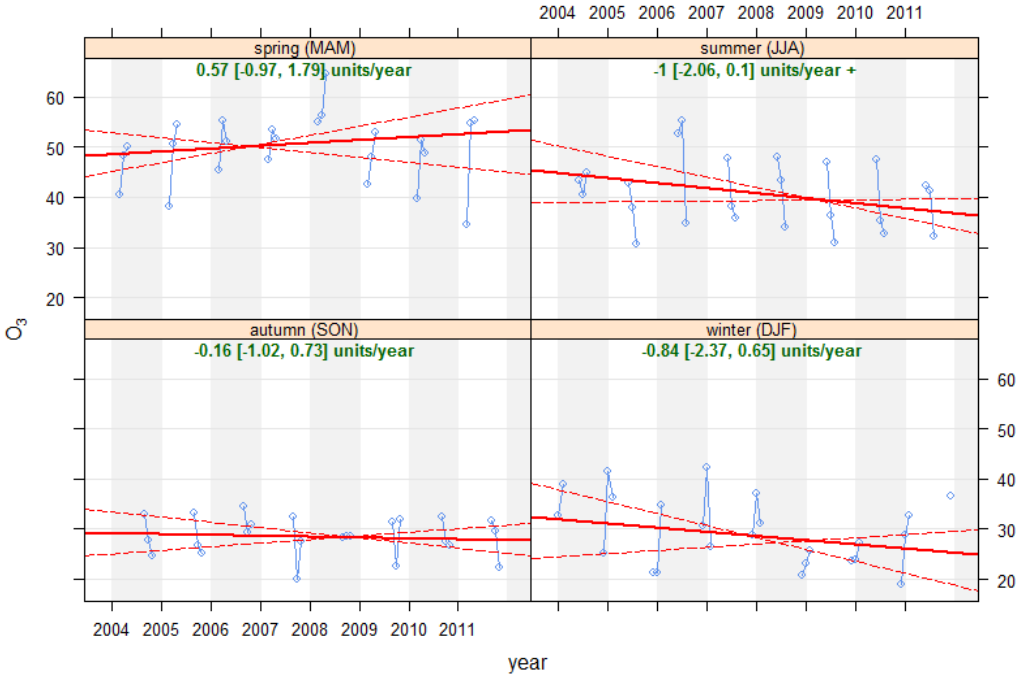
Site name	Non-deseasonalised				Deseasonalised			
	Slope	Lower	Upper	Sig. level	Slope	Lower	Upper	Sig. level
Rural Monitoring Sites								
Bottesford	-0.4	-1.19	0.42	ns	-0.04	-0.52	0.41	ns
B. Estate	0.06	-0.62	0.75	ns	0.46	0.11	0.78	*
E.D.muir	0	-0.78	0.79	ns	0.41	-0.09	0.89	+
Glazebury	-1.22	-2.24	-0.3	*	-0.87	-1.38	-0.41	***
GD Fell	-1.22	-1.93	-0.52	***	-1.03	-1.47	-0.46	***
Harwell	-0.57	-1.41	0.44	ns	-0.12	-0.81	0.57	ns
L. Navar	-0.3	-1.37	0.76	ns	-0.06	-0.54	0.49	ns
L. Heath	-2.1	-3.11	-1.23	***	-2.12	-2.67	-1.53	***
S. Vaich	-1.79	-2.8	-0.57	**	-1.19	-1.82	-0.65	***
M. Head	-0.43	-1.25	0.45	ns	-0.26	-0.57	0.07	ns
Sibton	-0.69	-1.62	0.25	ns	-0.28	-0.85	0.22	ns
Y. Wood	-0.74	-1.52	0.13	+	-0.43	-0.8	-0.01	+
Aston Hill	-1.71	-2.48	-1.03	***	-1.47	-2.16	-0.75	***
L.bower	-0.06	-1.09	1.29	ns	0.46	-0.26	1.05	ns
H Muffles	-0.78	-1.97	0.42	ns	-0.19	-0.81	0.39	ns
Average	-0.80				-0.45			
Urban Monitoring Sites								
Belfast	-0.72	-1.48	0.15	ns	-0.41	-0.79	0.03	+
Cardiff	-0.75	-1.65	0.12	ns	-0.62	-1.03	-0.23	***
Leeds	-1	-2.31	0.37	ns	-0.49	-1.17	0.02	+
Blombury	0.01	-0.99	0.87	ns	0.25	-0.14	0.64	ns
NC centre	-0.79	-1.74	0.02	+	-0.43	-1.02	0.12	ns
Average	-0.62				-0.34			

Note: ns – non-significant, Sig. codes: 0 - ***, 0.001 - **, 0.01 - *, 0.05 - +, alpha level 0.05 is applied to calculate confident intervals and level of significance.

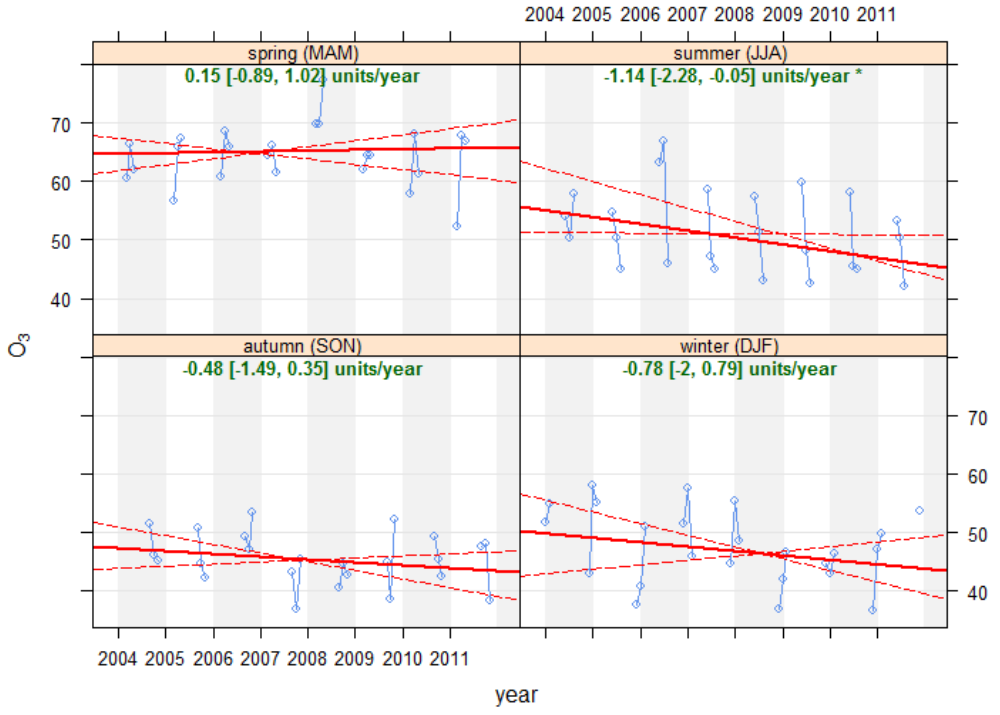
Table 10.3. Ozone trends at several other quantiles quantile 0.25, quantile 0.5 (median), quantile 0.75 and quantile 1(maximum) are shown in Table 10.3 during 2004 to 2011.

Site Name	Quantile 0.25	Quantile 0.5 (Median)	Quantile 0.75	Maximum
Rural Monitoring Sites				
Bottesford	0	0	0	-3.83
Bush Estate	0	0.37	0.5	-1.83
Eskdalemuir	0	0	0.14	1.1
Glazebury	-0.37	-1.2	-1.2	-2.91
Great Dun Fell	-1.07	-1	-0.58	-6.66*
Harwell	0	-0.14	-0.45	-1.5
Lough Navar	0	0	-0.17	-0.67
Lullington Heath	-1	-2	-2.53	-9*
Strath Vaich	-1.42	-1.55	-1.38	-1.47
Mace Head	-0.45	-0.34	0	-0.33
Sibton	0	-0.2	-0.73	-2.93
Yarner Wood	0	-0.14	0	0.83
Aston Hill	-1.33	-1.5	-1.42	-3.66
Ladybower	1.17	1	0.2	-1.21
High Muffles	0	-0.33	-0.4	-2
Average	-0.30	-0.47	-0.53	-2.02
Urban Monitoring Sites				
Belfast centre	-0.45	0	0.45	-0.75
Cardiff centre	0	-0.34	-0.62	-6*
Leeds centre	-0.31	-0.5	-0.78	-1.17
L Bloomsbury	0	0.73	-0.2	-3.1
Newcastle centre	-0.33	0.58	-0.67	-4.09
Average	-0.22	0.09	-0.36	-3.02

*Shows significant trends



(a) Urban sites 2004 to 2011, partitioned by season



(b) Rural sites 2004 to 2011, partitioned by season

Figure 10.5. Ozone trends at (a) urban and (b) rural sites from 2004 to 2011 for various seasons.

Table 10.4. Deseasonalised mean trend (µgm^{-3}/year) at rural and urban sites 2004 to 2011 for various seasons.

Site type	Spring (MAM)	Summer (JJA)	Autumn (SON)	Winter (DJF)
Urban	-0.3 (-1.07, 0.52)	-0.84 (-1.13, -0.56)***	0.03 (-0.18, 0.21)	-1.04 (-1.5, -0.35)*
Rural	-0.31 (-0.85, 0.35)	-0.83 (-1.1, -0.58)***	-0.28 (-0.6, 0)	-0.56 (-1.02, -0.1)*

Table 10.5 summarises mean ozone trends (µg/m^3) both adjusted and non-adjusted for the 8 years (2004 to 2011) period at both rural and urban monitoring sites. The seasonal trends both adjusted and non-adjusted are also shown in Table 10.5. The yearly adjusted (deseasonalised) and non-adjusted trends are both negative for the study period at both rural and urban sites. Furthermore, the adjusted trend for each season at both rural and urban sites is also negative. Similarly un-adjusted (non-deseasonalised) trends are negative at both rural and urban sites for most seasons, except spring, where the trend is positive. Therefore generally it can be concluded that ozone levels have declined during the last 8 years.

Most of the authors have reported positive ozone trends in the past (e.g., Carslaw, 2005; Derwent et al., 2007 and Jenkin, 2008), but the last three years (2009 to 2011) have not been included in the ozone trends study by the above authors, and therefore are being reported for the first time. Carslaw et al. (2011) have reported that NOx trends have stabilised during the last 7 - 8 years (as mentioned in the preceding sections) which is in agreement with Figure 10.3 that after 2004 NOx have stabilised, in fact NO_2 levels have gone up in the urban areas. Both NO and NO_2 are negatively correlated with ozone (Jenkin, 2001) and reduce ozone concentrations in urban areas due to their scavenging effect, therefore any increment in their levels will invariably result in ozone level to decrease in urban areas due to less scavenging effect. In rural areas NOx levels have decline from 1993 to 2011 and also during the last 8 years, i.e., 2004 to 2011 (date not shown).

Has ozone concentration declined as a result of continuous reduction in the emission of ozone precursors at European level and this negative trend in ozone will continue to the future; or is it a temporarily phenomenon caused by low ozone level during the last couple of years due to meteorology and ozone might increase again in the future? As the trend in ozone concentration during the last 8 years correlates well with NOx concentration, it might be possible that the negative trends are caused by reduction in its precursors and may continue to the future. However, Cape (2008) has stated that in some studies a pattern of decreasing concentrations during one decade may be followed by increasing concentrations in the subsequent decade, so the period over which the trend is assessed may determine the

apparent direction. Cape (2008) further reported that predicted (modelled) changes in emissions of precursors over the next 20–50 years imply serious increases in ozone concentrations across the whole Northern Hemisphere, to levels that would significantly affect both natural vegetation and crop yields. However, on these timescales it is also predicted that there will be subtle but important changes in climate that will act to mitigate the effects of increased precursor emissions on ozone formation. In particular, although increased temperatures are likely to increase emissions of biogenic VOCs, most ozone production is limited by the availability of NOx. Increased temperatures also increase the water vapour concentrations in the atmosphere, leading to faster ozone destruction, greater production of OH radicals, and consequent faster oxidation of ozone precursors (VOCs and NOx). However, ozone concentrations are predicted to increase significantly in future, even taking into account climatic changes, in regions where NOx concentrations are high, but may decrease where NOx emissions are low (Cape, 2008).

