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Ozone levels, changes and trends over Ireland – an Integrated Analysis

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STRIVE Report

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by

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The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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EXECUTIVE SUMMARY

Ozone is an important trace constituent in the atmosphere. While stratospheric ozone acts as an effective absorber of harmful ultraviolet radiation, the ozone found in the troposphere particularly at the surface acts as a pollutant and impacts on ecosystems (vegetation, forests and many crop species) as well as on human health. Ozone in the troposphere is the 3rd most important greenhouse gas affecting radiative forcing which therefore contributes to the heat budget of the planet and is a significant contributor to climate change. It is the main precursor of oxidizing agents in the atmosphere, the hydroxyl radicals, affecting the cleansing capacity of the atmosphere. Ozone (and its precursors) is one of the air pollutant species that is identified as a transboundary pollutant, by the Task Force on Hemispheric Transport of air pollution under the UNECE Convention on Long-Range Transboundary Air Pollution [CLRTAP]. It is also a priority pollutant under the EU Clean Air for Europe (CAFÉ) Programme. It was therefore fitting that a programme of research work was undertaken to analyse ozone levels, changes and trends over Ireland.

Surface ozone data at Irish sites with a relatively long data record (for more than 8 years) are analyzed to assess the overall ozone level, exposure exceedances and long term trends using statistical methods widely used for time analysis. The time series analysis shows that there is a decline in the occurrences of ozone peaks in recent years in urban as well as in rural areas – which is likely to be mainly attributable to the substantial decline in NO\textsubscript{x} and NMVOC (Non-Methane Volatile Organic Compounds) in background air composition. Except for the coastal marine sites of Mace Head and Valentia, all stations have shown an overall declining negative trend in ozone levels and also a negative trend in spring peaks, mainly in recent years. The rural sites in Ireland particularly Monaghan and Wexford may have responded to a regional reduction in ozone precursors and have shown the strongest negative decreasing trends in ozone levels during the 2000-2007 period. The data from Mace Head have shown a positive increasing trend of about 0.16 ppb/year over the period 1988-2007. Meteorological variability could be masking the impact of emission reductions on long-term ozone trends. This is indicated through European trends in NO\textsubscript{x} and VOC emissions which show a uniform decrease in ozone precursors across Europe but which are not directly reflected in observed ozone trends.
Hourly data (1994 – 2009) of surface ozone concentrations at eight monitoring sites have been analysed to assess critical level exceedances and their trend for human health, vegetation and forest. AOT40 (Accumulated exposure Over a Threshold of 40 ppb for daylight hours), and 8-hour average concentrations above 80 µg/m³ are calculated and analyzed. The critical level AOT40 for vegetation (6000 µg/m³/hr calculated from May to July) has been exceeded on an individual year basis at two sites – at Mace Head (for years 1996, 1997, 1999, 2006 and 2008) and at Valentia (for years 2001, 2003, 2006, 2008 and 2009). However, a 5-year running average results in just one year (2009) for exceedance >6000 µg/m³/hr, which occurs at the Mace Head site. The critical level for the protection of forest (20000 µg/m³/hr calculated from April to September) has not been exceeded for any site except at Valentia (with a value of 22690 µg/m³/hr) in the European summer heat wave year of 2003. Linear regression performed on a 11 year running average for AOT40-Vegetation shows a strong statistically significant negative trend at Cork-Glashaboy (-200 ± 18 µg/m³/hr per year) and at Lough Navar (-72 ± 14 µg/m³/hr per hour). Positive increasing trends were observed at Mace Head (80 ± 21 µg/m³/hr per year) and at Monaghan (28 ± 16 µg/m³/hr per year) sites. Critical level exceedances for human health (> 120 µg/m³ from a 8-hour running mean) have been observed in various years from almost all sites but their frequency of occurrence never exceeded the set limit of 25 exceedances in one year. Higher concentrations above 80 µg/m³ are found to be increasing at Mace Head while decreasing at Lough Navar, Cork-Glashaboy, and Monaghan sites.

Stratospheric ozone data from the Valentia ozonesonde programme and from a co-located Brewer spectrophotometer, together with satellite observations have shown a statistically significant positive trend of between 1.5% to 1.6 % increase per decade (during the period 1993-2009). The month of March is selected for each year for further analysis. The March integrated ozonesonde column ozone is found to be increasing at a rate of ~ 0.66% per decade, which compares with the Brewer and satellite increasing trends of ~ 5% per decade. In view of the sparcity of ozonesonde sites in the North East Atlantic region, the continuation of ozone-sonde measurements at Valentia Observatory is recommended.

A regional climate model is used to assess future changes in ozone for the years 2030, 2050 and 2100 relative to 2006. The simulations are evaluated against ozone measurements at Mace Head
for the year 2006, exhibiting good agreement between the model-predicted and the measured annual cycles (RMSE = 2.52 ppb). Under the RCP6 emission scenario used in these simulations, average ozone mixing ratios are set to reduce by 2.0 ppb over domains encompassing Europe and the North East Atlantic by 2100 with the most significant decrease occurring after 2050 due to the pattern in changing emissions. Peak reductions of more than 8 ppb are observed during summertime over mainland Europe by 2100. Model output was studied for three relevant subdomains, namely the North East Atlantic, Ireland and Europe. The relative contribution of both climate change and changing emissions is also assessed. Over the whole domain, changing emissions are predominantly responsible for changes in surface ozone although over the North East Atlantic domain, the changing emissions do not perturb surface ozone trends and the decrease in 2100 levels is entirely attributable to changing climate.

1.1. Introduction

The study of the behavior of surface ozone is of importance mainly because it has a negative impact on human health, agricultural crops, forests, and damaging of materials (WHO, 1987; Musselman et al., 2006; *US EPA*, 2006; Hazucha and Lefohn, 2007). Ozone in the troposphere is also a greenhouse gas affecting radiative forcing which therefore contributes to the heat budget of the planet and is a significant contributor to climate change (Ramaswamy et al., 2001). Ozone (and its precursors) is one of the air pollutant species that is identified as a transboundary pollutant, by the Task Force on Hemispheric Transport of Air Pollution under the UNECE Convention on Long-Range tranboundary Air Pollution (CLRTAP). It is the main precursor of oxidizing agents in the atmosphere, the hydroxyl radicals (Levy, 1971), affecting the cleansing capacity of the atmosphere. Most of the surface ozone originates from the troposphere itself but a significant source of ozone is also transport from the stratosphere due to a number of dynamical processes: seasonal variations at the tropopause, turbulence due to jet streams and diffusion across the tropopause causing stratospheric intrusion of ozone into the troposphere. This stratospheric flux is a maximum in the spring and through a large amount of tropospheric mixing contributes to the seasonal variation in tropospheric ozone at a particular site. Stratospheric ozone depletion might have an impact on the in-flux from the stratosphere to the troposphere (Treat et al., 2008; Ordóñez et al., 2007) and according to Fusco and Logan (2003), using GEOS-CHEM model analysis for the period 1970-1995, this flux may have decreased by a maximum of about 30 % from the early 1970s to the mid 1990s. But studies have shown that the decline in stratospheric ozone is due to a ban in the production and emission of ozone depleting chlorofluorocarbons by the Montreal and subsequent protocols (Newchurch et al., 2003; WMO, 2007). In the troposphere ozone can be produced or destroyed by chemical reaction. Ozone concentrations close to emission sources can be affected by destruction through NO (reaction of ozone with NO). Ozone is in equilibrium between its production and loss through NO\textsubscript{x} compounds. Anthropogenically emitted organic compounds can disturb this equilibrium by forming radicals. These radicals can provide an additional non-ozone destroying route through the reaction of NO to NO\textsubscript{2}. At very low NO\textsubscript{x} concentrations chemical destruction of ozone usually takes place. Dry deposition provides an additional sink of ozone. All these processes
together with transport and mixing determine ozone concentrations at a particular site. Surface ozone changes daily (diurnal variation), monthly (seasonal changes) and annually (long term changes). The seasonal cycle with a spring maxima and a summer minima is a very distinctive feature of ground level ozone in the Northern Hemisphere (Derwent et al., 1998; Monks, 2000; Wang et al., 2003). Though it depends on the location, chemical and transport processes at a particular site, it is consistent on a regional scale. Local pollution and boundary level meteorology are mainly responsible for diurnal variations (Coyle et al., 2002; Tarasova et al., 2007). Ozone changes at rural and remote locations might be affected by changes in hemispheric emissions and transport in the planetary boundary layer and changes in transport from the stratosphere. Jenkin (2008) discussed the effect of background ozone trends and regional trends caused by decreasing ozone precursor emissions on the trends in ozone concentrations at a receptor site.

Modeling and measurement studies have shown that baseline surface ozone levels in Europe are changing with time and are not consistent with changes in emission levels of ozone precursors on a regional scale (Jonson et al., 2006 and references therein). They suggested that the decrease in ozone levels due to regional changes in precursors is annulled by an increasing background level. Previous studies have indicated that background ozone levels are increasing at the background North Atlantic site at Mace Head (Simmonds et al., 2004) and in Europe (Naja et al., 2003). Several other works suggested that during the past century, anthropogenic photochemical precursors have been increasing and so have ozone background levels (Volz and Kley, 1988; Staehelin et al., 1994; Simmonds et al., 2004). Emission inventories and corresponding measurements have shown that ozone precursors such as NO\textsubscript{x}, CO and non-methane volatile organic compounds (NMVOC) have reduced significantly in North America and Europe since the late 1980s (Vestreng et al., 2004; Derwent et al., 2003; Solberg et al., 2004) and some authors suggested that this change may be ameliorating the increase in surface ozone levels (Ordóñez et al., 2005; Vingarzan, 2004; Oltmans et al., 2006; Lefohn et al., 2008). At the same time, emissions are found to be increasing from other parts of the world, mainly from Asia, and from other sources such as international shipping (Streets et al., 2003; Endresen et al., 2003). Oltmans et al., (2006) investigated changes in ozone levels at a network of surface ozone and ozonesondes monitoring sites scattered across the globe and provided a mixed picture of ozone trends at different sites suggesting significant regional differences. According to Oltmans et al.,
(2006), mid-latitudes of the Northern Hemisphere (North America, Continental Europe, and Japan) exhibited significant increase in tropospheric ozone in the 1970s and 1980s but have leveled off or declined during the recent decades. IPCC (2007) also suggested that long term background tropospheric ozone trends do not show any coherent picture for the changes in both magnitude as well as in sign and their possible causes. A recent study by Parrish et al., (2009) on ozone in the marine boundary layer has also indicated a stabilization in the ozone trend or even a negative trend (see Figure 12a of the above paper) at Mace Head after 2000. Another interesting result from the work of Parrish et al., (2009) is the difference in both the baseline ozone level and trends between Pacific marine boundary layer air masses entering the westcoast of America and Atlantic marine boundary layer air masses entering Europe (Mace Head). This study indicates that Mace Head ozone may not be considered as representative of hemispheric background ozone. Tarasova et al., (2009) studied ozone trend patterns at the Caucasian Kislovodsk High Mountain station site and at the Swiss Alpine site Jungfraujoch and showed that trends at the two sites have changed during the period 1997-2006 in comparison to the earlier period 1991-2001. They attributed these opposite trends during the two periods to the dramatic decline in emissions during 1990s in the former USSR and the introduction of more stringent emission regulations in Western Europe. Under these scenarios there appears to be no coherent picture about the trend in global or hemispheric background ozone. The widely changing scenarios in emissions of ozone precursors and of tropospheric ozone levels shifted the problem from a regional scale to a global scale. Emissions from Asia can influence ozone levels in North America (Lin et al., 2000; Fiore et al., 2002; Jaffe et al., 2003) and North American emissions can change ozone levels in Europe (Parrish et al., 1993; Moody et al., 1995; Stohl and Trickl, 1999; Wild and Akimoto, 2001; Li et al., 2002).

Ground-level ozone is currently measured in many rural and urban areas of Ireland but a long term record is only available and analyzed for the coastal station of Mace Head. Work by Oltmans et al., 2006; Scheel et al., 1997; Simmonds et al., 2004, Carslaw, 2005; Derwent et al., 2007 and by others on Mace Head ozone data have shown varying trends depending on the length of data considered and the methodology applied for their evaluation. In Ireland, ozone measurements are presently being carried out at 9 sites of the Environmental Protection Agency (EPA) ozone network, Valentia Observatory (Met Éireann), and at Lough Navar in Co. Fermanagh. Lough Navar site is part of the national Automatic Urban and Rural Network.
(AURN) set up by the UK Department of Environment, Food and Rural Affairs (DEFRA), (Jenkin, 2008). The ozone instrumentation at Mace Head was set-up by Peter G. Simmonds, funded through the UK Ministry of the Environment. There are many years of continuous records from these stations scattered around Ireland. Among them, Mace Head and Lough Navar have exceptionally long records with more than 20 years of data. There has been apparently no known coordinated integrated effort to analyze these data with respect to seasonal variability, or with respect to medium and long term changes. The objective of this paper is to present a detailed assessment of ozone levels and trends in Ireland on the basis of the statistical analysis of available surface ozone data.

1.2. Data and Methodology

1.2.1. Surface Ozone Data

Ozone at EPA stations, at Mace Head, Valentia Observatory, and Lough Navar is measured using a continuous ozone analyzer by UV Photometry. The ozone analyser is microprocessor-controlled and the principle of operation is based on the Beer-Lambert law for measuring ozone in ambient air. Ozone concentration data for Ireland are provided by the EPA for EPA measurement sites (Dublin Pottery Road, Dublin Rathmines, Cork, Wexford, and Monaghan). The ozone measurements at different sites in Ireland started in different years. In this analysis we consider the stations on the basis of their longer record and a range of stations such as urban, sub-urban, rural, and marine coastal sites are chosen. Table 1.1 shows the stations covered in this work and Figure 1.1 shows the approximate geographical location of observational sites.