Table 10.5. Summary of mean ozone trends (μg/m^3) at both urban and rural sites from 2004 to 2011.

Period	Urban	Rural	Adjusted	Metrics	Season
2004 – 2011	-0.62	-0.80	no	mean	Yearly
2004 – 2011	-0.34	-0.45	yes	mean	Yearly
2004 – 2011	0.57	0.15	no	mean	Spring
2004 – 2011	-1	-1.14	no	mean	Summer
2004 – 2011	-0.16	-0.48	no	mean	Autumn
2004 – 2011	-0.84	-0.78	no	mean	Winter
2004 – 2011	-0.3	-0.31	yes	mean	Spring
2004 – 2011	-0.84	-0.83	yes	mean	Summer
2004 – 2011	0.03	-0.28	yes	mean	Autumn
2004 – 2011	-1.04	-0.56	yes	mean	Winter

10.3.3 Ozone time variation in historic perspective

Figure 10.6 (top) shows time variation plots of ozone concentration at Leeds Centre before and after 2004, where it can be observed that ozone concentrations are higher after 2004, which are expected and are due to the positive trend until 2004. However, the increment in ozone concentration is different during different time period, particularly during different months of the year. For example, during August, September, and October, the difference in

ozone concentration before and after 2004 is minimal, in fact during August the increment is negative, showing slight decrement. In this section, therefore changes in time variations are further analysed.

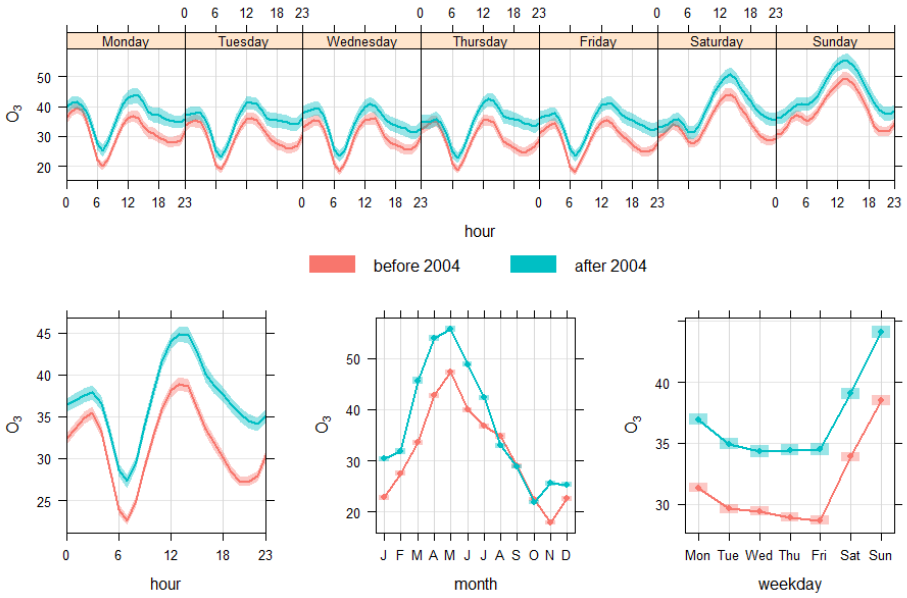
Ozone time variations in 1993 and 2011 at Leeds Centre (urban site) and Ladybower (rural site) are compared. Time Variations of ozone at rural and urban sites have been described in Chapter 5, here the aim is to compare the changes in ozone time variation from 1993 to 2011 at urban sites (represented by Leeds Centre) and rural sites (represented by Ladybower). Figure 10.6 (bottom) shows time variation plots of ozone concentration in 1993 ($O_3$93, red colour), in 2011 ($O_3$11, green colour) and the difference between the two years ($O_3$11- $O_3$93, blue colour) at Leeds Centre.

Figure 10.6 clearly indicate that ozone concentrations have generally increased over the 19 years period and the difference is positive over most of the time, except certain occasions where the difference is negative, particularly on Monday at about 06:00 hour and during the months of September and October. Figure 10.6 shows that the difference in ozone concentration between 1993 and 2011 varies during different hours of the day, days of the week, and months of the year. The difference seems to be more prominent on weekend. As explained in Chapter 7, on weekend generally traffic flow is low and traffic composition is different from that on weekdays, which might be affecting the trends differently during the weekend. During the diurnal cycle the difference seems to be more prominent during mid-day and non-significant during 04:00 to 06:00 am early in the morning. During the annual cycles, the difference is highest during April and July and lowest during September and October. General reasons for positive trends in ozone concentration at urban monitoring sites have been discussed above; however different trends during hours of the day, days of the week or months of the years may be linked with local micro-meteorological, local traffic flow and spatial variables.

Figure 10.7 shows ozone time variation for 1993, 2011 and the difference between the two years ($O_3$11- $O_3$93, blue colour) at Ladybower monitoring site, which is a rural site. Here again, the difference is positive and significant most of the time, except during June and August. In contrast to Figure 10.6, here the difference is more prominent at 18:00 hours and on Friday and Saturday. At Ladybower (Figure 10.7) the highest difference is shown during July, followed by April, which was the other way around at Leeds Centre (Figure 10.6).

It is worth mentioning that generally ozone concentration is higher at Ladybower than Leeds Centre during both 1993 and 2011, whereas the difference (increment during the 19 years period) seems the same or even greater at Leeds Centre, which indicate relative greater rate of ozone increment at urban monitoring site.

Table 10.6 shows the difference (ozone concentration in 2011 minus ozone concentration in 1993) and percent difference [(difference/O_3_93)*100] at both Ladybower and Leeds monitoring sites. Table 10.6 (top) shows difference and percent difference in ozone concentration (µg/m^3) on weekly basis. The difference was 9 µg/m^3 (38 %) and 8 µg/m^3 (16%) at Leeds and Ladybower, respectively. Average difference in ozone concentration at Leeds Centre is only 1 (µg/m^3) greater than that at Ladybower, but percent difference is much more at Leeds Centre than at Ladybower, due to low ozone concentration at Leeds Centre. Maximum percent difference was observed on Saturday (about 73%) at Leeds Centre and on Friday at Ladybower (25%). On daily basis mean % difference was 36 and 16 % at Leeds Centre and Ladybower, respectively. Furthermore, on annual basis mean 36% change was observed at the Leeds Centre and about 18% at Ladybower (see Table 10.6 for more details). This analysis again confirms that positive trend at urban monitoring sites is much greater than at the rural monitoring sites. This is in agreement with previous studies (e.g., Williams, 2007; AQEG, 2009), who reported that ozone concentration was increasing at a greater rate at urban than at rural monitoring sites.



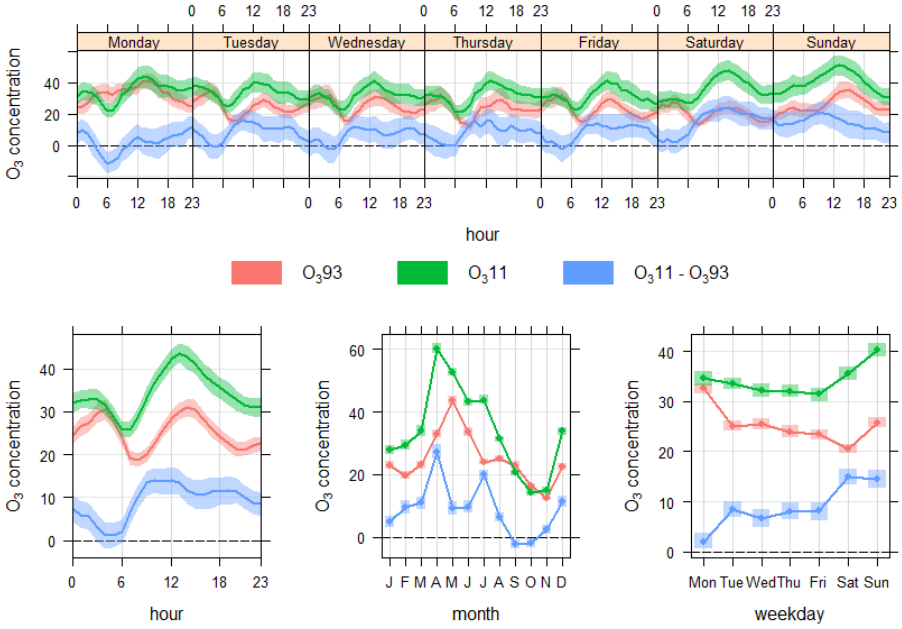


Figure 10.6. Comparison of ozone time variation in 1993 ($O_3$93) and 211 ($O_3$11) at Leeds Centre.

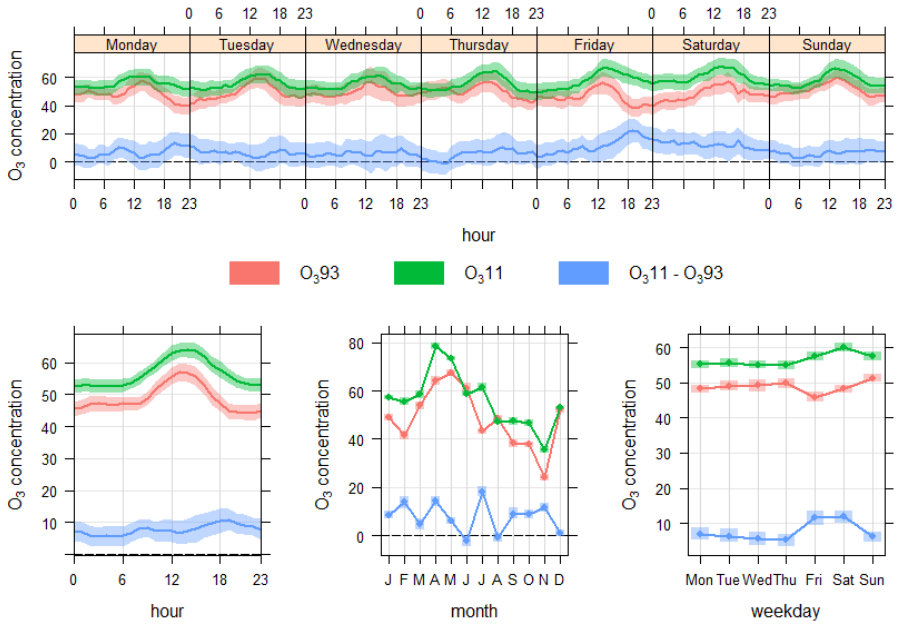


Figure 10.7. Comparison of ozone time variation in 1993 ($O_3$93) and 2011 ($O_3$11) at Ladybower.

Table 10.6. Showing difference (O_3_2011 – O_3_1993)and percent difference (%Diff) in ozone concentration (µg/m^3) at Leeds and Ladybower (LB) during different days of the week (top), months of the year (middle) and hours of the day (bottom).