Table 1.1. Name and abbreviations of stations, length of available data, and their category, used for the analysis.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Years of Measurement</th>
<th>Station Category</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dublin (Rathmines) DR</td>
<td>2002-2007</td>
<td>Urban</td>
<td>53.32</td>
<td>-6.26</td>
</tr>
<tr>
<td>Dublin (Pottery Road) DP</td>
<td>1994-2001</td>
<td>Suburb of Dublin city</td>
<td>53.27</td>
<td>-6.15</td>
</tr>
<tr>
<td>Cork (Glashaboy) CG</td>
<td>1995-2007</td>
<td>Near city rural</td>
<td>53.05</td>
<td>-8.69</td>
</tr>
<tr>
<td>Wexford WX</td>
<td>1999-2007</td>
<td>Near town rural</td>
<td>52.25</td>
<td>-7.14</td>
</tr>
<tr>
<td>Monaghan MN</td>
<td>1995-2007</td>
<td>Remote rural</td>
<td>54.19</td>
<td>-6.87</td>
</tr>
<tr>
<td>Lough Navar LN</td>
<td>1988-2007</td>
<td>Remote rural forest</td>
<td>54.44</td>
<td>-7.87</td>
</tr>
<tr>
<td>Valentia VA</td>
<td>2001-2007</td>
<td>Regional rural coastal</td>
<td>51.94</td>
<td>-10.23</td>
</tr>
</tbody>
</table>
Figure 1.1. Map of Ireland showing the approximate location of observational sites. The stations according to Table 1 are: MH (Mace Head), VA (Valentia), CG (Cork-Glashaboy), WX (Wexford), DP (Dublin-Pottery Road), DR (Dublin-Rathmines), MN (Monaghan), LN (Lough Navar). Scale is a close approximation.

Data shown in Table 1.1 are fairly representative of different regions in Ireland. Looking at the historical record for ozone measurements at these locations and taking the mean ozone values for a more complete record we have a very rough picture for different regions of Ireland. Hourly data are used to calculate daily means and the daily mean is used for monthly mean calculations. The annual mean is calculated from the monthly mean data. Figure 1.2 shows the mean values (mean of the annual means) of surface ozone at different stations considering the measurement records spanning 2002 to 2007, a common measurement period for all stations considered for analysis. The error bars shows one standard deviation. A six years average value at a polluted site (Dublin, Rathmines) shows a minimum ozone level of about 22 ppb whereas the maximum values are at the coastal sites of Mace Head and Valentia both at around 35 ppb. The rest of the ozone measurement sites show average means between 22 and 30 ppb. It is interesting to note that there is no significant difference (well within the error bars) in the mean of all records even if all measurement records of a particular station - irrespective of a common measurement period
- is considered for the calculation. On the basis of historical air quality data and from the geographical point of view, Ireland can be divided into different categories. The EPA divides

![Figure 1.2](image)

Figure 1.2. Average ozone values at measurement sites in Ireland for a common measurement period 2002-2007. Colour bars represents the category of the site on the basis of pollution levels and geographical location, with the most polluted Dublin City site depicted as red and clean marine west coastal sites depicted as blue. Orange represents the rural site close to the major city Cork and yellow represents the less polluted rural areas near the smaller town of Wexford. The green sites represent the remote rural Irish sites.

measurement sites according to the EU Directive 96/62/EC [CEC, 1996]. Stations are classified as either urban, suburban or rural and then one of traffic, industrial or background. Rural sites are further classified as near-city, regional or remote sites. West coast rural sites of Mace Head and Valentia are considered separately as coastal marine sites.
1.2.2. Cluster Analysis of Trajectories

Air samples measured for ozone at a particular site in Ireland can have a wide range of histories. They may be maritime clean Atlantic air due to westerly or south-westerly (190 – 300 degrees) winds or polluted European air due to easterly winds. The calculated air-mass trajectories arriving at a particular site provide information about the history of air-masses for four days back. For Mace Head and Lough Navar, both having a long record of data, trajectories were calculated using HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model), a transport and dispersion model provided by the NOAA Air Resources Laboratory (ARL) (Draxler and Rolph, 2003). NCEP/NCAR reanalysis data were used for the meteorological fields. 96 hour back-trajectories arriving at 1200 hours each day were calculated, with a final height of 100m, for the years 1987 until 2007. The algorithm used for the clustering process is given in Appendix I.

1.2.3. Statistical Analysis of time-series of ozone

Surface ozone data analyzed here are monthly averaged values of relatively long records (8 or more years of observations) of surface ozone measurements which form a time series. The data are averaged up to a monthly level to form a univariate (considering 12 months of the year distributed equally time-wise which is a good approximation for average monthly ozone values) time series for statistical analysis. Gaps in the resultant time series are replaced by the average of the adjacent seasonal values i.e. average of the values 12 months before and after. In time series analysis, one approach is to find a model that represents the data and can be used for future predictions. If data consist of an established periodicity or seasonality and possible trends (as with surface ozone), another approach may be to decompose the time series into trend, seasonal, and error components. The error components represent the periods in the series that might be affected by episodic pollution events.

Surface ozone data analyzed here exhibit well an established seasonal pattern with maxima during the spring and minima in summer. To examine the data for any long term trend, a very good method is to decompose the time series into seasonal, trend, and remaining components (Cleveland et al., 1990). The procedure used to decompose the time series is called seasonal trend decomposition (STD) procedure, which is briefly described in Appendix II.
Another time series modeling approach used here, based on Box and Jenkins (1970), is called autoregressive integrated moving average (ARIMA). This is a step-by-step procedure to identify the possible model which may closely represent the data series. The ARIMA model fit data contain the seasonal variation and trend components. The time series is first fitted to an appropriate ARIMA model, then the modelled data are de-seasonalized to remove seasonal variation. Linear regression is then performed on this deseasonalised data, which gives the trend prediction. A brief description of the ARIMA method is given in Appendix III.

1.3. Surface Ozone Results

To be consistent and accommodating for all lows and highs and to facilitate easier comparison between different stations, ozone values on the y-axis are plotted on the scale from 10 to 50 ppb for all inland stations including Dublin Rathmines (Figure 1.3); Dublin Pottery Road (Figure 1.4); Cork Glashaboy (Figure 1.5); Monaghan (Figure 1.7). Exceptions are for Mace Head and Lough Navar. Mace Head is plotted for 10 to 60 ppb to show its higher values, particularly for the Eastern sector (Figures 1.10). Lough Navar has shown exceptionally low values – sometimes below 10 ppb – and are plotted on a scale from 0 to 50 ppb (Figure 1.11). The time line on the x-axis is in the form mm-yy or yyyy, as needed. Trend lines shown in the following figures are from STD analysis.

A comparison is made of the mean value of surface ozone mixing ratios between sites. Figure 1.2 shows the mean of the annual mean, with an error bar of one standard deviation, for all sites that have a continuous record for the years from 2002 to 2007 inclusive - that gives a fairly good idea of ozone levels at a particular location. It is clear from this figure that the Rathmines site has the lowest ozone level of all sites.

1.3.1. Ozone at an Urban Polluted site: Dublin Rathmines

Ozone measurements in Dublin City started in 1994 at the EPA site in Pottery Road which is located in a southern sub-urban area and continued until 2002. In 2002, EPA changed its measurement location to a more polluted site near Rathmines and is still continuing. These two combined measurement sites give a total of 14 years of measurements in Dublin. The ozone data at the Dublin Rathmines site are analysed in this Section, and the Pottery Road data are analysed...
in Section 1.3.2. The data at the two stations show a different pattern which is discussed in Section 1.4.

Figure 1.3 shows the time series decomposition plot for the monthly mean data at Rathmines, Dublin showing model fits, original data and trend. Actual observed monthly mean data show that the values at high ozone spring peaks are well below 30 ppb after the exceptional peak of 2003. The STD model fits the data fairly well except for underestimation of the exceptional peak of 2003 and this may be attributed to a sunnier and a warmer spring-summer season as compared to other years. The trend component shows a decreasing ozone level since 2002, and the STD analysis shows a negative trend of about -0.33 ± 0.17 ppb per year. Part of this trend might be attributed to the peak year of 2003 with a spring seasonal maxima of ~33 ppb. The fact that seasonal values after 2003 have not exceeded 30 ppb cannot be ignored, and so the trend observed from decomposition analysis cannot be solely attributed to the 2003 seasonal peak.

The decomposition analysis also generates three accuracy measures in the fitted STD model to the measurements: Mean Absolute Percentage Error (MAPE) measures accuracy of fitted time series in percentage; the Mean Absolute Deviation (MAD) is expressed in the same unit as the data (ppb), and the Mean Squared Deviation (MSD) has the same unit as the data squared (ppb squared). These values are 9.5, 2.0 and 6.3 respectively for the Dublin Rathmines data decomposition plot. The relatively low values, particularly that of MAD, indicate that the model fit describes observations fairly well.

To understand better the ozone values and trend at the Dublin City Rathmines site, the ARIMA model analysis is also performed on the Dublin Rathmines data, to compare it with STD analysis. Figure 1.3 shows the model predicted time series plot of the two statistical approaches, STD and ARIMA, applied to the Dublin Rathmines time series, with both models fitting the measured data quite well. In a time series of monthly means, each data point represents the same season as the data point 12 steps away [for example the next June data are 12 steps away from this years June data] i.e. it has a seasonality of order 12. The Dublin Rathmines monthly surface ozone data show a very strong seasonality of order 12 which is not unexpected for ground level ozone. STD smoothes exceptional highs and lows for long term variations (e.g. the 2003 exceptional spring high values and the 2004 lower spring values have been smoothed to almost similar values) whereas ARIMA model fits follow values 12 months before (there is a lower
2003 ARIMA fitted spring value than the actual one because of a lower 2002 spring peak and there is a much higher 2004 spring peak compared to actual values because of an exceptionally high spring peak in 2003). The ARIMA model predictions show a negative trend of -0.26±0.14 ppb per year. This negative trend is less in comparison to -0.33±0.17 ppb per year predicted by the seasonal trend decomposition model, but nevertheless quite comparable, allowing for the prediction error bars. More details of ARIMA analysis and its comparison with STD are given in Appendix III.

Figure 1.3. Time series plot for the monthly mean surface ozone data at the polluted site of Dublin Rathmines, for the period 2002-2007. The plot shows original monthly mean data along with the STD and ARIMA model fits and the trend line: -0.33 ± 0.17 ppb per year. The trend line is from STD analysis. The X-axis shows months and year in mm-yy format.
Another important way to see the trend is from the annual mean ozone values. The annual mean ozone is calculated from the monthly mean data and a linear regression is performed. The linear regression analysis shows a negative trend of about \(-0.33\pm0.21\) ppb per year, in agreement within prediction errors with the two statistical model results. This result is in contrast to the results of Jenkin (2008), which shows an positive trend in the annual mean at a city site (Leeds) in the UK but with a larger time span (Leeds data 1994-2006 analyzed for annual means). Note, however, that the upward trend at Leeds is attributed to the negative trend in NO but during the measurement period at Dublin Rathmines, the NO\(_x\) concentrations had more or less stabilized (see Figure 1.12).

### 1.3.2. Suburban City site: Pottery Road, Dublin

Ozone levels at urban sites are dependent on the NO\(_x\) level via complex chemical reactions involving volatile organic compound (VOC) radicals driven by solar radiation in hot and sunny conditions. In Ireland, conditions are less favorable for solar radiation driven ozone formation and a major source of ozone is transport of prevailing Atlantic air passing over the country, mainly from the west and south-west directions. The ozone level is mostly controlled by NO\(_x\) through the reaction of NO with ozone. This effect is reduced at suburban city sites because of lower levels of NO\(_x\) than for a more polluted site. The EPA ozone record at this site is available for eight years from 1994 to 2001. Seasonal and trend decomposition analysis is performed for the monthly mean data and the results are shown in Figure 1.4.

Seasonal decomposition analysis shows that in contrast to the Dublin Rathmines site, the Dublin Pottery Road site shows a positive trend but is not very significant because of a large error margin (+0.09±0.16 ppb/ year). Strong peaks were observed at intervals such as in the late winter – early spring period (January, February, March) of 1994, 1997, 1998, 2000, and 2002, which might be due to meteorological conditions (e.g. such late winter – early spring periods are warmer than others), but do not contribute overall to a longer term change in ozone levels.

The linear regression of the annual means shows a strong positive trend of +0.38±0.26 ppb per year (see Table 1.5), not in agreement with monthly mean analysis. The strongest trend in the annual mean may partially be attributed to the very low values obtained during the years 1994 and 1995. No ozone records after February 2002 are available at this site. The positive trend observed at this site (though the monthly mean trend is not very significant) during the period
1994 - 2001 may be at least partially attributed to the negative trend of NO emissions in Ireland during that period, as shown in Figure 1.12.

**1.3.3. A rural site Glashaboy near Cork City**

EPA ozone records are available for a rural background site, at Glashaboy, in the north-east of Cork City. Ozone measurements in Glashaboy started in 1995 and still continue, and thirteen years of data (1995 to 2007) are analyzed and presented here. The monthly mean data along with STD and ARIMA model fits and trend lines from STD partial analysis are shown in Figure 1.5. Besides a few outliers and peaks, the monthly mean data from Cork are smooth and high spring ozone events did not occur during recent years and values of spring peaks appear to be

![Graph showing ozone levels from 1994 to 2001 with trend analysis results.](image)
diminishing after 2003. Seasonal decomposition analysis for this site shows a negative trend of -0.06±0.06 ppb per year. The trend calculated from ARIMA fit shows a very insignificant negative trend of -0.01±0.03 ppb per year. Trends observed from the two analyses are a little different and show no trend or a small negative trend in overall monthly ozone means from 1995 to 2007.

Statistical error estimates from the STD analysis are satisfactory and within reasonable limits and are shown in Figure 1.5. Similarly, the residuals for the STD also give a significant confidence in the analysis and will not be further discussed for this site.

There have been substantial variations since 1995 in NO\textsubscript{x} levels (see Figure 1.12) and ozone precursor emissions during different time periods are reflected by monthly mean ozone values in Figure 1.5. This prompted further analysis of the data by dividing the data into two different periods: before 2000 and after 2000. For the Cork Glashaboy site, there is a significant amount of data available before the year 2000 and therefore partial time series analysis is performed for this site to see if there is any change in trends. Figure 1.5 shows two trend lines estimated from the seasonal trend decomposition procedure for two time periods. During 1995-1999, monthly mean ozone at the Cork site shows a strong positive trend of +0.64±0.31 ppb per year but during the period 2000 to 2007 the trend is negative at -0.20±0.11 ppb per year. These two opposing trends in ozone levels during the two time periods give an almost insignificant negative resultant trend of -0.06±0.06 ppb per year for the entire period estimated by the two statistical analysis STD and ARIMA methods and is shown in Figure 1.5.

Annual mean ozone data are also analyzed by linear regression. The regression of annual mean data for the entire period show a negative trend of -0.07±0.12 ppb/ year, similar to that of STD and ARIMA analyses of monthly means. But when the annual mean data are regressed by dividing into two periods, they show positive and negative trends similar to that of monthly mean data but with larger error estimates. For the period 1995 to 1999, the positive trend is +0.58±0.73 ppb per year and for the period 2000 to 2007 the negative trend is -0.18±0.17 ppb per year. Because of large inter-annual variation in the annual mean, the associated error bars (+/- 1 standard deviation) may be larger than the trend, but this does not mean that the trend is not significant (see Jenkins, 2008 for example). The positive and negative trends during two time periods may be consistent with changes in NO\textsubscript{x} emissions, although NO\textsubscript{x} concentration levels are not known at the Glashaboy site. During the decreasing NO\textsubscript{x} period (decreasing titration) an
upward trend is obtained while during the NO\textsubscript{x} stabilization period a negative trend is observed. This indicates that the balance between ozone destruction and ozone production in the urban plume may be important for ozone levels at a particular site.

Figure 1.5. Monthly mean surface ozone values at the rural background site at Glashaboy, north-east of Cork City along with the model fits from seasonal trend decomposition (STD) and ARIMA. The figure also shows three trend lines - for the overall negative trend (1995-2007) of -0.06±0.06 ppb per year; the positive trend line from 1995 to 1999 of +0.64±0.31 ppb per year and the negative trend value of -0.20 ±0.11 for the period from 2000 to 2007 estimated from the seasonal trend decomposition procedure.

1.3.4. Wexford – a rural site near the town
Ozone levels in rural areas with a town background show a different picture than a more polluted city background site, where in general, ozone levels are higher than that in main cities. Ozone
measurements are available for the Wexford site from 1999 up to the present. Seasonal and trend decomposition model fitted results with actual monthly mean data are shown in Figure 1.6.

Figure 1.6. STD and ARIMA model fitted results of Wexford surface ozone along with actual monthly means for 1999-2007. The figure also shows the trend line of -0.80±0.11 ppb per year from STD analysis.

Figure 1.6 shows a clear decline in spring peaks since 2002. The trend component shows a negative slope of 0.067 ppb per month which is equivalent to a very strong negative trend of about -0.80±0.11 ppb per year which is also evident from raw data. The figure also shows the ARIMA fit to the monthly mean data. ARIMA analysis shows a first order of non-seasonal autoregression and a first order of seasonal moving average model with a first order of seasonal differencing. The ARIMA model fit also shows a similar negative trend of about -0.76±0.11 ppb per year, as a further confirmation of STD analysis. Raw data clearly show that before 2004 there is no evidence of the spring ozone maximum being below 38 ppb at this site. From 2004 to 2007, the monthly mean of ozone spring maxima stayed below about 35 ppb. The trend observed in this analysis cannot be completely rejected despite the fact that this very strong negative trend is enhanced due to a highest level of ozone during the spring peak in 2002, accompanied by a relatively high ozone level during the spring of 2003.
Moreover, the linear regression on annual mean data also shows a negative trend of -0.76±0.27 ppb per year as shown in Table 3.5, similar to the one from monthly mean analyses. Truncating the monthly mean time series by one year (from 1999-2007 to 2000-2007) gives an even stronger negative trend of -0.99±0.13 ppb per year from STD analysis as shown in Table 1.5.

1.3.5. Rural remote site - Monaghan

Ozone chemistry in rural areas can take different pathways than in urban areas (The Royal Society Report, 2008). In rural areas, NO\textsubscript{x} levels are not high enough in comparison to urban areas and the titration effect may not take place. In this scenario, ozone chemistry is sensitively controlled by the level of NO\textsubscript{x}. These regions are called NO\textsubscript{x} limited and NO\textsubscript{x} sensitive regions. A net ozone enhancement may take place in rural areas under these conditions, and intermediate radicals (such as CH\textsubscript{3}O\textsubscript{2} and HO\textsubscript{2}) can react with NO to form NO\textsubscript{2} which undergoes photodissociation and forms ozone. NO\textsubscript{x} levels in rural areas are usually at a regional background level and ozone formation generally takes place under NO\textsubscript{x}-limited conditions when \([O_3]/[NO_x] > 10\) but VOC-limited conditions when \([O_3]/[NO_x] < 10\), may also occur in air masses en route from rural to urban environments. However, observational data of relevant species (NO\textsubscript{2} = NO\textsubscript{y} – NO\textsubscript{x}) are needed in order to attribute the exact conditions for formation of ozone in a particular region.

Due to various European Union (EU) directives, pollution emissions from industries and automobiles have gone down and so has background NO\textsubscript{x}. There are several rural sites where the EPA has started ozone measurements in recent years. The rural site of Monaghan is selected here because of its relatively long measurement record. Ozone measurements at Monaghan started in 1995 and represent 12 years of measurement. As with all other stations, monthly means are calculated and analyzed for seasonal and long term variations.

The time series plots of decomposition analysis for the Monaghan site are shown in Figure 1.7. Figure 1.7 shows original monthly mean data, a decomposition model fit and trend line. The monthly mean spring peak values are below 40 ppb after 2003 except a little over 40 ppb in 2006. The Monaghan trend line has a negative slope of 0.0103 which is equivalent to about -0.12±0.07 ppb per year negative trend over the period from 1995 to 2007. To test the validity of the decomposition model, a residual analysis is also performed (not shown in figure). Monaghan site residual distributions are found to be close to a normal distribution and nearly all residuals
points fall within the 95% confidence intervals. The p-value for the analysis (0.09) is higher than the significance level of 0.05 (95% confidence interval), giving a significant level of confidence to the decomposition analysis.

Figure 1.7 also shows the comparison of ARIMA and decomposition model fits for the Monaghan data. The fitted values from both methods are in fairly good agreement. It is clear from Figure 1.7 that seasonal peaks have a major influence on the following years’ data for the

**Figure 1.7. Seasonal and trend decomposition (STD) and ARIMA fits for the rural site at Monaghan along with monthly mean (actual) data for 1995-2007. The figure also shows partial time period trend lines: -0.43±0.29 ppb per year for 1995-1999, -0.58±0.12 ppb per year for 2000-2007; and an overall trend line for the whole period from 1995-2007 of -0.12±0.07 ppb per year from STD analysis.**

ARIMA model, whereas in decomposition analysis, the following years values are not much influenced. The decomposition technique smoothes data more than the ARIMA analysis does. This difference between the two approaches results in slightly different predictions for the longer
term trend. For the Monaghan site, the ARIMA model shows a negative trend -0.07±0.05 ppb per year over the period from 1995 to 2007.

It would be interesting to see from the analysis, the difference in the trend before and after the year 2000. Figure 1.7 also shows three trend lines for the partial periods 1995-1999 and 2000-2007 and the entire period 1995-2007. During 1995-1999, the STD analysis shows a negative trend of -0.43±0.29 ppb per year. This was followed by four years of higher spring peaks and thereafter, the monthly mean ozone values mostly subside as seen in Figure 1.7. This again gives a very strong negative trend of -0.58±0.12 during the years 2000-2007. Because of a few high ozone years at the beginning of the period 2000-2007, the overall linear trend from 1995 to 2007 is reduced significantly and gives around -0.12±0.07 ppb per year from STD analysis. This also shows that a negative trend is more pronounced over the 8 years from 2000 than over the 5 years from 1995 to 1999, at the rural remote sites.

Linear regression for annual means for different time-periods is performed for this site as well. The trend during the entire period of 1995-2007 from annual mean data are found to be -0.14±0.16 which is similar to the monthly mean data analysis but with a higher error margin. The trend during 1995-1999 and 2000-2007 from the regression of annual means are similar to that of monthly mean analysis and are -0.55±0.89 and -0.58±0.24 ppb per year respectively. The trend from the annual regression has a larger error estimate (e.g. standard deviation from the mean), which is due to greater year to year variations. The decrease in mean ozone levels at the Monaghan site may be due a regional decrease in photochemical ozone production attributed to the EU controlled reduction in VOC and NO\textsubscript{x} emissions (see Figure 1.12 for NO\textsubscript{x} levels at the Dublin Rathmines site). However, definitive evidence for a reduction in NO\textsubscript{x} emissions at the Monaghan site is not available, due to the lack of NO\textsubscript{x} data at the site.

1.3.6. Marine coastal site - Valentia

Ozone observations at Valentia were started in 2001 by the Irish Meteorological Service (Met Éireann). The site is at the south west of Ireland near the coast. Data from 2001 to 2007 are analyzed using the seasonal trend decomposition procedure and the results are shown in Figure 3.6. ARIMA fitted data are also shown in Figure 1.8 and there is reasonably good agreement between the two analyses. Seasonal trend decomposition analysis of Valentia 2001-2007 data show a negative trend of -0.05±0.15 ppb/ year. This trend is not very significant because of large
error margins. A similar negative trend but with a much larger error margin is also shown by the linear regression of annual mean data as shown in Table 1.5. This might seem to be unusual in view of the positive trend at Mace Head during the same period (shown later). However, this discrepancy between the two stations will be discussed later when sector wind data of Valentia and Mace Head are compared in Section 1.3.8.

Figure 1.8. STD and ARIMA Model fit of monthly mean surface ozone data at Valentia Observatory during the period 2001-2007. Trend line shown of -0.05±0.15 ppb per year is from STD analysis.

1.3.7. Mace Head and Lough Navar: trajectory analysis

Because of the exceptionally long record of measurements available for the two sites of Mace Head and Lough Navar (in County Fermanagh, Northern Ireland), surface ozone data for these sites are analyzed in more detail. Both the sites have measurements available since 1988 resulting in 20 years of data up to and including 2007. These sites have different geographical locations and fall under different regimes of ozone chemistry. Mace Head lies at the westernmost
coast of Ireland facing the North Atlantic ocean whereas Lough Navar site is in an open rural landscape with surroundings of semi-mature forest and mature tree woodlands. Here, trajectory cluster analyses are performed for these two stations in order to determine any trend in the ozone level for different sectors. Backward trajectories are calculated using the HYSPLIT model, starting every day at 12 noon and going back 96 hours. These trajectories are then clustered using a non-hierarchical clustering algorithm, based on the work of Mattis (2002) and Dorling et al., (1992). The methodology is described in more detail in Appendix 1. The cluster analysis yields an optimal number of 10 clusters for Mace Head, and 11 for Lough Navar. These groups are then further combined to represent four main directions or sectors.

Table 1.2. Number of 96 hours back trajectories associated with the ozone measurements and percentage of the total number of trajectories for the four sectors for Mace Head and Lough Navar for the period 1988-2007.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Mace Head</th>
<th>Lough Navar</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of trajectories</td>
<td>6974</td>
<td>6709</td>
</tr>
<tr>
<td>No. of clusters</td>
<td>10 (indexed 0 to 9)</td>
<td>11 (indexed 0 to 10)</td>
</tr>
<tr>
<td>Eastern</td>
<td>644 (9.2%)</td>
<td>497 (7.4%)</td>
</tr>
<tr>
<td>Western</td>
<td>2689 (38.5%)</td>
<td>2515 (37.5%)</td>
</tr>
<tr>
<td>Northern</td>
<td>2299 (32.9%)</td>
<td>2015 (30.0%)</td>
</tr>
<tr>
<td>Southern</td>
<td>1342 (19.24%)</td>
<td>1682 (25.1%)</td>
</tr>
</tbody>
</table>

The distribution of trajectories and their percentage of the total number of trajectories analyzed are given in Table 1.2. The definition of four sectors is dependent on the direction of the centroids of the clusters. The clusters that seem to be from North America, and possibly from the west or south-west Atlantic marine region account for the Western sector. Note that a four days trajectory from the western sector most likely originates in the open ocean. The Arctic and Greenland directions (Polar Marine) are associated with the Northern sector. For the Southern sector, the associated trajectories are from tropical marine and tropical continental regions originating from the Atlantic Ocean and Northern Africa. The Eastern sector is associated with mainland Europe. These assignments and trajectories are shown in Figure 1.9. There are less than 10% of trajectories belonging to the eastern sector which shows that both sites are mostly
uninfluenced by polluted air coming from mainland Europe. Insufficient number of trajectories from the Eastern sector create gaps in the monthly mean data and the results from Eastern sector analysis may not be conclusive. Results from the Eastern sector analysis may therefore be considered only as a qualitative indication. A maximum number of trajectories are from the Western sector at both sites. After distributing the clusters to each sector, the trajectories belonging to each sector are combined together. Finally, each trajectory of a sector is associated with a particular day and the mean ozone value for that day. A monthly mean time series is formed for all four sectors. These monthly mean time series are analyzed for seasonal and trend variations for both the stations separately.

Figure 1.9. Clusters of trajectories assigned to a particular sector for the back-trajectories calculated for Mace Head. The sector assignment is shown with the letters E, W, N, and S for Eastern, Western, Northern, and Southern respectively. Trajectory length is 96 hours.

1.3.7.1. Mace Head

During the 20 year period (1988 -2007) only about 9% of air parcels are associated with the eastern sector, which does not give sufficient data in the ensemble of months for reasonably good monthly mean calculations. Sometimes data from the easterly direction are absent for many continuous months giving a large number of gaps in the monthly mean. If only few data are available in a month the mean values do not appropriately represent that particular month. This
makes Eastern sector analysis very difficult, and the results are not conclusive, which can be seen in Figure 1.10 having many gaps in the original monthly mean data for the Eastern sector.