Day	Leeds_Diff (µg/m^3)	% Leeds_Diff	LB_diff (µg/m^3)	% LB_Diff
Monday	2.05	6.28	6.88	14.24
Tuesday	8.46	33.69	6.38	12.99
Wednesday	6.69	26.33	5.67	11.48
Thursday	8.10	33.83	5.17	10.34
Friday	8.12	34.73	11.65	25.38
Saturday	14.96	72.73	11.88	24.64
Sunday	14.51	56.32	6.16	12.03
Mean	8.98	37.70	7.68	15.87

Month	Leeds_Diff (µg/m^3)	% Leeds_Diff	LB_Diff (µg/m^3)	% LB_Diff
January	4.84	21.03	8.57	17.57
February	9.52	48.15	13.92	33.35
March	10.86	47.04	4.74	8.78
April	27.31	82.59	14.23	22.10
May	9.08	20.81	5.95	8.83
June	9.69	28.97	-2.26	-3.70
July	19.81	82.51	18.10	41.83
August	6.37	25.51	-1.07	-2.22
September	-2.31	-10.12	9.05	23.67
October	-2.08	-12.75	8.87	23.53
November	2.32	18.56	11.38	47.47
December	11.31	50.23	1.12	2.15
Mean	8.89	35.67	7.72	17.57

Hour	Leeds_Diff ($\mu g/m^3$)	% Leeds_Diff	LB_Diff ($\mu g/m^3$)	% LB_Diff
00:00	7.46	30.45	7.24	15.91
01:00	5.97	22.44	6.87	14.89
02:00	5.53	20.20	5.82	12.37
03:00	3.05	10.27	5.45	11.49
04:00	1.12	3.68	5.95	12.68
05:00	1.28	4.61	5.70	12.16
06:00	2.03	8.52	5.80	12.32
07:00	6.46	33.40	6.49	13.75
08:00	10.10	54.29	7.88	16.71
09:00	13.38	67.34	8.33	17.00
10:00	13.95	61.13	7.20	13.95
11:00	13.74	53.49	7.23	13.49
12:00	14.02	49.48	7.31	13.12
13:00	13.52	44.95	6.62	11.56
14:00	11.76	37.93	7.24	12.75
15:00	10.75	35.13	8.00	14.39
16:00	10.57	37.53	8.98	16.94
17:00	11.30	43.69	9.72	19.55
18:00	11.52	47.73	10.48	22.11
19:00	11.63	51.52	10.86	24.00
20:00	11.46	53.90	9.87	22.23
21:00	10.22	48.10	9.11	20.48
22:00	8.86	40.35	8.73	19.70
23:00	8.47	37.61	7.81	17.37
Mean	9.09	36.10	7.70	15.91

10.3.4 Changepoint analysis

Changepoint detection estimates the point where the statistical properties of a sequence of observations (time series) change (Killick and Eckley, 2011). Several algorithms are available for detecting changepoints in a time series data, including Binary Segmentation (Scott and Knott, 1974), Segment Neighbourhoods (Auger and Lawrence, 1989) and Pruned Exact Linear Time (PELT) search algorithm (Killick et al., 2011). In this analysis the latter was preferred due to the fact that it produces exact results quicker than the Segment Neighbourhood and Binary Segmentation algorithms and can be applied to both normally and non-normally distributed data. For details on these methods see Killick and Eckley (2011).

The three changepoints detected in ozone concentration were in March 1998, January 2008, and May 2008. The output of multiple changepoint analysis is depicted in Figure 10.8 (top-left), which uses monthly mean ozone concentration ($\mu g/m^3$) at Leeds monitoring site from 1993 to 2011. The means of the four segments were 27, 36, 66 and 34 $\mu g/m^3$, which divide the dataset into to 3 main segments. First segment covers the time period from January 1993 to March 1998, when ozone concentration was relatively low (monthly average 27 $\mu g/m^3$). The second segment covers from March 1998 to January 2008, when ozone concentration was 36 $\mu g/m^3$. Third segment is a short one and consists of January 2008 to May 2008, when mean ozone concentration was highest (66 $\mu g/m^3$). Afterwards ozone concentration decreased in the last three years (2008 to 2011) and had a monthly mean value of 34 $\mu g/m^3$. The changepoint analysis indicates that monthly mean ozone concentration did not change significantly during 1993 – 1998. Ozone concentrations increased in March 1998 and then stayed at this level until 2008. During spring 2008 ozone concentration was significantly higher, however the concentration did not stay at this level for longer period and during the next three years ozone levels were even lower than the pre-spring 2008 period. This indicates that ozone concentration has stabilised during the last 14 years, except in March - May 2008. Using TheilSen function at each segment showed no significant trends.

Multiple changepoint analysis of NOx data (Figure 10.8, top-right) showed three break points in December 1998, August 2003, and October 2003 and the estimated mean NOx concentration ($\mu g/m^3$) for the four segments were 121, 77, 163, and 65, respectively. Single changepoint analysis was also performed for ozone (Figure 10.8, bottom-left) and NOx (Figure 10.8, bottom-right), which showed January 1998 and January 1999 as changepoints for NOx and ozone, respectively. Therefore both multiple and single changepoint analyses detect major break points in 1998 and 1999. Afterwards NOx concentrations have decreased and as a result ozone concentrations have increased. The negative association between NOx and ozone is well known (e.g., Jenkin, 2004 and Clapp and Jenkin, 2001) and is also shown

in Figure 10.9, that as NOx concentrations decrease ozone concentration increase and vice versa. However, the correlation is non-linear and the strength of correlation coefficients change at different NOx and ozone concentrations (e.g., see Munir et al., 2012 for more details).

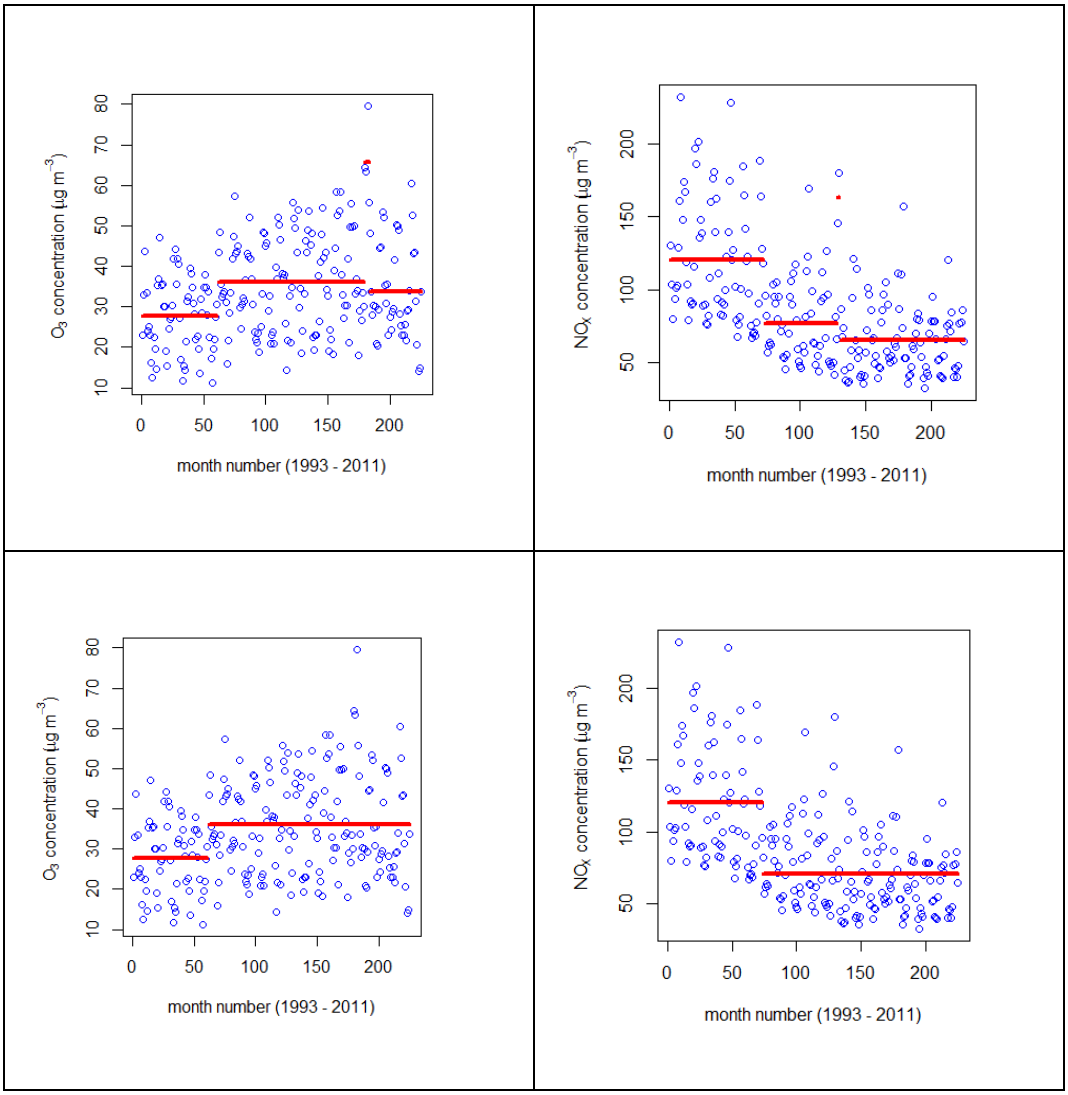


Figure 10.8. Showing changepoints in monthly mean ozone and NOx concentrations (µg/m^3) from 1993 to 2011 at Leeds monitoring site: (top-left) ozone multiple changepoints; (top-right) NOx multiple changepoints; (bottom-left) O_3 single changepoint; (bottom-right) NOx single changepoint.

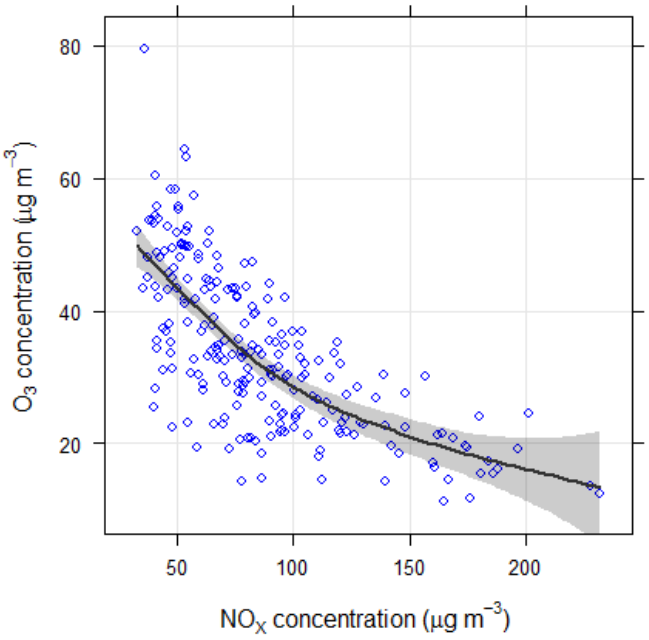


Figure 10.9. Scatter plot between monthly mean ozone and NOx concentrations (µg/m^3) from 1993 to 2011 at Leeds Centre monitoring site.

10.4 Measures undertaken to reduce pollutant emissions

The impact of air pollutant emissions on local air quality and human health is a major public policy concern and has stimulated a substantial body of research aimed at developing, implementing and evaluating emission reduction measures including improved underlying vehicle technologies, efficient traffic management schemes, and effective public policy actions. Our discussion on the measures carried out to reduce air pollutant emission is mainly based on Williams (2004) and the Air Quality Strategy (AQS, 2007), which provide a detailed account of different European and UK policies and measures to reduce air pollution. In order to protect human health and the environment as a whole, it is particularly important to combat emissions of pollutants at source and to identify and implement the most effective emission reduction measures at local and national levels. Therefore, emissions of harmful air pollutants could be avoided, prevented or reduced.