Figure 1.10 also shows the statistics of the decomposition analysis and fitted trend equations. Statistics for the Eastern sector show a poor quality of analysis with a mean standard deviation of 44 and 18% of a mean absolute percentage error (MAPE). In comparison, all other sectors have sufficient number of data points giving a much higher confidence in the analysis and results which are also reflected in the statistics. Statistically, the clean Northern and Western sectors show better results than the other two sectors.

Figure 1.10. Seasonal decomposition plots for four sectors, Eastern (top left), Western (top right), Northern (bottom left), and Southern (bottom right), of surface ozone (ppb) data for Mace Head along with actual data and trend lines of + 0.18±0.03, +0.17±0.03, +0.17±0.05, ppb per year for the Western, Northern and Southern sectors respectively and a trend line of +0.15±0.06 ppb per year for the Eastern sector. Statistical data are also shown.
Three of the four sectors show a positive trend of surface ozone at Mace Head of about +0.17 to +0.18 ppb per year while the Eastern sector has a less positive trend (+0.15±0.06 ppb per year). If we analyze for monthly mean data of ozone at Mace Head as a whole, without sector wise distribution, the positive trend using the STD approach comes out to be +0.16±0.04 ppb per year over a twenty year period (1987 – 2007). This is not very much different than the trend obtained from the Western, Northern, and Southern sectors, which is not surprising because more than 90% of data belong to these three sectors. From Figure 1.9, it is clear that the air parcels from these three sectors are mostly clean oceanic air giving a fairly good estimate of the trend in levels of ozone at Mace Head. Despite giving similar trends, these sectors have differences in levels of ozone. Ozone levels belonging to the Western and Northern sectors have higher values than the Southern sector, probably because of the origin of air masses represented by these sectors. Air parcels from Northern and Western sectors have a reasonable chance of constituting air masses being transported long range from a continental origin whereas the Southern sector (at least one part of it) belongs to the pure oceanic sector, and is one of the remoter regions of the atmosphere, which has very low NO\textsubscript{x} levels. This region corresponds to an ozone chemistry regime, which is characterized by an ozone loss rate due to removal of peroxo radicals (CH\textsubscript{3}O\textsubscript{2} and HO\textsubscript{2} are main constituents for ozone production) by their mutual reaction and net ozone removal. Though the ozone loss rate in this Southern region is small, nevertheless, it applies to a vast region of the troposphere and is an indicator of global ozone levels and trends (The Royal Society Report, 2008).

Analysis of the Mace Head clean sector (western sector) shows different trends during different periods as shown in Table 1.3.

Table 1.3. Ozone trend (ppb/year) for the clean western sector at Mace Head during different time periods from 1988 to 2007 from seasonal trend decomposition (STD) analysis of monthly mean data. Also shown in brackets are the trends of ozone values which are not segregated into different sectors.
The maximum trend is observed during the period 1993 to 2000 at +0.29±0.18 ppb per year similar to the four year trend from 1988 to 1992. But when eleven years of data for 1990 to 2000 are considered, the trend is reduced to +0.23±0.07 ppb/ year. This difference may be due to a rise in values during 1992, attributed to the 1991 Mount Pinatubo eruption, followed by a fall in values in 1993. The trend has further reduced to +0.21±0.09 ppb per year during the period 2000 – 2007, which brings down the overall trend for the Western sector at Mace Head to +0.18±0.03 ppb per year for the whole period 1988-2007. Though the trend is positive for each time period, it seems to be decelerating from 1988 to 2007. Raw (non-sectored) monthly mean values are highly dependent on pollution events – for example non-sectored monthly mean ozone values can be heavily impacted by episodic high values from the Eastern sector. However, in general they also follow the background trend value except for a relatively larger difference during the periods 1988 – 1992 (+0.52±0.26) and 2000 – 2007 (+0.27±0.18), as shown in brackets in Table 1.3.

### 1.3.7.2. Lough Navar

The Lough Navar site is located in a rural area of Northern Ireland, a short distance from a road and occasionally receives polluted air from vehicular movements depending on wind direction. This gives a significant source of NO for ozone removal processes. Another important ozone removal mechanism is local forest plant uptake for this site. Wind arriving at Lough Navar was divided into 11 clusters for backward trajectories and their assignment to a particular sector.

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<tbody>
<tr>
<td>1988</td>
<td>+0.29±0.18 (±0.52±0.26)</td>
<td>+0.19±0.06 (±0.20±0.07)</td>
<td>+0.18±0.03 (±0.16±0.04)</td>
</tr>
<tr>
<td>1990</td>
<td>+0.23±0.07 (±0.18±0.09)</td>
<td>+0.19±0.04 (±0.15±0.04)</td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>+0.29±0.13 (±0.34±0.15)</td>
<td>+0.19±0.05 (±0.18±0.05)</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td>+0.21±0.09 (±0.27±0.18)</td>
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</tr>
</tbody>
</table>
along with trajectories (not shown). Trajectory assignment criteria were the same as for Mace Head.

As shown in Table 1.2, during most of the time, air arriving at Lough Navar is from Western, Northern, and Southern directions. Only about 7% of the time it receives air from mainland Europe. This shows that not only Mace Head, but most of Ireland is free from high levels of pollution from mainland Europe during the large part of a year. Sector wise seasonal decomposition results are shown in Figure 1.11.

Figure 1.11. Seasonal decomposition plots for four sectors, Eastern (top left), Western (top right), Northern (bottom left), and Southern (bottom right), of surface ozone data for Lough Navar along with actual data and negative trend lines of $-0.05\pm0.04$, $-0.08\pm0.04$, $-0.05\pm0.05$, ppb per year for the Western, Northern and Southern sectors respectively and a negative trend line of $-0.03\pm0.05$ ppb per year for the Eastern sector. Statistical data are also shown.
Again the statistics of Eastern sector results are very poor and is mainly because of a large gap in such data. A sufficient number of points is assigned to all other sectors and the statistics shows reliable results. Despite the fact that higher % of trajectories are continen tally more influenced for Mace Head than Lough Navar the monthly mean data at the Lough Navar have comparatively more peaks and outliers. This is because of mixing of air from continental airmasses before arrival at the Lough Navar site irrespective of the direction they are coming from. This is shown in the poorer statistics for all sectors in comparison to the statistics for the Mace Head analysis. Mean standard deviation and mean absolute percentage error for the Mace Head cleaner sector (Western and Northern) are below 10 (shown in Figure 1.10) while for Lough Navar they are closer to 20 (shown in Figure 1.11). This shows that sector wise analysis for Lough Navar might not be so suitable for information about baseline ozone entering Europe, due to influence of continental air masses (mixing before sampled for measurement) at the site, but may be more useful for local regional ozone.

In general, ozone levels at the Lough Navar site are much lower than at other rural sites in Ireland. The Lough Navar average ozone level is at about 25 ppb whereas for Monaghan, the ozone level is 30 ppb and for Valentia it is 35 ppb (according to Figure 1.2). Forest plant uptake of ozone appears to be a determining factor for ozone levels at this site. All sectors of the Lough Navar site shows similar ozone levels at about 25 ppb. All the sectors show a slight negative trend with a maximum of -0.08±0.04 ppb per year for the Northern sector and a minimum of -0.03±0.05 for the Eastern sector. For the Western sector, the negative trend is -0.05±0.04 and for the Southern sector, the negative trend is -0.05±0.05 ppb per year. Lough Navar station is an inland station and air parcels for different sectors probed are mixed with local background air and therefore no definitive explanation can be provided for sector wise trends. Besides, except for the Northern sector negative trend, all other sectors’ trends are not very significant. The Northern sector’s negative trend may be attributed to a reduction of ozone levels in background air-parcels from the Northern oceanic and Greenland regions.

If the monthly mean data are considered as a whole without a sector wise distribution, the negative trend is about -0.07±0.04 ppb per year for the entire period [1988-2007], as shown in Table 1.5. The ARIMA fit model for the whole period also shows a negative trend of -0.08±0.02 ppb per year. This compares with Jenkin (2008) who reports a stronger negative trend of -0.17±0.13 ppb at Lough Navar based on annual average values for the data span of 1990-2006.
(see Table 1 of Jenkin, 2008). However, the 2000-2007 trend for this site is found to be slightly positive (+0.07±0.15) but not significant because of large error margins. A linear regression of annual mean data for the entire period also shows a negative trend of -0.07±0.05 ppb per year and a positive trend of +0.08±0.24 for the period 2000-2007 as shown in Table 1.5.

1.3.8. Further discussion of the two coastal marine sites: Mace Head and Valentia

From the above analysis of both sites it seems they show a significant difference in the trend though they are both on the west coast of Ireland and would appear to have similar meteorological conditions throughout the year. However, a closer analysis of data for both stations shows significant meteorological differences (mainly wind direction) between the two sites that probably explains the discrepancy between the results from the two sites. Back trajectories for Valentia for the period 2001-2007 are clustered in the same manner as for Mace Head. Table 1.4 shows sector wise contribution of air mass trajectories at Valentia and at Mace Head during 2001 – 2007.

Table 1.4. Sector wise distribution of 96 hours back trajectories at Mace Head and Valentia during the period 2001 – 2007.

<table>
<thead>
<tr>
<th>Trajectories Distribution (2001-2007)</th>
<th>Eastern</th>
<th>Western</th>
<th>Northern</th>
<th>Southern</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mace Head</td>
<td>235</td>
<td>929</td>
<td>849</td>
<td>484</td>
<td>2497</td>
</tr>
<tr>
<td></td>
<td>9.4 %</td>
<td>37.2 %</td>
<td>34.0 %</td>
<td>19.4 %</td>
<td></td>
</tr>
<tr>
<td>Valentia</td>
<td>490</td>
<td>902</td>
<td>388</td>
<td>727</td>
<td>2507</td>
</tr>
<tr>
<td></td>
<td>19.5 %</td>
<td>35.9 %</td>
<td>15.5 %</td>
<td>29.0 %</td>
<td></td>
</tr>
</tbody>
</table>

At Mace Head, the Western and Northern sectors are the dominant sectors whereas at Valentia the dominant sectors are Western and Southern. But the main difference is the contribution of the Eastern sector at Valentia which is twice that of Mace Head (19.5% compared to 9.4%). Because of the relative dominance of the Eastern sector at Valentia in comparison to Mace Head, Valentia is more affected by regional changes in ozone, compared to Mace Head. As shown in the earlier analysis, there is a negative trend in ozone at the inland Irish sites. The Valentia observational
site is close to the coast but is inland, as compared to Mace Head, and is in close proximity to a small Irish town (Cahirsiveen). Thus, although Valentia is near coastal, it also has characteristics of a rural site and is considered to be more influenced by regional ozone change. These differences between Valentia and Mace Head yield an almost insignificant negative trend at Valentia (-0.05±0.15) in contrast to the positive trend at Mace Head.

1.4. Surface Ozone Conclusions

Ground level ozone data at Irish sites, sampled mainly by the Environmental Protection Agency, and at Mace Head, Lough Navar, and Valentia are analyzed to assess the seasonality and any long term trends. The selected stations for the analysis have relatively longer data records (for more than 8 years) and cover a range of sites from urban, suburban, major towns, rural areas, and marine sites. Monthly mean data are analyzed using statistical techniques widely used for time series analysis - the seasonal and trend decomposition procedures (STD) and an ARIMA modeling approach. In general, both analytical methods have shown reasonable agreement in model fits and trends with slight differences owing to the difference in their treatment of time series. Deviation in trend predictions between the two methods were noticed when raw data have large variations.

Monthly mean data show that, in general, the occurrences of ozone peaks in recent years showed stable or in some cases declining (e.g. Wexford site) values. Trend and seasonal variations in ozone levels at any location are mainly dependent on ozone precursors and a recent review (UNECE, 2007) has shown that the emissions of NO$_x$ and NMVOC (Non-Methane Volatile Organic Compounds) in Europe and North America have declined substantially which may have resulted in a decrease in ozone levels. Except for the coastal marine sites of Mace Head and Valentia, all stations analyzed here show an overall declining trend and also a negative trend in spring peaks.

This decline in ozone values has occurred in recent years, mainly after 2000. A very strong negative trend is observed at Rathmines, Dublin (data collected since 2002) and almost no trend for the Dublin Pottery Road site (data available from 1994 to 2001) is such an example. The ozone concentrations at rural and urban sites are influenced differently by changes in local and regional pollution levels as well as by hemispheric background ozone concentrations (The Royal
Figure 1.12. Decreasing levels of annual mean NO\textsubscript{x} concentration (ppb) at the Dublin Rathmines site during the period 1988 to 2000. Levelling off in annual NO\textsubscript{x} levels occurs after around the year 2000. Error bars shown are one standard deviation for annual mean calculations.

During the period 2000-2007, there is little change in NO\textsubscript{x} concentration levels at the Dublin Rathmines urban site (Figure 1.12) where annual mean values range from ~ 17-19ppb for years 2000, and for 2002 – 2007, with the only exception being for 2001 with an annual mean of ~ 30ppb. Thus the negative trends may be attributed to the decrease in the severity of regional scale photochemical ozone production [Jenkins, 2008] and may also be due to a decelerating trend in baseline ozone. The seasonal peak of monthly mean ozone at the Dublin Rathmines site has also declined significantly in recent years (Figure 3.1) and this decline is likely to be a consequence of reduction of photochemical ozone events during the period of observations. A similar decrease in
annual maximum ozone concentration at the urban site at Leeds, UK as well as in the rural site of Lullington Heath is described by Jenkin (2008).

Ozone values in rural areas are more influenced by regional changes in precursor emissions and hemispheric background ozone levels and are least influenced by local NO concentrations. The data from Mace Head are representative of ozone levels in airmasses entering Europe from the Atlantic which show a positive trend. The rural sites in Ireland have responded to a regional reduction in ozone precursors and almost all the rural sites have shown a decreasing trend with different negative trend values over the period from 2000 to 2007. The only exception is the forest woodland site of Lough Navar, which has almost no trend in the 2000-2007 period. The rural sites of Wexford and Monaghan have shown the strongest negative trends for the 2000-2007 period. The rate of negative trend is dependent on the period of data analyzed. All sites, except for the coastal marine sites and Lough Navar, have shown a very strong negative trend during the period 2000-2007. Trends from monthly mean analyses are in good agreement generally with regression analysis of annual mean data, as shown in Table 1.5.