Actions to manage and improve air quality in the UK are largely driven by European legislation. The 2008 ambient air quality directive (2008/50/EC) sets legally binding limits for air pollutant concentrations of major air pollutants that impact public health such as particulate matter (PM_{10} and $PM_{2.5}$) and NO_2. The 2008 directive replaced nearly all the previous EU air quality legislation and was made law in England through the Air Quality Standards and Regulations 2010. Previous directives include: Council Directive 96/62/EC

on ambient air quality assessment and management; Council Decision 97/101/EC establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution; Council Directive 1999/30/EC relating to limit values for SO_2, NOx, particulate matter and lead in ambient air; Directive 2000/69/EC of the European Parliament and of the Council relating to limit values for benzene and carbon monoxide in ambient air; Directive 2002/3/EC of the European Parliament and of the Council relating to ozone in ambient air; and the 4th air quality daughter directive (2004/107/EC) that sets targets for levels in outdoor air of certain toxic heavy metals and polycyclic aromatic hydrocarbons.

The UK government has introduced a mechanism to control emissions from the significant sources of air pollution, in particular from the transport, industry sectors and domestic premises. The main measures undertaken to reduce air pollutant emissions include: (1) Road transport is a key source of many air pollutants, particularly in urban areas. Emissions of key air pollutants from road transport have fallen by about 50% over the last decade, despite increases in traffic, and are expected to reduce by a further 25% or so over the next decade (AQS, 2007). This is mainly a result of progressively tighter vehicle emission and fuel standards agreed at European level and set in UK regulations. The Vehicle Certification Agency ensures that all new models of cars coming onto the UK roads meet EU emissions standards and that all types of existing vehicles must go through an emission check as part of the annual MOT testing procedures. Regulations were introduced in 1997 in England and Wales to allow local authorities to check vehicle emissions by the roadside and issue fixed penalties if vehicles do not meet the legal limits. In Scotland, the 2003 Regulations allow any local authority to apply to the Scottish Ministers for designation to undertake roadside emissions testing and to instruct drivers of parked idling vehicles to switch off their engines. The UK government encourages the use of cleaner fuels and vehicles, rewarding those who choose to buy clean, fuel-efficient vehicles through lower vehicle excise duty and company car tax rates. The UK Highway Agency tries to influence its effect on air quality through: contributing to strategic planning; road improvements; integrating transport and encouraging sustainable travel; providing better information for improved operation; and working with local authorities to deliver the Air Quality Strategy; (2) industrial sources: The Pollution Prevention and Control Act 1999 ensures implementation of the EU IPPC Directive (96/61/EC) and establishes the main mechanisms for minimising air pollution from industrial sources. IPPC covers some 4,300 installations in England and Wales. These include large-scale installations, such as oil refineries, power stations, chemical plants and large food and drink processing plants; (3) Local authorities have been empowered for tackling localised air quality problems, leading to an overall improvement of air quality across the UK; (4) The Environment Act 1995 and the Environment (Northern Ireland)

Order 2002 introduced the system of local air quality management. Since then, local authorities have had to periodically review and assess the current and likely future air quality in their areas against national air quality objectives for seven air pollutants. Local air quality management areas have been declared and action plans developed to address the air quality exceedences problem in each local area. For example, a number of English local authorities have established a "Low Emissions Strategies Group", to help scope and develop practical knowledge on the implementation of low emissions zones and measures; (5) The Government Beacon Scheme 'Delivering Cleaner Air' theme, annual air quality grant programme, and integration of Air Quality Plan with Local Transport Plan are some of the measures which helped improve air quality at local levels in the UK, and perhaps have lead to reduction in ozone concentration during the last several years. For details on different measures and policies for improving air quality in the UK see AQS (2007).

10.5 Summary

Previously ozone trends have been mostly analysed at rural monitoring sites and therefore indicate trends in background ozone concentrations, which are mainly controlled by regional and global emissions of the ozone precursors. To quantify the effect of national and local precursors emissions on ozone concentration, urban ozone trends are needed to be quantified and compared with rural trends. Urban trends are not only affected by the background trends but also by NOx scavenging effect, which are apparently decreasing with time. In contrast to previous studies, this project uses data from many monitoring sites, not available to earlier authors. This chapter not only quantifies temporal trends in annual average and several quantiles of ozone concentrations but also analyses how ozone diurnal, weekly and seasonal cycles have changed with time. Furthermore, this project uses a nonparametric approach which is based on median and various quantiles and hence is not affected by outliers or few high or small values, and therefore presents a more robust approach.

In this chapter ozone trends for the last 2 decades (1993 to 2011) at both rural and urban sites have been investigated. Hourly data from 5 urban and 15 rural sites, which are part of the UK AURN have been analysed for zone trends. Trends show significant variability at different statistical metrics (e.g., mean, median, maximum and selected quantiles). The maximum trends were found to be negative; whereas median and mean trends were positive during the period at both rural and urban sites. The negative trends in high episodic ozone during the summer are believed to be caused by reduction in the emissions of ozone precursors (e.g., NOx and VOCs) in the Europe since 1990; whereas the positive trends in mean ozone are believed to be controlled by hemispheric baseline ozone levels. Urban and

rural trends have different rates and indicate that urban decrement (the difference in ozone concentration between rural and urban areas caused by gas phase titration of ozone by locally produced NOx) has been decreasing over the period. Trends of decreasing urban decrement have also been reported by several authors (Williams, 2007 and AQEG, 2009).

Observed ozone trends during 1993 to 2011 and 2004 to 2011 showed different pattern, i.e., average ozone trends at both urban and rural sites are positive for the former and negative for the latter case. Statistical analysis indicated that NOx trends have been stabilised during the last 8 years or so in urban areas and could have caused the ozone trends to change. Multiple and single changepoint analyses indicate significant increase in ozone concentrations in 1998, afterwards ozone concentrations have either remained constant (1998 to 2008) or decreased (2009 to 2011), except in spring 2008 when ozone monthly mean concentration was significantly higher. Changepoint analysis is used for the first time for ozone trend analysis and provides a good tool for recognising break point in ozone time series. If the recent negative trend in ozone, is not a temporarily phenomenon and is rather a turning point in ozone trends and continue to the future then it is a good indication and can reduce ozone concentrations in the future. However, modelling studies (Cape, 2008) have reported that the emission of ozone precursors might still increase for the next 20-50 years and may result in ozone concentration to further increase in both rural and urban areas. In this case the negative trend in ozone concentration might be an apparent temporarily phenomenon caused by some short term effects and ozone trend may turn positive again in the future that can have some serious policy implications.

CHAPTER 11: SUMMARY AND FURTHER WORKS

11.1 Introduction

This chapter summarises the whole PhD project, focusing on the main findings and contributions of the project. Further work has been suggested in the light of the findings and constraints of this project. Section 11.2 summarises how the project was carried out and what are the main contributions of the project to the field of air quality, particularly ground level ozone in urban areas; and section 11.3 describes the main recommendations of the project for the future work, which is the work that could not be done in this project due to data, time and resources constraints or was out of the scope of this project.

11.2 Summary of this thesis

The main aim of this PhD project was to characterise the spatial and temporal variability of traffic-related ozone concentration with the help of historical ozone data from rural and urban monitoring sites, spatial characteristics (easting and northing coordinates, altitude, distance from the coast and site types), road traffic characteristics (traffic flow, vehicle speed and fleet composition), other air pollutants (e.g. NOx, CO, VOCs, $PM_{2.5}$) and meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction). The project differs from traditional approaches in several ways: (1) the statistical models employed are applicable to non-normal ozone distribution and can handle non-linearities in the association of ozone and covariates; (2) it focuses on the whole ozone distribution in contrast to the traditional men-focused approach; (3) it characterises ozone as an urban air pollutants (known as traffic-related ozone) rather than rural air pollutant; (4) it considers a large range of covariates, which in addition to ozone precursors and meteorological variables include traffic characteristics and spatial parameters.

This project uses data from two sources: (1) Kirkstall monitoring site in Leeds, which is part of the facilities for monitoring air quality and traffic flow at the Institute for Transport Studies, University of Leeds. Traffic data (traffic flow, vehicle speed and fleet composition) were used from Kirkstall monitoring site. Meteorological variables (temperature, solar radiation, relative humidity, wind direction and wind speed) and traffic related air pollutants (NOx, NO, NO_2, HC, CO and $PM_{2.5}$) data were also used from Kirkstall monitoring site; (2) The UK Automatic Urban and Rural Network (AURN), which is established by the UK Department for Environment, Food and Rural Affairs (DEFRA) and monitors several air pollutants including ozone, NOx, NO_2, NO, CO, HC, PM_{10}, and $PM_{2.5}$. Data regarding

spatial parameters (easting and northing coordinates, altitude, distance form coast and site type) used in this project were obtained from 80 ozone monitoring sites, which are part of the UK AURN.

The project mainly employs graphical presentations (scatter plot, time variation plots, histogram, box plot, polar plot, etc.), general statistics (e.g., correlation analysis, Shapiro-Wilk test, Kolmogorov-Smirnov, multiple regression analysis) and two advanced models: quantile regression model (QRM), and generalised additive model (GAM). R programming language with several specialist packages (e.g., openair, quantreg, mgcv, loa, circStats and lattice) were used to do most of the statistical analysis. In addition, MS Excel 2007, Google Earth 2011 and QGIS 2011 have also been used in the project for data analysis, getting spatial data and mapping procedure. Where suitable code was not already available, dedicated code was purpose written in-house for this project. This included specialist functions for a range of operations, such as estimating the local and global goodness of fit for QRM, modifying the outputs of the GAM and estimating temporal trends for selected quantiles.

11.2.1 Synthesis of main results

The main results are discussed with reference to the research objectives that were presented in Chapter 1.

Objective 1: To analyse ozone frequency distribution to determine whether ozone concentration is normally distributed. This is important to decide whether to apply parametric or non-parametric statistical tests.

Frequency distributions of ozone and independent variables were investigated in chapter 5 to determine whether the distributions were normal or not. The aim was to establish whether to apply parametric or non-parametric statistical tests. The data distributions exhibit variations in time and space, however statistically the distributions of ozone and independent variables were non-normal. Therefore it was decided to apply non-parametric statistics that can be applied to both normal and non-normal distributed data. Furthermore, the behaviour and interaction of ozone with its predictors vary at different parts of ozone distribution indicating a nonlinear association; therefore it was ensured that the statistical test applied can handle the non-linearities in the association of ozone and its predictors.

Objective 2: To analyse the diurnal, weekly and seasonal cycles of ozone and characterise the variations with the help of meteorological variables, other air pollutants (especially NOx) and road traffic characteristic.

In Chapter 5 the diurnal, weekly and seasonal cycles of ozone have been analysed in details. Ozone data from four monitoring sites (Leeds centre, Harwell, Marylebone, and Strath Vaich) for year 2008 were obtained. The four monitoring sites have different topographical and meteorological characteristics. The aim here is to obtain a broad picture of ozone variations at roadsides, urban centres, rural and remote areas. Ozone concentrations seem to have been affected by both meteorological conditions and sources of fresh NO (as explained below). Generally ozone concentrations are found to be higher at rural and remote sites (Harwell and Strath Vaich) and lower at urban and roadside monitoring sites (Leeds and Marylebone). The lowest ozone concentrations are exhibited by Marylebone monitoring site which is located approximately one meter from the edge of Marylebone road (A50). This road has six lanes and has a flow of 80,000 vehicles per day (UK-AIR, 2012). Most probably titration of ozone by fresh NO emitted by road transport keeps ozone concentrations low at this site.