Table 1.5. Ozone trends at Irish sites from seasonal trend decomposition (STD) analysis of monthly mean data. Trends during 2000-2007 are shown separately. Corresponding trends in annual mean are also shown. The stations show reasonably good agreement for trends, analyzed from both monthly mean data and annual mean data, except for the Dublin-Pottery Road site.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Trend in monthly mean in ppb/year</th>
<th>Trend in annual mean in ppb/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dublin-Rathmines (2002-2007)</td>
<td>-0.33±0.17</td>
<td>-0.33±0.21</td>
</tr>
<tr>
<td>Dublin-Pottery Road (1994-2001)</td>
<td>+0.09±0.16</td>
<td>+0.38±0.26</td>
</tr>
<tr>
<td>Cork (1995-2007)</td>
<td>-0.06±0.06</td>
<td>-0.07±0.11</td>
</tr>
<tr>
<td>2000-2007</td>
<td>-0.20±0.11</td>
<td>-0.18±0.17</td>
</tr>
<tr>
<td>Wexford (1999-2007)</td>
<td>-0.80±0.11</td>
<td>-0.76±0.27</td>
</tr>
<tr>
<td>2000-2007</td>
<td>-0.99±0.13</td>
<td>-0.99±0.30</td>
</tr>
<tr>
<td>Monaghan (1995-2007)</td>
<td>-0.12±0.07</td>
<td>-0.14±0.16</td>
</tr>
<tr>
<td>2000-2007</td>
<td>-0.58±0.12</td>
<td>-0.58±0.24</td>
</tr>
</tbody>
</table>
The monthly mean data from Mace Head and Lough Navar were analyzed using trajectory cluster analysis in order to compare the contribution of different sectors to the ozone level. The clean sector data of Mace Head – Northern and Western – were analyzed for trend and seasonality. The results show a positive trend of +0.18±0.03 ppb per year and +0.17±0.02 ppb per year for Western and Northern sectors respectively over the period 1987 – 2007. Polluted Eastern sector and other non-eastern sectors for Mace Head have shown different seasonal patterns with the polluted Eastern sector lagging behind the cleaner sectors by about two months for maxima and by about four months for minima. The Western sector is also analyzed for trends during different time periods, partially to see the variation in ozone trends for background Atlantic air masses. Positive trends in the background ozone concentration (Mace Head Western sector) were larger during the partial periods before 2000 (e.g. +0.29 ppb per year for 1993-2000 and +0.23 ppb per year for 1990-2000) and have seemingly reduced when the period 2000 to 2007 is included (Table 1.3). The deceleration in the positive trend in ozone at Mace Head is also noticed in non-sectored data analysis.

This work shows that the increasing baseline ozone concentration in the Atlantic marine boundary layer seems to have stabilized in recent years as per some indications given by Oltmans et al., (2006) and show a deceleration in the positive trend in contrast to the continuous positive trend reported in other studies (Simmonds et al., 2004; Derwent et al., 2007; and others). These changes have occurred mostly over the past decade and may partially be attributed to changes in the level of ozone precursors in North America and Europe. There is a negative trend in ozone values in Ireland at most sites, which may be attributed to regional changes in emissions and may be up to some extent due to the decelerating trend in baseline ozone entering Europe as discussed above. But because the

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lough Navar (1988-2007)</td>
<td>-0.07±0.04</td>
<td>+0.07±0.15</td>
<td>-0.07±0.05</td>
<td>+0.08±0.24</td>
</tr>
<tr>
<td>Mace Head (1988-2007)</td>
<td>+0.16±0.04</td>
<td>+0.27±0.10</td>
<td>+0.16±0.04</td>
<td>+0.27±0.18</td>
</tr>
<tr>
<td>Valentia (2001-2007)</td>
<td>-0.05±0.15</td>
<td>-0.06±0.37</td>
<td>-0.05±0.15</td>
<td>-0.06±0.37</td>
</tr>
</tbody>
</table>
ozone precursor emissions may not necessarily have stopped or decreased substantially in around 2000, the possible stabilization in ozone level observed in this work may not completely be attributed to changes in precursor emissions. Moreover, meteorological variability could be masking the impact of emission reductions on long-term ozone trends (Wilson et al., 2012; EEA, 2007). This is indicated through European trends in NOx and VOC emissions which show a uniform decrease in ozone precursors across Europe but which are not directly reflected in observed ozone trends (Wilson et al., 2012, EEA, 2009).

Further observational and modeling research is needed to address this complex problem. Most of the Irish sites started observations after 2000 and relatively few years of data are available which does not necessarily give a reliable long term trend in ozone levels and accordingly the trends are just indicative. The analysis underlines the need for further continuous measurements of ozone at different sites along with systematic ozone precursor measurements coupled with detailed meteorological analyses, in order to assess long term ozone variations in the region and to assess future impacts of government and EU directives for emission controls.
2. **Stratospheric Ozone**

2.1 Introduction

The Montreal protocol and its subsequent amendments led to a decrease in the global production of ozone depleting substances (ODS) and halogen loadings in the stratosphere (Wallace and Livingston, 2007; Froidevaux et al., 2006) and consequently led to a possible slowdown in decline and recovery of ozone in the upper stratosphere (Reinsel et al., 2002; Newchurch et al., 2003) and in total column ozone (Hadjinicolaou et al., 2005; Reinsel et al., 2005; WMO, 2006). The changes in ozone level, particularly in mid-latitude, however, may not be totally attributed to the changes in the production of ODS because of many other influences e.g. solar cycle, changes in stratospheric circulation, climate variability contributing to the total column ozone level. Arctic ozone depletion and subsequent mixing with local air masses (Tripathi et al., 2006, 2007; Leblanc et al., 2006) also play an important role in establishing the northern mid-latitude column ozone level. The largest fraction of the ozone layer that protects us from harmful ultraviolet radiation lies in the lower stratosphere between 10 and 25 km (WMO, 1999). Determining any change in the ozone amount in this region of the stratosphere is essential for the evaluation of the thickness of the protecting ozone layer. Yang et al. (2006) analyzed ground based and satellite data up to the year 2005 for Northern Hemisphere mid-latitudes and found an increasing trend in the lower stratosphere at different altitude ranges. The Arosa Umkehr record shows that the trends above 33 km and below 24 km were negative before 1995 and then reversed to a positive trend during 1996-2004 (Zanis et al., 2006). A significant change in the trend in northern mid-latitudes was also observed by Miller et al. (2006) from ozonesondes’ data in the altitude range from 13 to 18 km. The analysis by Krzyscin and Rajewska-Wiech (2009) indicates a significant decline in the total ozone downward trend in European mid-latitudes. The same study also found a significant upward trend in column ozone when the EESC (Equivalent Effective Stratospheric Chlorine) time series is used as a proxy for the anthropogenic trend pattern. An investigation by Angell and Free (2009) using different sources of column ozone measurements as well as ozonesonde data have shown a decline and subsequent increase in mid-latitude ozone values. Harris et al. (2008) used advanced multiple regression from ozonesonde data and atmospheric models and long term ozone
data sets in their analysis and have shown an almost negative trend (which was statistically significant) from the late 1970s to the mid 1990s, and then followed by an increase.

Met Éireann has a long record of ground based and balloon borne ozone observations conducted since around 1994 at Valentia observatory which is located on the south west coast of Ireland. Despite Valentia being a part of GAW (Global Atmosphere Watch) network and a prominent mid-latitude station located on the northwestern extreme of Europe, these ozonesonde data have never been systematically analyzed for column ozone variations. The observational periods which coincide with the possible ozone recovery period discussed above give added importance to this analysis. In this Report, ozonesondes’ data along with co-located Brewer column ozone data are analyzed and compared with the total column ozone derived from satellite total ozone observations for changes in column ozone since the mid 1990s.

2.2. Data and Methodology

2.2.1 Valentia Ozonesonde Programme

Under this Project, Met Éireann’s Valentia Meteorological and Geophysical Observatory (Caherciveen, Co. Kerry) extended its existing Ozonesonde programme (originally running from December through to March) into a year round programme. The preparation of an ozonesonde is a very manual intensive exercise. Three detailed quality assurance stages are performed over a seven day period prior to launch. Each of the stages requires the use of testing equipment known as an ‘Ozonizer’ (manufactured by the Science Pump Corporation). If the ozonizer were to fail, it would result in the suspension of the ozonesonde launches at Valentia. To remove the dependence on this single point source, Met Éireann funded the purchase of a new ozonizer and associated accessories, thus providing redundancy to the quality assurance preparations of an ozonesonde. As of yet, there is no globally accepted international standard operating procedure for the preparation of ECC 6A ozonesondes (i.e. the type used at Valentia). Preparation guidelines do exist but the finer details are left to the individual ozonesonde agencies. Under the ERC project, Lerwick Observatory in the Shetland Islands was visited. Here a detailed inter-comparison of the three stage preparation of an ozonesonde was conducted.
Incorporating this along with the standard operating procedures obtained from Environment Canada (home of the World Ozone and Ultraviolet radiation Data Centre [WOUDC]) Valentia verified that its ozonesonde preparations met with best international practices. After the completion of an ozonesonde ascent, a data file is generated containing all relevant ozone data and metadata associated with the flight. Based on information obtained in Lerwick and other sources from within the international ozonesonde community, Valentia designed and developed quality control software to test and profile these ozone data files. This has greatly aided the quality control of ozonesonde data before its submission to the international data centre (WOUDC). Also located on site at Valentia Observatory is Met Éireann’s ground level ozone analyser. This analyser continually monitors ground level ozone, contributing its measurements to an EPA national network. As a final quality assurance check before launch, the ozone value obtained from the ozonesonde is compared to the ozone value obtained by this ground level analyser. If a major discrepancy is found between the two, the launch can be suspended and the discrepancy resolved rather than incurring the cost of a failed ascent. Standard international launch times for ozonesondes are at noon UTC (often called the 12z ascent). This is so they double up with scheduled radiosonde weather balloons used for weather forecasts. Although the ascent is called the 12z ascent it is in fact launched at 11:15 UTC. This is standard practice. It comes from the fact that an ascent is typically around 90 minutes long and the need to be approximately halfway through your ascent by 12 noon.

The ozonesonde program at Valentia started in 1994 using ECC ozonesondes and has continued since then on a regular basis. Before 2007, the launches were usually made during the winter and spring months only, but since June 2007 this launch schedule was extended to a weekly regime as part of the EPA (Ireland) Ozone Project. As part of the GAW (Global Atmosphere Watch) global ozone observing system, the ozonesonde program at the observatory has played an active role in EU funded research projects including: SESAME (the Second European Stratospheric and Mid latitude Ozone Experiment), TOASTE (the Tropospheric Ozone and Stratospheric-Tropospheric Exchange), THESOE (the Third European Stratospheric Ozone Experiment) and currently participates in the MATCH campaign. The observed ozonesonde ozone profile
is integrated to yield total column ozone. Only ozone profiles with a burst level of 30 km (geopotential height) or above is considered for this work. Above the burst level of the sonde, the residual ozone is calculated using climatological mean data by McPeters et al. (1997). Known instrumentation uncertainty between individual sondes e.g. decreasing efficiency of pump with decreasing pressure (Komhyr and Harris, 1965; Logan et al., 1999; Tarasick et al., 2005) is corrected for during prelaunch calibration or as in the case of pump efficiency, is automatically corrected by universal Vaisala ECC6A pump correction tables during the ascent. For this study the integrated ozonesonde profiles were also normalised by applying a normalisation correction factor as is common practice (Fioletov et al., 2006; Keim et al., 2009). The normalization correction factor is the ratio of the integrated ozone from the ozonesonde profile and the column ozone observed from a ground based instrument (here the co-located Brewer spectrophotometer column ozone value is used). The corrected profile is the product of the observed profile and the correction factor. The standard deviation of the correction factor from 443 launches is 0.065 which gives an estimated uncertainty in non-corrected profiles of 6.5%, which is slightly lower than the one estimated by Fioletov et al., (2006) (7.6% from 5500 ECC flights that reached at least 26 km). The uncertainty in corrected profiles is between 4 to 5% taking into account that the standard uncertainty of total ozone spectrophotometer values is less than 3% (see e.g. Basher, 1982; Fioletov et al., 2006).

### 2.2.2 Total column ozone analysed data

Satellite derived column ozone data for Valentia are taken from the COST-726 data base having daily gridded total ozone data with 1° x 1° resolution over Europe [the rectangle 31°N-80°N, 25°W-35°E] for the period since 1950 and available at http://private.igf.edu.pl/~jkrzys. The database comprises statistically reconstructed total column ozone for the period 1950-1978 from a limited number of ground based sites. For the period after 1978, it has assimilated column ozone from the measurements through various satellites (Krzyscin, 2008) and the more recent data since 2005 is from the Ozone Monitoring Instrument (OMI) on-board the Aura satellite. Satellite data can be accessed for any particular station either from the value at the closest grid point or the interpolated value from the stations’ latitude and longitude coordinates. Interpolated values are used for this analysis.


2.2.3 Brewer spectrophotometer

Ground-based monitoring of total column ozone is continuously conducted at Valentia Observatory, using a MKIV Brewer spectrophotometer. These data contribute to the daily analysis of Northern Hemisphere total column ozone as produced by the WMO Daily Ozone Mapping Centre (Thessaloniki, Greece) and the WOUDC. A number of Brewer data were also obtained from 'zenith sky (ZS)' observations that are supposed to be less accurate than direct sun (DS) observations. ZS is a proxy total column measurement made on cloudy days when no direct sun is visible. A DS measurement is a very accurate ozone measurement derived from direct sunlight. Quite a few ZS days on the west coast of Ireland are obtained. However as our Brewer is well looked after and calibrated every two years, the ZS measurements compare quite well to the high quality DS measurements. Quite often, the DS and ZS measurement is compared as a quality check exercise. A typical random quality check for the month of July 2010 shows an average DS column ozone of 353.0 DU as compared to 353.2 DU for an average ZS value. A recent study of the performance of the ground based column ozone measurement instruments including the Valentia instrument was carried out by Fioletov et al. (2008). Daily and monthly averages of satellite and Brewer observations are in very good agreement at Valentia. Integral column ozone from corrected ozonesonde profiles is also in good agreement with Brewer and satellite observations. The mean deviation between satellite and Brewer data is found to be 1.3% whereas between satellite and sonde data it is 2.6 %, which is well below the uncertainty limit described in Fioletov et al. (2008). Because the ozonesonde data is normalized to the Brewer data, the mean deviation between the two data sets is much lower at 0.4%. It should be noted that the best available (daily mean) column ozone value from the Brewer was used in the calculation of the normalisation factor of the ozonesonde profiles.

2.2.4 Solar and dynamical variables

Additional emphasis is given to the analysis of ozonesonde data measured at Valentia. For this, apart from EESC, we also used the following solar and dynamical proxies to analyze springtime (March) total column ozone calculated from ozonesonde profiles: the
solar flux, the quasi-biennial oscillation index (QBO), and the North Atlantic Oscillation (NAO) index. The solar radio flux signal arriving at the surface of the earth changes every day. The flux density at 2800 MHz using a radio telescope is recorded every day at local noon at Penticton, B.C., Canada. The data are available in the form of monthly and daily means. The monthly mean data for the month of March is used here. For the QBO index, we used monthly mean zonal wind at 50hPa measured over Singapore (1° 22’ N, 103° 55’ E). The North Atlantic Oscillation (NAO) exerts a strong control on the winter climate of Northern Hemispheric winters and may consequently impact column ozone. The difference between the normalised sea level pressure over Gibraltar and the normalised sea level pressure over Southwest Iceland is used as the index of the strength of the NAO [Jones et al. 1997].

2.2.5 Methods used for Stratospheric Ozone data analysis

Statistical methods are used to investigate the slowdown and possible recovery of column ozone over Valentia observatory. Dynamical and radiative factors like the quasi-biennial oscillation (QBO) and the 11-year solar cycle play a very important role in ozone column amount. QBO has a time period of about 23 months and solar cycle signals of about 11 years. The effect of these signals on data spread can be minimized by using an 11-year running average on annual mean time series. Monthly mean time series e.g. from Brewer and satellite observations have strong seasonal variations with a frequency of 12 months. Time series also have a long term change in data level called trend. These two components - seasonal variations and trend - are separated using the procedure specified by Cleveland et al. (1990), the Seasonal-Trend decomposition procedure based on Loess (STL) smoothing. STL is a filtering procedure consisting of a sequence of applications of loess smoothing (locally weighted scatterplot smoothing). Total column ozone over northern mid-latitudes has a very strong seasonal variability with a strong trend in the spring period and an almost near-zero trend in the autumn. The STL technique gives the trend average annual trend estimate. For more details of the procedure, FORTRAN code and various parameter settings, see Cleveland et al. (1990). STL is used for monthly mean time series. There are different sources of year to year variation in column ozone at a particular location. Besides a decreasing trend in the equivalent effective stratospheric
chlorine (EESC), solar and dynamical influences were analyzed using multiple variable linear regression analysis. The simple multi-linear model used can be described as:

\[ O_3 = M_{EESC} \cdot EESC + M_{SOL} \cdot SOL + M_{QBO} \cdot QBO + M_{NAO} \cdot NAO + C + \text{Error} \]

where \( O_3 \) is total column ozone, \( M_{xxx} \) are the multiplying factors, EESC is the equivalent effective stratospheric chlorine value, SOL is the solar signal. QBO and NAO are the values described above, \( C \) is a constant and Error is the error term.

### 2.3. Stratospheric Ozone Results

#### 2.3.1. Ozonesonde and Brewer column ozone

Ozonesonde weekly launches in Valentia started in 1994 and until 2007 launches were made mainly during the winter-spring months (December to April). Since June 2007, the launches are made over the full year on a weekly basis. Figure 2.1 (a), (b) and (c) shows the comparison of weekly ozonesonde integrated column data with Brewer observations for Valentia, together with satellite data. Figure 2.2 shows a comparison of monthly mean values from ozonesonde ozone profiles and Brewer observations from Valentia, along with satellite data. Ozonesonde profiles are first adjusted for instrumental performance error using a correction factor calculated using co-located Brewer data. The corrected profile is then integrated for column ozone. The profiles with a burst height of 30 km or above are considered for calculation. However, monthly mean calculations can only be regarded as approximate, since the monthly values are based on relatively few (either 4 or 5) weekly values. Figure 2.2 also shows mean correction factors corresponding to each monthly mean values. The ozonesonde column ozone compares well with satellite and Brewer data except for some outliers. There may be several reasons for these outliers mainly: there are relatively few launches in the month, with fairly very high or very low correction factors. It is clear from Figure 2.2 that some of the deviations occurred only for values with high or low correction factors.
Figure 2.1. (a) Comparison of Valentia ozonesonde integrated column ozone and Brewer observations in 2007, and satellite COST data.

Figure 2.1. (b) Comparison of Valentia ozonesonde integrated column ozone and Brewer observations in 2008, and satellite COST data.
Figure 2.1. (c) Comparison of Valentia ozonesonde integrated column ozone and Brewer observations in 2009, and satellite COST data.

Figure 2.2. Monthly mean comparison of total integrated column ozone from ozonesondes and from the Brewer instrument observed at Valentia Observatory from 1993 to 2009, with satellite column ozone data. The correction factors (in red) applied to integrated column ozone are shown on the secondary y-axis.

2.3.2. Long term changes in column ozone

Concentrations of parameterized anthropogenic ODS combining the destructive power of all chlorine and bromine containing species weighted to their ozone depleting potential is
the equivalent effective stratospheric chlorine loading or EESC. Figure 2.3 shows global averaged EESC from atmospheric observations of ozone depleting substances: CFCs, chlorinated solvents (CH3CCl3 and CCl4), methyl chloride, methyl bromide, halons, and HCFCs from 1970 to 2007. Data are taken from the State of the Environment publications of the Department of the Environment, Water, Heritage and the Arts of the Australian Government. Total stratospheric chlorine peaked in the mid 1990s (1996 as shown in the Figure) and is now declining. Figure 2.3 also shows the 11 year running mean of column ozone over Valentia Ireland from satellite measurements (after 1978) and model reconstructed data before 1978 (including dates when satellite data are not available after 1978). To minimize the effect of QBO and the solar signal, a 11-year running average assuming the solar signal of period 11 year is preferred. The running mean is centrally averaged and therefore the value for 2003 is an average of the annual means from 1998 to 2009 and so on. The beginning of the decline in EESC is coinciding
average are given. The Figure also shows the global observations of equivalent effective stratospheric chlorine (EESC) which peaks in the year 1996 over the recent decade.

with the upward trend in column ozone. This upward trend starts 5 years later in the case of backward averaging and therefore coincidence should be considered cautiously. The beginning of the upward trend in column ozone, if any, may be between these two extremes.

2.3.3. Monthly mean Brewer and satellite column ozone

Monthly mean time series from daily mean data of satellite (COST) and Brewer are created and analyzed for changes in column ozone level from 1993 to 2009. The time series is first decomposed into seasonal, trend and error components using the STL method described above. The trend component contains a slow variation in ozone levels from 1993 to 2009. The trend component, when linearly regressed, shows $+0.53\pm0.08$ DU per year variation from satellite data and $+0.48\pm0.07$ DU per year from Brewer observations from 1993 to 2009.
Figure 2.4. Annual mean of accumulated percentage change in column ozone in satellite data (COST) and from Brewer observations at Valentia, Ireland since 1993, calculated from the trend component of decomposed monthly mean time series using the STL method. This accounted for $+1.6\pm0.25\ %$ and $+1.5\pm0.24\ %$ change per decade for satellite and Brewer respectively at an average ozone level of 325 DU.

Accumulated variation in trend component is calculated from the regressed value in January 1993. The 12 month average accumulated percentage annual change from the two data series is shown in Figure 2.4. The error bars show one standard deviation from the 12 month mean on each side. The Figure shows a continuous positive change in ozone levels up to the year 2004 and then a negative change followed by a positive change again from 2007 to 2009. Lowest ozone levels are observed in the year 1993 with a maximum negative change and then a continuous positive change until a dip in the year 2005. The maximum negative anomaly in 1993 and then an upward trend is also reported by Harris et al. (2008) for ozone trends at northern mid-latitudes. Note that the change is calculated with respect to the regressed level in the year 2003 and therefore an almost equal value during 2006 to 2009 in Brewer data indicates no change in ozone levels.
during this period. Satellite data also agree with the Brewer except for a slight upward shift in the year 2009. When only March mean data are analyzed using the 11 year running average, the trends are much stronger of $+4.8\pm0.5\%$ per decade during the period 1993 to 2009 at an average March level of 355 DU from both sources.

2.3.4. Ozonesonde data since 1994

Ozonesonde data at Valentia for the months December, January, February and March (DJFM) are available since the year 1994. Figure 2.5 shows the ozone profile during DJFM from 1994 to 2009. The launch started in January 1994 so there are no data for December 1993 that constitutes winter/spring data of 1994(D). Similarly no launches were conducted during 2005 (DJF), 2006 (J) and 2007 (J) as the gaps in the Figure indicate. The data are in milliPascal (mPa) and the y-axis shows geopotential height in km. As shown in the figure, most of the ozone is in the lower stratosphere between 15 and 26 km. Elevated ozone levels are observed in this layer during recent years particularly in the springs of 2007 and 2009. In the nineties, an elevated ozone level is observed only in the spring of 1999 between 18 and 21 km as shown in the Figure.

Ozone profiles for the period 1994 to 2009 are integrated partially for three layers: ground to 15 km, 15 km to 26 km, and above 26 km, in order to understand ozone changes in different layers of the atmosphere. Because of the absence of some months during 2005 to 2007, only March profiles are considered for partial integration. Figure 2.6 shows annual March mean column ozone values for the three partial regions of the atmosphere. Large uncertainties shown in the trend (see Figure 2.6) for all regions is due to strong interannual variations of column ozone. A 11-year running mean for the 3 column height regions are calculated in order to reduce the uncertainty and the effect of solar cycle and QBO. A 11-years running mean from 1994 to 2009 gives only 6 data points. The linear regression is used on these points and the result in DU per year is shown in Table 2.1. The 11-year running average shows a positive trend for all three atmospheric regions with a maximum trend in the 15 to 26 km region ($+9.2\pm3.2\%$ per decade at an average level of 180 DU in this region) with a reasonable confidence level. For the 0-15 km region, the trend is $+3.7\pm7.4\%$ per decade but is not statistically significant with almost a double error estimate. Above 26 km, the positive trend observed
is +4±1.6 % per decade with significant statistical confidence. Note that the ‘11-year’ running mean smooths data and reduces the inter-annual fluctuation, as compared with the trend results shown in Figure 2.6, but it does not reduce uncertainty. Another cause of concern for the above 26 km result comes from the approximation used for this part of the atmosphere. The ozone in this band is a combination of measured ozone and additional ozone as approximated by McPeters [1997] climatology. This additional contribution is to account for the missing ozone between burst height and top of the atmosphere. However McPeters [1997] climatology is based on 12 years of Nimbus7 satellite data measured between 1979 and 1990. From Figure 2.3 we see that the ozone average over Ireland very different than now during this period. Our trend result for 'above 26km' band may have a possible contaminant. Table 2.1 also shows Brewer and satellite trends for the same period with similar analysis for comparison.

Figure 2.5. Ozone profiles from the winter-spring months of December, January, February and March (DJFM) from 1994 to 2009 observed from ozonesonde launches at
Valentia, Ireland. There was no launch in December 1993 (D part of 1994). No ozonesonde launch occurred during 2005 (DJF), 2006 (J), and 2007 (J).

Another objective of the work is to understand the relative contribution of different variables on the recent trend in atmospheric column ozone observed in the ozonesonde exercise at Valentia Observatory and to underline its continuous operation. A multiple linear regression is performed for March mean column ozone values as dependent variables. The four major independent variables included are solar signal, QBO index, NAO index, and EESC. Independent variables are considered in different sets, for example (1) only solar signal is considered as an independent variable, (2) solar signal and QBO are considered as independent variables, (3) solar signal, QBO, and NAO are considered, and finally all four are considered. The values of the independent variables are used as is and are not normalized, so the multiplying factors (M) for different contributors should be considered independent to each other. They do not show their relative contribution. The exercise is aimed to show that anthropogenic as well as solar and dynamical factors have influenced the data.

Table 2.2 shows the results of some of the sets, including coefficient of determination ($R^2$). The coefficient of determination is a measure of the effectiveness of the model if used for the prediction. It is observed that the coefficient of determination is a maximum when all the independent variables are taken into account instead of subsets of them. It shows that besides EESC, other factors also contribute to the total column ozone. It is further observed that in all cases (subsets) the signs of the correlation (positive or negative) are not changed. The EESC has always been negatively correlated, regressed either alone or with other variables. Similarly, the solar signal has always positively contributed to the column ozone as shown in Table 2.2. The signs of contributions of QBO and NAO have always been negative. In the case when EESC alone is considered as the independent variable, only 9.3% ($R^2=0.093$) of variation in data can be explained by the regressor (EESC) i.e. the model performed poorly. Similarly for other cases where only solar and dynamical variables are considered as regressor, the performance is very poor as shown in Table 2.2. Significant improvement is shown when
Figure 2.6. Partially integrated column ozone from ozonesonde profiles between ground level to 15 km, 15 km to 26 km, and above 26 km geopotential heights. Monthly averages for the month of March are shown. Linear regression lines and trend values are also shown.