Ozone concentrations at all sites follow a typical twenty four hours cycle i.e. lower during night-time and early morning hours and higher during day times. The highest concentrations are achieved during the afternoon from 12:00 to 14:00 hours, most probably caused by photochemical ozone formation as a result of higher amount of ultraviolet (UV) radiation during these hours. Harwell and Strath Vaich sites have slightly different daily cycles than Marylebone and Leeds. At Marylebone and Leeds in addition to night times low, there is a further reduction in ozone concentrations in the morning (about 06:00), which cannot be observed at the other two sites. This effect is most probably caused by the early morning traffic which emits NO that reacts with ozone and further reduces its concentrations.

It is observed that the diurnal cycle of ozone concentrations varies during different seasons of the year due changes in meteorological characteristics (e.g., temperature or the level of solar radiation). Therefore diurnal cycle of ozone varies during spring, summer, autumn and winter. Average ozone concentration is highest during the spring season (March, April, May), followed by summer (June, July, August). Furthermore, the day-night variation in ozone concentration is considerably higher in spring than in winter. In winter due to low levels of solar radiation, hardly any photochemical ozone formation takes place and most probably due to this reason ozone concentration in the afternoon is almost the same as during night time. The highest concentrations are observed in March, April and May and lowest in December. December shows ozone concentrations during day time significantly lower than night time, which is most probably due to the lack of ozone formation during day time and ozone being further depleted by the freshly produced NO. On the other hand during night time due to low level of road traffic flow, ozone depletion by NO is minimal and hence ozone concentrations are higher than day time. June and July exhibit considerably

greater day-night variation most probably due to the high level of solar radiation in these months. It is worth re-emphasising that average ozone concentrations in these months are still lower than that in March – May, which is probably more to do with the level of ozone precursors than solar radiation. The rest of the months make a group showing characteristics of a typical urban diurnal cycle.

To analyse the diurnal cycle of ozone further, k-means clustering analysis was applied to divide the diurnal cycle of ozone concentrations (ppb) into various clusters and analyse their similarities or dissimilarities with the seasonal or monthly cycle of ozone. Firstly ozone data are divided into 365 diurnal cycles and then using k-means these are grouped (clustered) into 4 and 12 clusters. The reason for selecting 4 and 12 clusters was to make comparison easy with seasonal and monthly diurnal cycles. The diurnal cycles for the 4 clusters vary considerably in some aspects from the seasonal diurnal cycle. The diurnal cycles of the 4 clusters are evenly distant from each other, in contrast to seasonal diurnal cycles where two distinct groups can be observed. The diurnal cycle for spring is entirely different from the other 3 seasons, which seems closely related. Cluster 1 and cluster 4 look almost the same as winter and spring, but the rest of the two clusters (cluster 2 and 3) exhibit different characteristics from summer and autumn. Cluster 2 show ozone concentration during afternoon time lower than the early morning hours (0 to 5 am) and looks more like a typical winter urban diurnal cycle, whereas cluster 3 has very high afternoon peak ozone concentration compared to early morning hours and looks more like a typical summer urban diurnal cycle. The diurnal cycles of 12 clusters vary from those of monthly cycles. Within the 12 clusters, again 4 distinct groups can be identified. This analysis shows that apart from seasonal and monthly variations in the diurnal cycles of ozone there are some mixed days that show different characteristics within the same season. Therefore cluster analysis provides further insight into the ozone diurnal cycle.

On a weekly basis generally weekend and Monday exhibit higher, whereas Wednesday and Thursday show relatively lower ozone concentrations. For instance, mean ozone concentrations ($\mu g/m^3$) at Marylebone site were 20 and 12 and at Harwell site were 47 and 55 on Sunday (weekend) and Thursday (midweek), respectively. High level of ozone during weekend is a well known phenomenon and is referred to as ‘ozone weekend effect (OWE)’ in the literature, e.g. Jenkin (2008) and the references therein. Low levels of traffic during weekend is considered to be the main cause of OWE, as low levels of fresh NO reduce local ozone removal. Compared to other weekdays, higher level of ozone on Monday is probably due to the carry over effect of ozone from weekend. At Strath Vaich monitoring site the difference in ozone concentrations during different days is negligible, probably because the site is remote and is not affected much by road traffic emissions.

Ozone concentrations show a clear seasonal effect. Ozone concentrations are higher during March, April and May and lower during autumn and winter months at all four sites. For instance, monthly mean ozone concentrations ($\mu g/m^3$) at Marylebone site were 35 and 7 and at Leeds site were 79 and 17 for May and December, respectively. Cloudy and cold weather conditions during winter months result in very low UV radiation in the UK, which reduce photochemical ozone formation. Ozone titration by NO and low tropospheric – stratospheric exchange of ozone caused by the stagnant atmospheric conditions further reduces ground level ozone concentrations, which explain low level of ozone in the winter months. In spring when UV radiation increases, it increases photochemical ozone formation and hence ozone level increases in the atmosphere. The point which needs further attention is that UV radiation are generally higher in June, July and August, however after May ozone levels decrease gradually and in August reach a level which is normally observed in winter months. Most probably the reason for this is that for photochemical ozone formation in addition to UV radiation, the presence of ozone precursors (e.g., VOCs) is essential whose oxidation by hydroxyl radicals in the presence of NOx leads to ozone formation. Data collected at Harwell and Marylebone monitoring sites show that hydrocarbons accumulate in the atmosphere during winter months and reach the highest level in February. In March when the level of UV radiation increases, this consumes hydrocarbon concentrations through photochemical ozone formation and hydrocarbons levels gradually decrease. In August in spite of relatively high level of UV radiation, photochemical ozone formation is restricted by the limited availability of hydrocarbons.

Objective 3: To investigate the relationship between ozone and traffic related air pollutants (NO_2, NO, CO, VOCs, and $PM_{2.5}$) and, ideally, better understand their role in controlling the variations in ozone concentrations in the UK.

The effect of traffic related air pollutants on ozone concentration was analysed in chapter 6, using graphical presentation, correlation analysis and quantile regression model. Traffic related air pollutants (e.g., NO, NO_2, CO, HC, and $PM_{2.5}$) play important role in controlling ozone variations, therefore their association with ozone was investigated. Among these air pollutants, NOx seems to exert the dominant effect. NOx, or more strictly its main constituents NO and NO_2 act as both precursor and a local sink of ozone and therefore may contribute positively or negatively to ozone concentration. However, at local level the latter effect (as a sink) is more dominant in which freshly emitted NO reacts and reduces ozone concentration. Statistical analysis shows that the effect of NOx on ozone varies during different months of the year, days of the week and hours of the day. The correlation coefficients were much stronger during colder months and night hours for NO, NO_2 and their sum (NOx). Furthermore, it was observed that the association of NOx and ozone

changes at different ozone and NOx concentrations. QRM shows stronger effect of NO_2 than NO on ozone concentration. The effect of HC, CO and $PM_{2.5}$ on ozone concentration was negative and significant at all quantiles of the ozone distribution. HC and CO are considered the precursors of ozone and therefore as ozone photochemistry increases it consumes HC and CO and causes their levels to decrease, which probably explains the negative association. $PM_{2.5}$ may provide a surface for dry ozone deposition which reduces ozone concentrations. QRM reveals that sometimes only the strength of effect changes (e.g. CO), whereas other times both strength and nature (negative or positive) changes at different quantiles of ozone distribution, indicating that the association is non-linear and more complicated than thought before.

Objective 4: To investigate the effect of local road traffic characteristics (traffic flow, vehicle speed, and fleet composition) on traffic related ozone concentrations and quantify their contributions to ozone concentrations on local levels.

The effect of road traffic on ozone concentration is not well documented particularly in the UK. Literature review (Chapter 3) shows that existing studies on the topic carried out mostly in Europe, have certain limitations in their approaches, such as using parametric statistics, mostly linear regression, ignoring the background effect, and using surrogates for traffic or ozone data. In this project (Chapter 7) two approaches have been adopted to quantify the effect of road traffic on ozone concentration: Firstly the differences in ozone concentration between rural and urban monitoring sites (urban decrement) have been analysed in the whole UK using a QRM model; Secondly using hourly traffic characteristics and ozone data from Kirkstall site. Statistical analysis shows that on average (5 years average – 2007 to 2011) ozone concentrations are about 26 % higher in rural areas than in urban areas. The urban decrement varies at different quantiles of ozone concentration and ranges from 10.5 $\mu g/m^3$ (25%) to 21.56 $\mu g/m^3$ (30%) at quantile 0.1 and 0.99, respectively. The results of QRM show that based on the 5 years average data up to 90% ozone variations between rural and urban sites can be explained with the help of road traffic characteristics. Cars are the dominant traffic category and are the main emission source; however using normalised levels buses are shown to have the strongest positive effect on urban decrement. In other words buses are the traffic component with the strongest sink contribution for ozone concentrations at urban sites. Various traffic scenarios and their effects on ozone concentrations have been investigated. The findings favour the use of public transport (e.g. buses) in urban areas for better air quality management, especially ground level ozone.

Objective 5: To quantify the association of ozone and meteorological variables, taking into account the whole ozone distribution.

Meteorology plays a vital role in photochemical ozone formation (e.g. temperature and solar radiation) and ozone transport and dispersion (e.g. wind). The effects of meteorological variables (temperature, solar radiation, relative humidity, wind speed and wind direction) on ozone concentration have been investigated using data from Kirkstall and Marylebone monitoring sites. Statistical analysis shows that the relationship between ozone and meteorology changes considerably during different hours of the day and seasons of the year. Generally temperature and wind speed demonstrate positive effect, whereas relative humidity demonstrates negative effect on ozone concentration. The effect of wind direction is more complicated and being a circular variable needs to be handle differently. The effect of meteorology also varies spatially, for instance ozone at Marylebone and Kirkstall site responds differently to meteorological variables probably due to some local factors (e.g., tall buildings, street canyon effect, and traffic volume), which can affect the flow of wind, recirculation of pollutants and the chemistry of ozone. Furthermore, as revealed by QRM, the effect of meteorology varies at different ozone concentrations. Sometimes the strength of effect changes but the nature (positive or negative) remains the same as in the case of wind speed, other times both strength and nature change as in the case of solar radiation. The effect of meteorology on ozone is also investigated using graphical presentation and correlation analysis.

Objective 6: To model the spatial variability of ozone in the UK with the help of geographical (spatial) parameters and to investigate as to how ozone concentration is affected by the associated variables (e.g., altitude, distance from the coast etc).

Ozone spatial variations in the UK are analysed in chapter 9. Ozone concentrations demonstrate considerable spatial variation throughout the UK. Spatial variations of ozone can be linked with several phenomena, including ozone titration by freshly emitted NO, dry deposition (to ground surface, plants and other materials), vertical and horizontal movement, and photochemical ozone formation. However, the balance of these different phenomena can be influenced by local factors: for instance, ozone titration by NOx is higher in urban areas; dry deposition is lower to water surfaces; photochemical ozone formation rate is higher in sunny areas of the country; and higher altitudes exhibit higher average ozone concentration. Therefore, here a spatial ozone model has been proposed for the UK using such spatial parameters, distance from the coast, easting & northing coordinates, altitude of the site, and NOx concentration. The model is implemented as a generalised additive model (GAM) because the GAM is an advanced regression model that relaxes some of the restrictions imposed by linear regressions (e.g. linearity and normality assumptions). The model is simple to set up. The model can therefore be readily applied to a location or region where NOx measurements or predictions are available to provide an estimate of associated

ozone concentrations, and by inference the negative feedback associated with different NOx mitigation activities.