Table 2.1. Trend in column ozone in the month of March from 1994 to 2009 at different layers of the atmosphere integrated from ozonesonde measurements at Valentia Observatory, Ireland. Total column ozone trends from Brewer observations and from satellite for the month of March are also given for comparison.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0-15 km</td>
<td>+0.37±0.84 DU/Year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-26 km</td>
<td>+1.02±1.07 DU/Year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>above 26 km</td>
<td>+0.38±0.41 DU/Year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>+1.77±2.00 DU/Year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level</td>
<td>Change (DU/year)</td>
<td>Change Rate (%)</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Above 26 km</td>
<td>+0.37±0.15</td>
<td>+4.0±1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-26 km</td>
<td>+1.66±0.59</td>
<td>+9.2±3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-15 km</td>
<td>+0.29±0.58</td>
<td>+3.7±7.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>+2.32±1.24</td>
<td>+6.6±3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1.75±0.25</td>
<td>+4.9±0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1.84±0.25</td>
<td>+5.1±0.7</td>
<td></td>
</tr>
</tbody>
</table>

EESC is included with solar and dynamical variables. The relatively better result is shown when all the independent variables are included and then about 26% of the variation could be accounted for.
Table 2.2. The multi-linear regression is performed for the total column ozone (O3) integrated from the ozonesonde profile for the month of March since 1994 to 2010 considering different sets of independent variables. The coefficient (contribution) of different variables ($M_{xxx}$) for each set and Coefficients of Determination ($R^2$) are shown in this Table. The linear model if all variables are included may be described as:

$$O3 = M_{EESC} \cdot EESC + M_{SOL} \cdot SOL + M_{QBO} \cdot QBO + M_{NAO} \cdot NAO + C + \text{Error}$$

<table>
<thead>
<tr>
<th>Cases</th>
<th>$M_{EESC}$</th>
<th>$M_{SOL}$</th>
<th>$M_{QBO}$</th>
<th>$M_{NAO}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EESC</td>
<td>-0.070±0.056</td>
<td></td>
<td></td>
<td></td>
<td>0.093</td>
</tr>
<tr>
<td>SOL</td>
<td></td>
<td>+0.010±0.014</td>
<td></td>
<td></td>
<td>0.032</td>
</tr>
<tr>
<td>EESC + SOL</td>
<td>-0.091±0.058</td>
<td>+0.017±0.014</td>
<td></td>
<td></td>
<td>0.175</td>
</tr>
<tr>
<td>EESC + SOL + QBO</td>
<td>-0.090±0.060</td>
<td>+0.019±0.015</td>
<td>-0.024±0.055</td>
<td></td>
<td>0.187</td>
</tr>
<tr>
<td>SOL + QBO</td>
<td></td>
<td>+0.012±0.015</td>
<td>-0.028±0.058</td>
<td></td>
<td>0.048</td>
</tr>
<tr>
<td>SOL + QBO + NAO</td>
<td>+0.012±0.017</td>
<td>-0.028±0.065</td>
<td>-0.006±2.274</td>
<td></td>
<td>0.048</td>
</tr>
<tr>
<td>EESC + SOL + QBO + NAO</td>
<td>-0.133±0.073</td>
<td>+0.024±0.016</td>
<td>-0.053±0.062</td>
<td>-2.661±2.550</td>
<td>0.255</td>
</tr>
</tbody>
</table>

2.4. Stratospheric Ozone Conclusions

Column ozone data from ground Brewer spectrophotometer, satellite, and ozonesonde observations from 1993 to 2009 are analyzed to support recent ozone recovery at mid-latitude station Valentia Observatory in Ireland. All sources of data show varying amounts of positive trend during this period. Monthly mean analysis for Brewer and satellite data show statistically significant trends of about 1.5% to 1.6% increase per decade [during the period 1993-2009] at an average ozone level of 325 DU. This accounted for ~2% increase from 1993 to 2009 including contributions from all sources: anthropogenic, radiative and dynamical. Krzyscin and Rajewska-Wiech [2009] used a simple EESC model to show a statistically significant anthropogenic component trend of ~+1% from 1995 to 2008. The largest increase of ~+4.8% per decade is found in the March months for the period 1993 to 2009 from both sources using a 11-year running average. Note that the 11-years running mean reduces the effect of radiative and QBO contributions and therefore is indicative of changes due to anthropogenic sources.
Ozonesonde observations for the month of March only from 1994 to 2009 are also analyzed for the direction (whether positive or negative) of total ozone recovery and relative contributions from three layers (0-15 km, 15-26 km, and above 26 km) of the atmosphere. The maximum change in the lower stratosphere for the 15 to 26 km region underlines the strong relative contribution of atmospheric dynamics to total ozone change. The total integrated column ozone trend for ozonesonde data is found to be ~+6.6% per decade – in reasonable agreement with Brewer and satellite March data each showing ~+5% per decade. Multiple linear regression analysis shows that neither EESC or solar and dynamical signals are enough to explain the variation in the column ozone observed by the ozonesonde at Valentia. Although EESC may be a major contributor to the total column ozone trend, the inclusion of solar and dynamical variables with EESC in the multi-linear model significantly improves the prediction.

In summary, this study has shown that reduced emissions of ozone depleting substances have a significant positive impact on stratospheric ozone and that ozone levels in mid-latitudes have leveled off and are now in a recovering stage. Maximum change is occurring in winter/spring months. The changes may be attributed to the reduction in ODS and to changes in the variation in solar and dynamical factors of the atmosphere, but a more detailed theoretical (modeling) and experimental data analysis on a global basis is required for the apportionment of these relative contributions. As shown in Figure 2.3, there is still a very long way to go to achieving 1980s levels again, and prediction of when this might occur will require prolonged measurements and continuing analysis of ozone and meteorological data.
3. Exposure Levels of Ozone for protection of human health, vegetation and forest in Ireland

3.1 Introduction

Tropospheric ozone is known to be an important pollutant and it has been established that ozone has significant impact on human health globally, and in the European Union 21,400 premature deaths each year are associated with ozone (EEA, 2007). An informative review chapter on the effects of ozone on human health is given in the Royal Society Report (2008) some of whose conclusions are: (i) health effects of ozone increase with increasing concentrations (ii) health impacts have been observed at around ambient concentrations (~70 µg/m$^3$) (iii) the existence of a threshold concentration, below which ozone has no effect on humans is not yet determined. Despite the lack of clear evidence of a threshold, nevertheless, the World Health Organisation (WHO), based on epidemiological time-series studies and on chamber and field studies, have set a new air quality guideline and interim target of 100 µg/m$^3$ (daily maximum 8-hourly mean), WHO (2006). The ambient air quality and Cleaner Air For Europe (CAFÉ) Directive [2008/50/EC], (CEC, 2008) has been adopted, and sets an ozone target concentration value of 120 µg/m$^3$ not to be exceeded for the protection of human health.

Tropospheric ozone is also known to affect forest, vegetation, and many species of crops (Fuhrer, 1994; Sanders et al., 1994; US EPA, 1996; Hayes et al., 2007; Mills et al., 2007; Schaub et al., 2005; Bassin et al., 2007). Experimental studies have shown that besides a visible impact on growth, ozone exposure also affects the reproductive capacity, biomass allocation, and biological aging (senescence i.e. a change in the biology of an organism as it ages after its maturity) (Davison and Barnes, 1998; Fuhrer and Booker, 2003; Bassin et al., 2007). The severity of ozone on vegetation and forest depends on the concentration, duration of exposure, and activity level (stomatal conductance) during the time of exposure. The stomatal conductance depends upon various climatic parameters e.g. temperature, humidity, vapour pressure deficit, and availability of light as well as soil water potential and phenology (Emberson et al., 2000; LRTAP Convention, 2004; Pleijel et al., 2007). Assessment and quantification of the impacts of ground-level ozone on terrestrial vegetation relies primarily on empirical exposure-response relationships
between ozone concentration and changes in crop yield, derived mainly from chamber studies (Royal Society Report, 2008). Hourly averaged data are analyzed in different ways for the assessment of the impact of ozone exposure on vegetation. In the US, as per 2008, standard concentration based parameters such as a 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations (should not exceed 75ppb or 150µg/m$^3$) are used for this purpose (US EPA, 2009) whereas in Europe a target level approach is used. The UN Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) has set out an exposure level for long term injury and damage to vegetation (and human health), (Fuhrer et al, 1997). The target level is referred to as AOT40 (Accumulated exposure Over a Threshold of 40 ppb – more detail is given in Section 3), whose target value for the protection of vegetation is AOT40 18,000 ug/m$^3$*hr, (CEC, 2008).

As a result of legislation to reduce emissions of ozone precursors, downward trends of high ozone concentrations have been reported in various areas of Europe (Monks et al., 2003; Solberg et al., 2005) and most recently in Ireland (Tripathi et al., 2010) during the last two decades. Surface ozone levels in Europe and in Ireland are controlled mainly by two sources: the internal formation and loss processes due to local variation in precursor emissions and ozone transported to Europe mainly entering from the west from the North Atlantic, often referred to as background ozone. Peak ozone concentrations are mainly affected by local production and loss processes and are controlled mainly by local changes in precursor emissions whereas mid-percentile ozone level (between 40 and 60 percent) is determined by the ozone entering from outside the region and strongly controlled by broader global emissions. Furthermore, several meteorological variables such as temperature, pressure, wind speed, humidity, cloud cover etc may impact ozone concentration (Camalier et al., 2007) particularly at urban sites. Variation in these parameters affects seasonal and interannual variability in ozone concentration at a particular site.

Exposure analysis for Ireland was first performed by Kluizenaar et. al (2001) based on three years of ozone data (1995 to 1997) just after systematic monitoring of ozone in Ireland started in 1994. Since then, no integrated approach for ozone exposure analysis of ozone data in Ireland has been made. In this work, we determine for the first time, based
on some 16 years of hourly ozone concentration data (1994-2009) if the new target ozone values and long-term objectives for human health and protection of vegetation are being met in Ireland. Furthermore, we analyze ground level hourly ozone data at eight sites in Ireland to study trends in ozone exposure levels to humans and to vegetation, as well as examining changes in diurnal variation of ozone concentration, over an 11 year time span.

### 3.2. Ozone Target values for Human Health and Vegetation

The methods used for analysis is in compliance with the ambient air quality and Cleaner Air For Europe (CAFÉ) Directive [2008/50/EC] for ozone levels in ambient air (CEC, 2008) which has been adopted into Irish law in 2011 by the Air Quality Standards Regulations 2011 (S.I. No. 180 of 2011), [http:www.epa.ie]. The Directive defines the criteria, target values and long term objectives for the protection of human health and vegetation and use $\mu$g/m$^3$ as the unit of ozone concentration in the ambient air. For ozone, two $\mu$g/m$^3$ is equivalent to one ppb and $\mu$g/m$^3$. For protection of human health, the target limit is based on a maximum daily 8-hour running mean. The running mean is calculated from hourly data and is assigned to the day on which the period ends i.e. first value of the running average on any day is the average from 1700 hrs on the previous day to 0100 hour on that day.

Earlier standard protocols provided different critical levels for injury and damage to crops, forest and semi-natural vegetation (Werner and Spranger, 1996; Karenlampi and Skarby, 1996). The approach is based on the hypothesis that long term damage results from cumulative exposure over a certain limit during the growing season, and has shown to be appropriate for several economically important vegetation species (Fuhrer et al, 1997). The limit is derived from the European Open-top Chamber Program which showed a correlation ($R^2 = 0.91$) between crop yield decline and cumulative exposure above an ozone concentration of 80 $\mu$g/m$^3$ (40 ppb) (CLAG, 1994; Fuhrer, 1994, Fuhrer et al, 1997).

For the protection of vegetation, AOT40 acts as the basis for target values and long term objectives. AOT40 is the sum of the difference between hourly concentration greater than 80 $\mu$g/m$^3$ and 80 $\mu$g/m$^3$ over a given period of time. Only daylight measurements
between 0800 hrs and 2000 hrs central European time (CET) are included in the AOT40 evaluation because the vegetation is physiologically active and most susceptible to damage during daylight. Two time periods, May to July when the vegetation is assumed to be most sensitive to ozone (Werner and Spranger, 1996) and April to September for the purpose of forest protection, are considered for AOT40 calculations.

The CEC (2008) Directive requires 90% or more of one hour values over the time period defined for calculating the AOT40 value, and for calculating the number of exceedences. The calculated parameters, maximum daily eight hour running average and AOT40, are annually scaled to the total possible number of hours to compensate for missing hourly data. The annual hourly data are considered for analysis if at least 80 % of the possible no. of hours are present in the measured data. The calculations may be considered as reasonably reliable if 90 % or more measured hours are present in the dataset. In some cases for completeness less than 80% data present are also taken into account and the cases are mentioned and flagged specifically if less than 80 % of measured data are used in figures. The presence of less than 90 % data in the scaling procedure does not make the result automatically unreliable, it only means that the results may be only indicative and quantitatively suspect. The scaled or estimated values are calculated as follows, in accordance with CEC (2008):

\[
V_{\text{est}} = V_{\text{cal}} \times \frac{N_{\text{poss}}}{N_{\text{meas}}},
\]

where

\( V_{\text{est}} \) is the estimated annual value of parameter AOT40
\( V_{\text{cal}} \) is the calculated annual value of AOT40, based on measured hourly concentrations > 80 µg/m³ summed over the relevant vegetation or forest protection period
\( N_{\text{poss}} \) is total possible no. of hours for the calculation in a year
\( N_{\text{meas}} \) is no. of hours of measured data available in a year

In a year for AOT40 (vegetation) the \( N_{\text{poss}} \) is 1104 hrs and for AOT40 (forest) the \( N_{\text{poss}} \) is 2196 hrs which is 12 hours per day (0800 hrs to 2000 hrs) from May to July and April to September respectively. For the maximum 8 hour running average for a typical 365 days year, the value of \( N_{\text{poss}} \) is 8760 i.e. all 24 hours per day are considered.
3.3. Results

Hourly averaged ozone concentration data have been analysed for the period of 1994-2009 for eight monitoring sites. The list of monitoring sites, their type, and coordinates are shown in Table 1.1. The approximate geographical location of each site is indicated in Figure 1.1.