A GAM model using these inputs exhibits characteristics consistent with established ozone behaviour. Annual average ozone level has a pronounced northeasterly component, i.e. ozone levels increase towards north and decrease towards east. Ozone concentration is negatively correlated with the distance from the coast within a range of 0 to 60 km, a trend associated with relatively less dry deposition of ozone molecules on water surfaces. Furthermore, there is a positive association between the altitude of monitoring site and ozone level, most likely due to local topographical effects. NOx, which is mainly derived from road traffic and other combustion sources in urban areas, is negatively correlated with ozone and appears to provide a more sensitive alternative to the monitoring site type (rural or urban) as a model input. The scores of the metrics (e.g., FAC2, RMSE, NMB) and validation process place confidence in the model performance. The model was validated both temporally and spatially and the predicted ozone showed strong correlation with observed ozone concentration. The use of the model as an impact assessment tool was demonstrated, and based on 2020 NOx projections it was estimated that the average ozone in urban areas would increase by 26% over the same period, however this increment differ in various geographical region. The highest increment was shown in London Bloomsbury (53 %) and London Marylebone (46 %).

Objective 7: To characterise temporal trends in ozone concentrations in urban and rural areas, analyse their differences, characterise the factors responsible, and discuss their implications for future ozone-related air quality management practices.

In chapter 10 ozone trends are calculated to determine how the concentrations of air pollutants might have changed over time using data from 15 rural and 5 urban monitoring sites during 1993 to 2011. The sites were chosen on the basis of data availability over the 19 years period. Ozone trends during the last 8 years (2004 to 2011) have also been investigated for the same monitoring sites to investigate how ozone trends have changed most recently. Trends have shown significant variability at different statistical metrics (e.g., mean, median, maximum and selected quantiles). The maximum trends were negative at both rural and urban sites; and median and mean trends were positive during the period. The negative trends in high episodic ozone during the summer are believed to be caused by reduction in the emissions of ozone precursors (e.g., NOx and VOCs) in the Europe since 1990; whereas the positive trends in mean ozone are believed to be controlled by hemispheric baseline ozone levels (Jenkin, 2008; Derwent et al., 2010). Urban and rural trends have different rates and indicate that urban decrement (the difference in ozone concentration between rural and urban areas caused by gas phase titration of ozone by

locally produced NOx) has been decreasing over the period. Observed ozone trends during 1993 to 2011 and 2004 to 2011 showed different patterns, i.e., average ozone trends at both urban and rural sites are positive for the former and negative for the latter case. Statistical analysis indicated that NOx trends have been stabilised during the last 8 years in urban areas and could have caused the ozone trends to change from positive to negative. If the recent negative trend in ozone, is not a temporarily phenomenon and is rather a turning point in ozone trends and continue to the future then it is a good indication and will lead to less human health and environmental impact. However, modelling studies (Cape, 2008) have reported that the emission of ozone precursors might still increase for the next 20-50 years and may result in ozone concentration to further increase in both rural and urban areas. In this case this negative trend in mean ozone is an apparent temporarily phenomenon caused by some short term effects and ozone trend will turn positive again in the future that can have some serious policy implications.

11.3 Further work

Ozone is a complicated air pollutant and its concentration in the atmosphere is dependent on many factors, including meteorological variables (temperature, solar radiation, relative humidity, wind speed, wind direction, cloud cover, the amount of precipitation), other air pollutants (NOx, NO, NO_2, CO, SO_2, $PM_{2.5}$ and PM_{10}, and VOCs), the sources of ozone precursors (road traffic and other combustion processes), and spatial characteristics (such as altitude, distance from the coast, site type). In addition, ozone concentration is affected by stratospheric-tropospheric exchange (STE), regional and global transportation and local topographical characteristics. Therefore ozone concentration demonstrates substantial spatiotemporal variations in the UK. Interaction of ozone with so many factors makes its modelling a challenging task and there are many uncertainties in ozone modelling. Different models are required for ozone modelling at global, regional or local levels. Data availability, data quality, uncertainties in quantifying the amount of ozone precursors (including anthropogenic and natural sources), the amount of ozone dry deposition, and the amount of STE are some of the constraints in accurate ozone modelling.

In this project the intention was to characterise ozone at local and national levels with the help of meteorological variables, road traffic characteristics and traffic related air pollutants using hourly data from Kirkstall monitoring site and the UK AURN. As part of this work, a GAM model for annual average ozone modelling in the whole UK has been proposed using spatial parameters and NOx concentration data. QRM model is proposed for modelling ozone at local levels. This project has provided some new insight into urban chemistry, most notably more comprehensive characterisation of the relationship between ozone and its

controlling factors (e.g., atmospheric factors and traffic characteristics) in light of their non-linear association and a highly flexible and simple to use modelling strategy for ozone mapping.

The following recommendations are made which can provide further insight into ground level ozone and help further understand its behaviour:

1. The contribution of STE to ground level ozone concentration: To quantify the contribution of STE to ground level ozone is out of the scope of this project. This requires further consideration using modelled or monitored data from the vertical movement of the atmosphere. The points that need further works are: What are the main meteorological processes responsible for ozone vertical transport, particularly for ozone downward movement? What are the relative contributions of STE to ground level ozone and how this contribution varies during different meteorological conditions? How frequently does STE increase ozone concentrations near the surface? What regions are most likely to be affected by STE?

2. Dry deposition: Different rates of dry deposition occur to different surfaces, which needs to be quantified for accurate ozone modelling, particularly the variation of ozone dry deposition to living materials including plants leave.

3. Global and regional contribution: The regional and global contributions of different processes to ozone concentrations need quantifying.

4. I this PhD project several meteorological parameters were considered (see chapter 8 for details), which are considered more important for controlling ozone concentration. However, in future other parameters can be considered including precipitation and cloud cover which could be sourced from the Met Office. In addition it is suggested to investigate the effect of boundary layer height on ozone concentration in the future.

5. Although the effect of different vehicle categories (cars, vans, buses, articulated heavy vehicles, cars with trailers and motorcycles) on ozone concentration has been investigated, the effect of different fuel types (e.g., petrol, diesel, alternative fuel types) has not been considered in this project. Furthermore, the vehicle age, engine size, and driver behaviour were not considered. The vehicle speed limit on Kirkstall road is 48 km/hr, therefore it is suggested to further investigate the relationship of ozone with vehicle speed using traffic data from a site where a much broader range of speeds are encountered.

6. A comparative analysis of the results of the models developed in this project, comparing its outputs with those from more advanced air quality models (e.g., ADMS-Urban or a three-dimensional ozone chemistry transport models, e.g. CTMK), may be useful to further verify the applicability and potential usefulness of the model for ozone data analysis.

11.4 Summary

This PhD project aimed to characterise the spatiotemporal variability of ground level ozone in the UK using meteorological variables, road traffic characteristics, traffic related air pollutants, historical ozone data and spatial parameters data. The effect of these parameters on ozone is described using mainly quantile regression and generalised additive models. It is shown that these parameters play a vital role in controlling ozone concentrations; however the effects vary in space and time and with the concentrations of ozone. The project provides a great insight into the behaviour of ozone and its interaction with other factors. Statistical models have been employed to investigate the association of ozone with several covariates at local and national levels in the UK. The project concludes that ozone concentrations are increasing at greater rates in urban areas than in rural areas, which may be more challenging for policy makers and pose greater risks for building materials and human health in the urban environment. The project recommends further investigation to quantify the contribution of STE, global and regional transport, and dry deposition to ozone concentrations. The effects of different fuel types, engine size, vehicle age, and driver behaviour on ozone concentration require further consideration. Furthermore, a comparative analysis of the results of the models developed in this project with advanced air quality models may provide further insight into the performance of the model and its potential for ozone prediction in the UK.

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LIST OF ABBREVIATIONS

µg/m^3	Microgram per cubic meter
abs	Absolute
AEA	Atomic Energy Authority
AOT40	Accumulated ozone concentration Over a Threshold of 40 ppb
API	Application Programming Interface
AQEG	Air Quality Expert Group
AQEG	Air Quality Expert Group
AQRM	Amalgamated Quantile Regression Model
AQS	Air Quality Strategy
Auc	Auchencorth
AURN	Automatic Urban and Rural Network
BAM	Beta Attenuation Monitor
Bir	Birmingham
BP	Black pool
Br	Bromine
Br	Brighton
BrO	Bromine Oxide
C	Ozone Concentration (molecules cm^{-3})
C Mem	Coventry Memorial
CFC	Chlorofluorocarbons
CH_4	Methane
Char	Charlton
Cl	Chlorine
ClO	Chlorine Oxide
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DEFRA	UK Department for Environment, Food and Rural Affairs
DJF	December, January, February
DoE	Department of Environment
e.g.	for example

EA	Environment Agency
EC	European Community
Ed St	Edinburgh Saint
EEA	European Environmental Agency
EPA	Environmental Protection Agency
EPAQS	Expert Panel on Air Quality Standards
EU	European Union
FAC2	Factor of 2
FDMS	Filter Dynamics Measurement System
GAM	Generalised Additive Models
GDF	Great Dun Fell
H_2O	Water
H_2O_2	Hydrogen peroxides
H_2S	Hydrogen Sulphide
H_2SO_4	Sulphuric Acid
HA	Highway Agency
HB	High Muffles
HC	Hydrocarbon
HNO_3	Nitric acid
HO_2	Hydroperoxy radicals,
Hrm	Hour Running Mean
HVS	High Volume System
I	Light intensity after absorption by ozone
I_0	Light intensity at zero ozone concentration
ICP	International Cooperative Programme
IPCC	Intergovernmental Panel on Climate Change
IPPC	Industrial Pollution Prevention and Control
ITS	Institute for Transport Studies
JJA	June, July, August
km	Kilometer
KS	Kolmogorov-Smirnov
L	Path-length (cm) of the cell

L	London
LB	Ladybower
LVS	Low Volume System
M	An un-reactive molecule such as nitrogen (N_2)
m asl	Meters Above Seas Level
M	Market
m	Meters
m/s	Meter per Second
MAM	March, April, May;
Man	Manchester
Max	Maximum
MB	Mean Bias
mg/m^3	Milligram per cubic meter
MGE	Mean Gross Error
MH	Mace Head
Min	Minimum
N	Nitrogen Atom
N	North
N_2	Nitrogen Molecule
N_2O	Nitrous Oxide
NA	Not Available
NACIS	North American Cartographic Information Society
NAEI	Nationl Atmospheric Emission Inventory
NMB	Normalised Mean Bias
NMGE	Normalised Mean Gross Error
NMHC	Non-Methane Hydrocarbons
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_3	Nitrate
Nor	Norwich
NOx	Oxides of Nitrogen

O	Atomic Oxygen
O (^{1}D)	High energy oxygen atom
O (^{3}P)	A ground state or low energy oxygen atom
O_2	Oxygen Molecule
O_3	Ozone
^oC	degree Celsius
OH	Hydroxyl Radicals
OH	Hydroxyl radicals
Oi	Observed value
OLS	Ordinary Least Square regression
OWE	Ozone Weekend Effect
PELT	Pruned Exact Linear Time
Pi	Predicted value
PM	Particulate Matter
PM_{10}	Particulate Matter of size 10 micron
$PM_{2.5}$	particulate matter of size 2.5 micron
PORG	Photochemical Oxidant Review Group
Port T	Port Talbogh
ppb	Parts Per Billion
ppm	Parts Per Million
q	value of a quantile
QA/QC	Quality Assurance and Control
QGIS	Quantum Geographic Information System
QRM	Quantile Regression Models
R	Correlation coefficient
R	Alkyl radicals (e.g. CH_3)
R^1 (τ)	local goodness of fit
R^1	Global goodness of fit
R^2	Coefficient of determination
RB	Rural Background
RBA	Rural Background Agriculture

Red Ne	Reading New
RH	Hydrocarbons (e.g. CH_4)
RMSE	Root Mean Square Error
RNM	Rural Background Nature
RO_2	Oganic peroxy radicals
ROOH	Alcohols
S L	Sunderland
S W	Sandwell West
SO_2	Sulphur Dioxide
SO_3	Sulphur Trioxide
SOMO35	the Sum of Ozone Means Over 35 ppb
SON	September, October, November
SOT	Stoke-On-Trent
Southamp	Southampton
STE	Strato-Tropospheric Exchange
STL	Seasonal Trend decomposition using Loess
SU	Suburban
SW	Shapiro-Wilk test
T	Tyburn
TEOM	Tapered Element Oscillating Microbalance
UB	Urban Background
UI	Urban Industrial
UI	Urban Influence
UNECE	United Nation Economic Commission for Europe
UT	Urban Traffic
UV	Ultra Violet
VOCs	Volatile Organic Compounds
WB	Weybourne
WF	Wicken Fen
WGPM	Working Group on Particulate Matter
WHO	World Health Organisation
WRAC	Wide Range Aerosol Classifier

α	Specific ozone molar absorption coefficient
τ	quantiles

APPENDICES

Appendix 1

Ozone annual mean (µg/m^3) from 2007 to 2011 and 5 years mean for 80 monitoring sites. UB stand for urban background, UT for urban traffic, UI for urban industrial, SUB for suburban, RB for rural background, RBA for rural background agricultural and RBN for rural background nature.

Site Name	Type of Site	Annual Mean ozone11	Annual Mean ozone10	Annual Mean ozone09	Annual Mean ozone 08	Annual Mean ozone 07	5 years Mean Ozone
Aberdeen	UB	42.69	44.15	42.00	50.19	46.86	45.18
Aston Hill	RBA	61.29	56.12	63.75	69.86	63.41	62.89
Auchencorth Moss	RB	55.82	56.12	55.51	60.24	58.18	57.17
Barnsley Gawber	UB	39.07	35.20	43.29	46.26	43.52	41.47
Belfast Centre	UB	42.65	37.72	37.75	39.40	42.70	40.04
Birmingham Tyburn	UB	40.11	36.69	38.26	41.89	35.29	38.45
Birmingham Tyburn Roadside	UT	32.71	28.48	33.21	NA	NA	31.47
Blackpool Marton	UB	57.00	32.10	49.76	57.08	54.95	50.18
Bottesford	RB	48.30	44.98	45.85	48.77	45.42	46.66
Bournemouth	UB	53.04	49.22	50.64	54.61	50.87	51.68
Brighton Preston Park	UB	51.64	45.88	52.94	51.34	49.74	50.31
Bristol St Paul's	UB	43.31	39.62	44.03	43.99	42.77	42.74
Bush Estate	RBN	58.80	56.62	56.23	57.65	55.61	56.98
Cardiff Centre	UB	39.06	35.57	40.97	43.17	39.57	39.67

Charlton Mackrell	RB	58.93	55.08	55.22	45.71	NA	53.74
Coventry Memorial Park	UB	45.13	41.30	44.37	47.69	45.35	44.77
Cwmbran	UB	48.21	47.12	50.93	54.79	50.36	50.28
Derry	UB	51.32	44.91	48.80	52.63	48.00	49.13
Edinburgh St Leonards	UB	40.42	32.53	52.24	49.03	47.75	44.39
Eskdalemuir	RBN	53.18	54.96	56.22	56.88	54.46	55.14
Exeter Roadside	UT	39.36	30.97	37.79	41.97	45.90	39.20
Fort William	SUB	53.56	47.27	53.48	56.32	53.73	52.87
Glasgow Centre	UB	34.06	26.81	31.92	32.68	36.22	32.34
Glazebury	RB	41.82	37.69	39.49	44.51	41.10	40.92
Great Dun Fell	RBN	53.61	58.36	55.52	58.57	62.22	57.66
Harwell	RBA	54.96	52.43	49.40	49.98	48.00	50.95
High Muffles	RBN	57.82	60.37	62.72	56.56	52.87	58.07
Hull Freetown	UB	28.40	32.47	39.84	55.74	42.73	39.83
Ladybower	RBN	56.18	58.13	53.60	58.32	52.90	55.83
Leamington Spa	UB	45.85	35.04	32.00	40.91	38.98	38.56
Leeds Centre	UB	34.84	32.62	35.23	43.20	37.24	36.62
Leicester Centre	UB	35.63	23.45	39.49	41.14	38.30	35.60
Leominster	SUB	49.59	42.73	46.91	51.17	47.71	47.62
Lerwick	SUB	69.21	65.25	70.44	70.09	64.38	67.88
Liverpool Speke	UB	50.38	42.71	40.89	46.62	44.42	45.00
London Bloomsbury	UB	27.27	22.58	25.93	28.28	23.73	25.56
London Eltham	UB	39.61	37.75	37.89	40.15	39.06	38.89
London Haringey	UB	28.49	32.49	37.47	41.09	38.76	35.66

London Harlington	UI	35.13	33.48	34.87	35.13	32.29	34.18
London Hillingdon	UB	26.07	25.30	25.69	31.11	30.18	27.67
London Marylebone	UT	17.03	18.36	14.07	15.73	17.30	16.50
London N. Kensington	UB	39.30	34.41	37.12	38.64	36.48	37.19
London Teddington	UB	48.99	44.29	45.15	47.45	42.35	45.65
London Westminster	UB	35.75	34.67	33.80	34.55	34.00	34.55
Lough Navar	RB	51.63	47.89	46.40	49.10	45.90	48.18
Lullington Heath	RBN	48.97	54.71	57.80	59.07	54.45	55.00
Mace Head	RB	72.75	70.13	74.06	75.63	73.62	73.24
Manchester Piccadilly	UB	30.32	26.74	23.57	28.83	20.60	26.01
Manchester South	SUB	46.05	34.26	31.54	32.74	30.61	35.04
Market Harborough	RB	39.39	46.54	53.20	56.55	54.53	50.04
Middlesbrough	UB	48.39	44.35	45.98	48.12	45.99	46.57
Mold	SUB	50.67	38.48	36.76	NA	NA	41.97
Narberth	RB	59.94	58.65	60.37	61.84	59.90	60.14
Newcastle Centre	UB	40.30	42.31	34.95	41.82	42.98	40.47
Northampton	UB	51.26	44.55	47.24	47.83	45.62	47.30
Norwich Lakenfields	UB	40.99	35.78	32.90	NA	NA	36.56
Nottingham Centre	UB	34.42	31.99	34.08	38.46	34.47	34.69
Peebles	UB	54.17	51.36	44.80	NA	NA	50.11
Plymouth Centre	UB	44.90	39.90	43.03	42.33	40.75	42.18
Port Talbot Margam	UI	51.58	50.54	52.10	57.20	40.95	50.48

Portsmouth	UB	46.59	43.04	48.22	52.10	47.29	47.45
Preston	UB	43.54	34.93	42.04	49.93	42.39	42.57
Reading New Town	UB	40.63	39.21	42.50	46.01	42.74	42.22
Rochester Stoke	RB	46.43	41.55	42.79	45.50	45.86	44.43
Salford Eccles	UI	36.99	29.37	18.79	23.62	34.58	28.67
Sandwell West Bromwich	UB	50.13	41.05	44.97	48.14	42.04	45.26
Sheffield Centre	UB	42.14	38.10	38.42	43.78	37.66	40.02
Sibton	RBA	55.03	53.03	51.66	60.74	49.55	54.00
Southampton Centre	UB	36.49	33.27	33.44	32.37	31.38	33.39
Southend-on-Sea	UB	37.23	40.76	46.43	52.19	45.36	44.39
St Osyth	RB	50.25	47.38	51.58	53.85	54.93	51.60
Stoke-on-Trent Centre	UB	41.62	36.74	39.28	40.65	47.22	41.10
Strath Vaich	RBN	63.51	61.23	66.80	72.81	68.39	66.55
Sunderland Silksworth	UB	51.24	46.61	50.30	46.75	50.23	49.03
Thurrock	UB	38.08	37.60	37.57	38.50	37.33	37.82
Weybourne	RB	68.30	68.22	66.87	63.46	65.11	66.39
Wicken Fen	RB	43.39	44.34	49.16	50.73	54.48	48.42
Wigan Centre	UB	42.42	38.18	39.44	46.35	45.88	42.45
Wirral Tranmere	UB	45.28	38.53	43.81	48.65	46.91	44.64
Yarner Wood	RBN	61.38	59.92	61.72	60.70	58.54	60.45
Average		45.90	42.44	44.72	47.99	45.52	45.20

Appendix 2

Ozone AOT40 values (µg/m^3 hr) from 2007 to 2011 and 5 years average for 80 monitoring sites. UB stand for urban background, UT for urban traffic, UI for urban industrial, SUB for suburban, RB for rural background, RBA for rural background agricultural and RBN for rural background nature. The highlighted values are exceeding the critical value.

Site Name	Type of Site	AOT40 2011	AOT40 2010	AOT40 2009	AOT40 2008	AOT40 2007	5 years Mean AOT40
Aberdeen	UB	608	454	1256	7096	1898	2262
Aston Hill	RBA	1936	1650	7214	8212	2492	4301
A. Moss	RB	1770	1794	2480	8060	1596	3140
B. Gawber	UB	248	590	2046	4690	1500	1815
Belfast Centre	UB	946	536	506	1238	1154	876
B. Tyburn	UB	1950	3564	3592	7270	932	3462
B. T. Roadside	UT	830	1380	1430	NA	NA	1213
B. Marton	UB	4866	0	4566	6992	4164	4118
Bottesford	RB	3562	3270	3562	9030	2464	4378
Bournemouth	UB	4560	3234	3792	12642	4992	5844
Brighton Preston Park	UB	4262	2628	7242	5946	4916	4999
Bristol St Paul's	UB	2034	2344	6018	4880	2392	3534
Bush Estate	RBN	2738	1818	1840	5202	878	2495
Cardiff Centre	UB	1052	1436	4020	4296	1392	2439
Charlton Mackrell	RB	5128	5688	6070	NA	NA	5629

Coventry Memorial Park	UB	2810	3806	4256	7496	3192	4312
Cwmbran	UB	2124	3216	7508	5200	2864	4182
Derry	UB	1760	814	1600	6202	502	2176
Edinburgh St Leonards	UB	108	98	1822	4814	1578	1684
Eskdalemuir	RBN	1750	1860	5442	8826	1584	3892
Exeter Roadside	UT	574	132	0	1766	1854	865
Fort William	SUB	1826	896	3208	8552	794	3055
Glasgow Centre	UB	138	196	244	830	570	396
Glazebury	RB	2000	3180	1980	4464	2276	2780
Great Dun Fell	RBN	102	630	1446	5682	2248	2022
Harwell	RBA	4656	5954	4344	6062	3120	4827
High Muffles	RBN	4256	3866	11476	8926	3300	6365
Hull Freetown	UB	90	290	1388	20306	2766	4968
Ladybower	RBN	3216	3964	2554	8402	2662	4160
Leamington Spa	UB	4058	3854	2526	5572	1620	3526
Leeds Centre	UB	802	1102	586	8128	1222	2368
Leicester Centre	UB	486	12	4144	7194	2546	2876
Leominster	SUB	3430	3096	4198	6116	2630	3894
Lerwick	SUB	4238	996	5746	8366	1926	4254
Li. Speke	UB	2872	3270	994	3054	1256	2289

L. Bloomsbury	UB	640	710	280	1232	124	597
L. Eltham	UB	2354	3312	3072	6012	2354	3421
London Haringey	UB	3328	164	5024	9854	2580	4190
L. Harlington	UI	2220	3010	3676	5082	896	2977
L.Hillingdon	UB	966	622	2374	6296	2830	2618
L.Marylebone	UT	6	166	0	648	140	192
L. N. Kensington	UB	4598	2480	3240	6450	2604	3874
L.Teddington	UB	9140	6870	6328	11706	3300	7469
L.Westminster	UB	1760	2100	1348	3264	1262	1947
Lough Navar	RB	1892	1686	544	3918	1384	1885
Lull. Heath	RBN	1684	0	4952	10392	3086	4023
Mace Head	RB	3206	2308	5506	8314	5546	4976
Man Piccadilly	UB	380	746	104	814	362	481
Man South	SUB	2318	870	470	1050	628	1067
M.Harborough	RB	2318	4190	6624	11428	4672	5846
Middlesbrough	UB	2326	1840	1182	3668	1552	2114
Mold	SUB	1744	530	NA	NA	NA	1137
Narberth	RB	1458	2140	5594	6252	NA	3861
Newcastle Centre	UB	674	2452	336	2694	828	1397
Northampton	UB	5458	3776	5060	9366	2860	5304
Norwich Lakenfields	UB	1050	1816	NA	NA	NA	1433

Nottingham Centre	UB	1128	1962	1936	4502	920	2090
Peebles	UB	2498	2344	NA	NA	NA	2421
Plymouth Centre	UB	690	312	1296	1238	922	892
Port Talbot Margam	UI	2866	1616	5436	7708	NA	4407
Portsmouth	UB	1908	2464	5834	11310	3602	5024
Preston	UB	1170	678	2324	6922	660	2351
Reading New Town	UB	3426	4226	6558	7678	2470	4872
Rochester Stoke	RB	2866	1782	1056	5150	3794	2930
Salford Eccles	UI	588	1020	0	302	862	554
Sandwell West Bromwich	UB	4856	4054	4248	6942	2270	4474
Sheffield Centre	UB	1234	1416	418	1864	1946	1376
Sibton	RBA	6000	5384	5994	12810	1888	6415
Southampton Centre	UB	798	772	832	296	100	560
Southend-on-Sea	UB	904	2070	6694	13622	3248	5308
St Osyth	RB	3502	3386	6186	7832	11000	6381
Stoke-on-Trent Centre	UB	1158	994	1468	2870	3254	1949
Strath Vaich	RBN	2318	2318	2554	8622	5016	4166

Sunderland Silksworth	UB	3004	1614	1798	3412	2748	2515
Thurrock	UB	2644	2830	3028	5686	2198	3277
Weybourne	RB	9972	12666	9802	11016	10720	10835
Wicken Fen	RB	2854	5962	7888	11684	4238	6525
Wigan Centre	UB	1958	2944	2822	4938	3546	3242
Wirral Tranmere	UB	1484	1464	2536	4730	1750	2393
Yarner Wood	RBN	3188	7108	7712	7496	3668	5834
Average		2379	2309	3444	6381	2453	3337

Appendix 3

Ozone SOMO35 values (µg/m^3 hr) from 2007 to 2011 and 5 years average for 80 monitoring sites. UB stand for urban background, UT for urban traffic, UI for urban industrial, SUB for suburban, RB for rural background, RBA for rural background agricultural and RBN for rural background nature. The highlighted values are exceeding the critical value.

Site Name	Type of Site	SOMO35 2011	SOMO35 2010	SOMO35 2009	SOMO35 2008	SOMO35 2007	SOMO35 5 years Mean
Aberdeen	UB	746	687	916	2541	1190	1216
Aston Hill	RBA	2075	1349	3161	4282	2694	2712
Auchencorth Moss	RB	1354	1365	1539	2822	1632	1742
Barnsley Gawber	UB	293	179	1130	1460	824	777
Belfast Centre	UB	722	384	411	1190	985	738
Birmingham Tyburn	UB	1172	1151	1278	2190	633	1285

Birmingham Tyburn Roadside	UT	489	309	578	NA	NA	459
Blackpool Marton	UB	3274	0	2081	2938	2608	2180
Bottesford	RB	2807	1447	1629	2389	1382	1931
Bournemouth	UB	2608	1987	2139	3630	2553	2583
Brighton Preston Park	UB	2824	1401	3004	2656	2583	2494
Bristol St Paul's	UB	1410	1157	1872	1648	1554	1528
Bush Estate	RBN	2040	1694	1668	2519	1340	1852
Cardiff Centre	UB	669	591	1261	1446	950	983
Charlton Mackrell	RB	2967	2492	2496	115	NA	2018
Coventry Memorial Park	UB	1646	1429	1795	2166	1987	1805
Cwmbran	UB	1586	1562	2512	2958	2054	2134
Derry	UB	1391	982	1184	2235	680	1294
Edinburgh St Leonards	UB	232	162	1920	1942	1419	1135
Eskdalemuir	RBN	1590	1625	2651	2560	1720	2029
Exeter Roadside	UT	532	216	577	1125	1470	784
Fort William	SUB	1780	1294	2225	3350	1573	2044
Glasgow Centre	UB	277	109	644	397	492	384
Glazebury	RB	1379	1196	921	2147	1480	1425
Great Dun Fell	RBN	614	1258	1003	1846	2011	1346
Harwell	RBA	2402	2255	1644	1911	1402	1923
High Muffles	RBN	2706	2389	5784	3505	1582	3193
Hull Freetown	UB	140	209	960	5207	1394	1582
Ladybower	RBN	2056	1935	1423	2423	1875	1942
Leamington Spa	UB	1983	1163	834	1448	1030	1292
Leeds Centre	UB	610	370	391	2324	668	873

Leicester Centre	UB	584	59	1593	1694	1279	1042
Leominster	SUB	2206	1527	1805	2484	1856	1976
Lerwick	SUB	3333	2273	3730	3745	2148	3046
Liverpool Speke	UB	1981	1504	713	1694	945	1367
London Bloomsbury	UB	401	153	158	374	312	280
London Eltham	UB	1360	1184	1151	1606	1427	1346
London Haringey	UB	1624	479	1551	2248	1683	1517
London Harlington	UI	1154	858	1331	1284	970	1119
London Hillingdon	UB	480	321	770	1526	1249	869
London Marylebone	UT	96	98	31	200	243	134
London N. Kensington	UB	1957	876	1270	1716	1491	1462
London Teddington	UB	3282	2508	2234	2923	1878	2565
London Westminster	UB	1005	582	795	989	1044	883
Lough Navar	RB	1766	1638	487	1491	728	1222
Lullington Heath	RBN	1414	6	2823	3503	2331	2015
Mace Head	RB	4277	3642	4850	5361	4771	4580
Manchester Piccadilly	UB	331	264	36	348	97	215
Manchester South	SUB	1437	343	178	282	188	486
Market Harborough	RB	710	1561	2571	3186	2518	2109
Middlesbrough	UB	1452	1082	1032	1593	1125	1257
Mold	SUB	1372	253	16	NA	NA	547
Narberth	RB	2201	2015	2633	2889	517	2051

Newcastle Centre	UB	606	1317	482	1296	1194	979
Northampton	UB	2587	1394	1997	2460	1826	2053
Norwich Lakenfields	UB	726	535	1	NA	NA	421
Nottingham Centre	UB	603	518	832	1239	647	768
Peebles	UB	2153	2036	129	NA	NA	1439
Plymouth Centre	UB	795	437	695	597	643	633
Port Talbot Margam	UI	1994	1446	2121	3155	190	1781
Portsmouth	UB	1386	1045	2099	3323	2149	2000
Preston	UB	1022	341	1200	2385	810	1152
Reading New Town	UB	1617	1409	2157	2271	1524	1796
Rochester Stoke	RB	1503	1050	1018	1771	1908	1450
Salford Eccles	UI	485	407	0	120	535	309
Sandwell West Bromwich	UB	2400	1487	1672	2077	1262	1780
Sheffield Centre	UB	770	621	446	1181	710	746
Sibton	RBA	2686	2237	2260	4709	1444	2667
Southampton Centre	UB	477	365	462	216	150	334
Southend-on-Sea	UB	693	849	2427	3644	1721	1867
St Osyth	RB	1795	1333	2378	2981	3676	2433
Stoke-on-Trent Centre	UB	842	492	548	1009	1990	976
Strath Vaich	RBN	2742	2557	3189	5238	3660	3477
Sunderland Silksworth	UB	2043	877	1601	1394	1705	1524
Thurrock	UB	1346	1134	1224	1524	1320	1310
Weybourne	RB	4225	5235	4703	4282	4419	4573

Wicken Fen	RB	1795	2117	2708	3209	3040	2574
Wigan Centre	UB	1488	1250	1362	2076	2270	1689
Wirral Tranmere	UB	196	785	1196	1685	1244	1021
Yarner Wood	RBN	2900	3070	3347	2906	2846	3014
Average		1533	1174	1571	2201	1539	1582

Appendix 4

4.1 Code for calculating local R1 for Quantile Regression MOdel

```
localR1 <- function(mod){
        tau <- mod$tau ## here tau means quantiles used in the model, e.g., 0.1, 0.2, ...
1.
        mod.y <- mod$y ## y stands for dependent variable (ozone)
        quantiles<-quantile(mod.y, tau) ## quantile is the value of each tau
        p<-predict(mod) ## p is predicted variable
tempfun <- function(i=1){
    x1<-tau[i]*(mod.y-p[,i])
    y1<-((1-tau[i])*(mod.y-p[,i]))
    test<-ifelse(mod.y>=p[,i], abs(x1), abs(y1))
    SSerr<-sum(test) ## sum of square of residuals (error)
    temp<-ifelse(mod.y>=quantiles[i], abs(tau[i]*(mod.y-quantiles[i])), abs((1-
tau[i])*(mod.y-quantiles[i])))
    SStotal<-sum(temp) ## total sum of square
    R1<-1-(SSerr/SStotal) ## R1 is the local R^2
    R1
  }
 ans <- sapply(1:length(tau), tempfun)
  names(ans) <- names(quantiles)
 rq$localR1 <- ans
  rq$quantiles <- quantiles
        rq
}
```

```
##now just run the model

For Example

rq<-rq(o3~carflw+vanflw+busflw+articflw+trailerflw+mcycleflw, data=traffic1hdata, tau=c(.1, .2,.3,.4,.5,.6,.7,.8,.9,.99))

rq<-localR1(rq)

rq$tau

rq$localR1

rq$quantiles
```

4.2 Code for calculating global R^1

```
globalR1 <- function(mod){

tau <- mod$tau

mod.y <- mod$y

quantiles<-quantile(mod.y, tau)

  p<-predict(mod,newdata)

mean<-mean(newdata$o3, na.rm=TRUE)

newdata$test <- cut(newdata$o3, c(min(newdata$o3, na.rm=TRUE)-1, quantile(newdata$o3, c(.1, .2,.3,.4,.5,.6,.7,.8,.9,.99,1))) )

#added extra column because one more level than quantiles in mod.out

p <- cbind(p, NA)

myfun <- function(x) {

    p[x, as.numeric(newdata$test[x])]

}

ans <- lapply(1:length(newdata$o3), myfun)

ans <- do.call(rbind, ans)

newdata$ans <- ans ## add ans to newdata

ans<-newdata$ans

o3<-newdata$o3

SSerr<- sum(na.omit(c(o3-ans)*(o3-ans)))

SSreg<- sum((ans-mean)*(ans-mean))

SStotal<-sum((o3-mean)*(o3-mean))

globalR1<-1-(SSerr/SStotal)
```

```
mod$globalR1 <- globalR1

mod

}

## Example

traffic1hdata<-import()

newdata<-selectByDate(traffic1hdata, month="May", year=2008)

rq<-rq(o3~carflw+vanflw+busflw+articflw+trailerflw+mcycleflw,          data=traffic1hdata,
tau=c(.1, .2,.3,.4,.5,.6,.7,.8,.9,.99))

rq<-globalR1(rq)

rq$globalR1

rq$quantiles

rq$tau
```