3.3.1 Ozone Diurnal Variation

Daily ozone concentrations show a large spatial and temporal variation and depend on the site’s location and altitude. Figure 3.1 shows the mean diurnal variations during two time periods, 1996 to 1998 and 2007 to 2009 for four selected sites of Lough Navar, Monaghan, Cork-Glashaboy, and Mace Head. Time periods are selected in such a way that respective years are 11-years apart to account for the effect of solar signal. The solar cycle represents a periodic change in solar irradiation experienced by the Earth and has a period of about 11 years. So two time periods having about 11-years of separation may be considered as experiencing a similar phase of the solar cycle or about a similar amount of solar irradiation. Three years averages are calculated for May to July (MJ-969798 and MJ-070809) and April to September (AS-969798 and AS-070809). The determining factor of ozone concentration at a particular site is its coupling with the well mixed planetary boundary layer (Fowler et al., 1994; Zhang and Rao, 1999). At very high altitude sites

![Diagrams](image-url)
Figure 3.1. Diurnal variation of ozone concentrations for four monitoring sites (a) Lough Navar (b) Monaghan (c) Cork-Glashaboy (d) Mace Head. Each curve is a three years average value between May to July (MJ-969798 and MJ-070809) and April to September (AS-969798 and AS-070809) representing the variation during the growing season (most vulnerable period) for Vegetation and Forest respectively. Two time periods of three years (1996, 1997, 1998 represented as for example MJ-969798 and 2007, 2008, 2008 as for example MJ-070809) with a 11-years separation were considered to see changes in the 11 years period. The x-axis represents hours of the day and the y-axis represents ozone concentration in µg/m³.

like mountain tops where background air is well mixed with the planetary boundary layer, ozone concentration virtually remains constant or shows a very small diurnal variation (Stull, 1989; Loibl et al., 1994). The Monaghan site, a remote hilly area with altitude of 170m may come under this category, showing only a small diurnal variation as shown in Figure 3.1. Mace Head also shows a very small variation. Mace Head is a remote coastal station which is less influenced by night-time inversions and onshore breezes helps to keep air-masses fairly well mixed during night time advecting ozone rich marine air over the land (Entwistle et al., 1997). Ozone levels show a large variation with maximum concentration in remote rural areas during early afternoon (Casado et al., 1994; Sunwoo et al., 1994; Millan et al., 1996; Pedersen and Lefohn, 1994). Lough Navar shows a typical diurnal variation with lowest concentration in the morning hours, gradually increasing after sunrise and reaching highest values during early afternoon. At Lough Navar which is a remote clearing site near a semi-mature forest, the ozone loss by dry deposition during night time exceeds the supply of ozone from above leading to a sharp decline during night time. Cork-Glashaboy also shows a typical diurnal variation but less stronger than Lough Navar probably because it is located at a down-wind site.
(north-east) of a large city – that of Cork. Because of its location downwind of a large city, it shows a characteristic of urban diurnal variation having a minimum during the morning peak traffic hours due to ozone depletion by \( \text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2 \), (Coyle et al., 2002).

Changes in diurnal variation of ozone concentration during a period of about a decade (between 1996-98 and 2007-09) is clearly shown in Figure 3.1. Two kinds of sites have shown opposing patterns in the diurnal changes. The sites which are mostly influenced by background tropospheric ozone are showing least change in diurnal variation in a 11 years time period like Mace Head and Monaghan. Mace Head has shown an increase in peak afternoon ozone concentration from 1996-98 average to 2007-09 average by about 3-4 µg/m³ for both May to July and April to September data. On the other hand the sites like Lough Navar and Cork-Glashaboy, which are relatively more influenced by local ozone production and loss processes are showing a strong negative change in afternoon ozone levels in the 11 years period from 1996-1998 to 2007-2009. For the Cork-Glashaboy site May to July averages have decreased by about 6 µg/m³ and April to September averages have decreased by 10 µg/m³. The Lough Navar afternoon average is reduced by about 7 µg/m³ for both May to July and April to September averages. The Cork-Glashaboy site is even showing a decrease in ozone levels over each of the 24 hours. Almost in all cases, the May to July (MJ) averages are higher than the April to September (AS) averages except for the 1996-98 period of the Monaghan and Cork-Glashaboy sites when opposing patterns were observed at some points. This maybe because of some missing data during the peak period from May to July for these sites during 1996-98.

3.3.2 Accumulated Ozone Concentration (AOT40)

Yearly accumulated ozone above a threshold of 40 ppb in Ireland widely varies from one site to another and it also varies from one year to another. Irish ozone measuring sites analyzed here can be classified in two categories – one having high AOT40 values and the other having low values. The sites such as Mace Head, Valentia, Monaghan and Wexford may be classified as high AOT40 sites and are shown in Figure 3.2. Figure 3.3 shows other four sites Dublin-Pottery Road, Dublin-Rathmines, Lough Navar, and Cork-Glashaboy where normally low AOT40 values were observed. Figures 3.2 and 3.3 show
AOT-Vegetation and AOT-Forest values in separate column bars which are calculated from May to July and April to September each year respectively. Dotted columns using the right hand side axis show the percentage of number of hours the measured data are available each year. Note that the AOT40 values are adjusted values calculated according to the method discussed in Section 3.2.

Figure 3.2. AOT40 for vegetation (AOT-Veg, represented by blue bars) and for forest (AOT-For, represented by yellow bars) calculated for each year from 1994 to 2009 for ozone monitoring sites (a) Mace Head, (b) Valentia, (c) Monaghan, and (d) Wexford. Missing years indicate that ozone monitoring has not been started at the site. AOT-Veg are calculated from the observations made between May and July (MJ) and AOT-For between April and September (AS). Hourly concentrations starting from 0800 hr (average of 0700 hr to 0800 hr, where hr stands for hour) CT (Central European Time) to 2000 hr CT (total 13 hours) are included. Overlapping dotted lines (for the right hand side y-axis) show the percentage of hours the actual observations were made and is used to adjust AOT40 for missing observations. The x-axis represent years, y-axis (left) indicate AOT40 in µg/m^3*hr, and y-axis (right) represents percentage of total possible hours when observations were made for respective AOT40 calculations. Only for Valentia (b) the AOT-For has exceeded the value of 16000 µg/m^3*hr (actual value is 22690 µg/m^3*hr and is truncated in the figure) during 2003.
Figure 3.3. Same as Figure 3.2 but for monitoring sites of (a) Dublin-Pottery Road, (b) Dublin-Rathmines, (c) Cork-Glashaboy, and (d) Lough Navar. Note that observations in Dublin started in the year 1994 at Pottery Road site (a suburb of Dublin) but in 2002 the monitoring operation was moved to another site Rathmines, closer to the city centre. The sites fall under different categories and therefore are shown separately. The suburb site of Dublin-Pottery Road shows larger AOT40 values than that of the city site of Dublin-Rathmines.

The Dublin-Rathmines site has shown the lowest values of AOT40 during all of the years and the maximum AOT40-Vegetation, about 2000 µg/m³·hr is recorded for the year 2006. The Dublin-Pottery Road site which is a suburb of Dublin with an observational record from 1995 to 2001 shows slightly higher values than Rathmines with a maximum value of more than 4000 µg/m³·hr during the year 2000 for AOT40-Vegetation. But this value may not be reliable as the percentage of measured hours is below 80 %. The maximum AOT40-Vegetation value for Lough Navar was observed during the years 1995 and 1996 at a level of slightly less than 4000 µg/m³·hr and after that values kept below 4000 µg/m³·hr levels. AOT40-Forest levels for Lough Navar have been around
4000 µg/m³*hr except for 1995 and 1996 when they reached a level of more than about 7000 µg/m³*hr.

The long-term objective value for AOT40 for the protection of vegetation has been set at 6000 µg/m³*hr, and the target value for vegetation protection has been set at 18,000 µg/m³*hr, averaged over five years, CEC (2008). Exceedances > 6000 µg/m³*hr for vegetation at Mace Head have occurred for five years (1996, 1997, 1999, 2006 and 2008) out of sixteen years of measurements. However, a five year running average calculation results in just one year (2009) for exceedance > 6000 µg/m³*hr. For the vegetation target protection limit of 18,000 µg/m³*hr, no exceedances have been observed during 16 years of analyzed data at Mace Head calculated from April to September. The next highest AOT40 value site is Valentia where ozone measurements started in 2001. Valentia exceeded the long-term objective value for vegetation protection for four years (2001, 2003, 2006, 2008, and 2009) out of nine years of measurements. The critical value for the protection of forest was exceeded only once – during the European heat wave summer of 2003 – at Valentia (the value is 22690 µg/m³*hr and is truncated in the Figure). The other two high value sites of Monaghan and Wexford never exceeded either the target limit or long-term objective value for vegetation protection, based on a five year running average. On an individual year basis, Monaghan site was close to the long-term objective value only in 2006 (about 5990 µg/m³*hr) as shown in Figure 3.2. The low AOT40 values sites shown in Figure 3.3 never exceeded the CEC (2008) target and long-term objective values during the entire period of measurement. On an individual year basis, the site of Cork-Glashaboy was closest to the vegetation limit in 1995 (5595 µg/m³) but the percentage of measured data for this calculation is low – just around 70 % as shown in Figure 3.3.

Four observational sites, Cork-Glashaboy, Monaghan, Mace Head, and Lough Navar, having fifteen or more years of measurement record are chosen to calculate trends in AOT40 values. To account for interannual changes in ozone concentration due to variation in solar signals, an 11-year central running mean of AOT40-Vegetation and AOT40-Forest are calculated and are shown in Figure 3.4. The error bars show one
standard deviation each side from the calculated mean. Calculated 11-year running average values falls almost on a straight line showing that 11-year running mean eliminates year to year variation and is a very good approximation for a trend calculation. A linear regression is performed on the 11-year running average. The slopes which represent the trend values are indicated in the figure along with standard error in slope calculation. Mace Head and Monaghan show a positive trend for AOT40-vegetation of about $+80 \pm 21$ and $+28 \pm 16 \, \mu g/m^3*hr$ per year respectively. Sites like Lough Navar and Cork-Glashaboy have shown a strong statistically significant negative trend. For Cork-Glashaboy the negative trend value has been found to be $-200 \pm 18 \, \mu g/m^3*hr$ per year whereas for Lough Navar it is lower at $-72 \pm 14 \, \mu g/m^3*hr$ per year. Similar trends were also observed for AOT40-Forest (April to September calculation). The trend for AOT40-Forest at Mace Head of about $+194 \pm 36 \, \mu g/m^3*hr$ per year is found to be significantly stronger than for AOT40-Vegetation. For Cork-Glashaboy and Lough-Navar the trend values for AOT40-Forest are found to be negative ($-334\pm49$ and $-198\pm39 \, \mu g/m^3*hr$ per year respectively) and stronger than those of AOT40-Vegetation. Monaghan does not show any significant trend. These trends have analogous characteristics similar to the diurnal change in ozone levels and can be explained on the basis of the relative contribution of local, regional and free tropospheric influences on the hourly record.
Figure 3.4. 11-years running averages are calculated for AOT-Veg and AOT-For for four monitoring sites and the trend results are shown here. Top panel (a) is for AOT40-Vegetation trend and the bottom panel (b) is for AOT40-Forest trend. Trend values for four monitoring sites Mace Head (MH), Monaghan (MN), Cork-Glashaboy (CG), and Lough Navar (LN) shows the slope and standard error (one standard deviation each side) of linearly regressed line on 11-year running average values in $\mu g/m^3/hr$ per year. Y-axis represents respective AOT40 in $\mu g/m^3/hr$ per year.
3.3.3 Maximum Daily 8-hour Means Exceedances

To assess the ozone exposure to population for the protection of human health, an 8-hours running average is calculated from all hourly data available for the eight ozone monitoring sites and the results are shown in Table 3.1. The critical value of concentration for the protection of human health is set at 120 µg/m\(^3\) (CEC, 2008) and the no. of days are calculated when the maximum daily 8-hour running average exceeds this limit. To understand the trend in mid-percentile (between 40 and 60 percent) level ozone concentration, calculations are also performed for the no. of days when the 8-hour average concentration remained in the range 100 - 120 µg/m\(^3\) and 80 – 100 µg/m\(^3\). Linear regression is performed on the total no. of days (exceedances) in a year when the mean concentration was between these limits and also on the no. of days for more than 80 µg/m\(^3\) and the result for four stations having the longer data records are shown in Table 3.1.

Mean concentrations exceeded the critical limit of 120 µg/m\(^3\) for almost all stations during some years but never exceeded the target exceedances set by CEC which is more than 25 exceedances per calendar year averaged over three years. Dublin-Rathmines exceeded 120 µg/m\(^3\) limit only once in year 2006 during the entire 8 years of observations. Maximum exceedances (21) were recorded at the Monaghan site in the year 1995. Trend values shown in the last column have an unit of days/year and indicate no. of days per year in which mean ozone concentrations are changing. Concentration exceedances between 100 – 120 and 80 – 100 have been decreasing for all inland sites (Cork-Glashaboy, Monaghan, and Lough Navar) since 1994 (or 1995) except for the coastal site of Mace Head which recorded an increasing trend. The negative trend of concentrations exceedances between 80 and 100 µg/m\(^3\) (-1.6 ± 0.09 days/year) is found to be stronger than the trend of exceedances between 100 and 120 µg/m\(^3\) (-0.8 ± 0.3 days/year) for Cork-Glashaboy with a significant statistical confidence. This means that higher ozone concentrations exceedances are not decreasing as fast as lower level exceedances i.e. once the concentrations exceeded 80 µg/m\(^3\) chances are more that it will cross 100 µg/m\(^3\) instead of staying between 80 and 100 µg/m\(^3\). A similar trend is observed for Monaghan (-1.5 ± 1.6 days/year and -0.1 ± 0.3 days/year) and Lough Navar (-0.8 ± 0.9 days/year and -0.6 ± 0.2 days/year) sites but the results for these sites are
3.4. Ozone Exposure Levels – Conclusions and Discussion

Average ozone levels in Ireland vary between 50 to 80 µg/m³ which is almost half of the average concentration levels in central Europe but CEC criteria for protection of human heath, vegetation and forest are the same throughout Europe and apply equally to Ireland. The criteria set by CEC (2008) should not be regarded as a minimum ozone level for biological effects on humans and on vegetation; lower ozone concentrations than set limits may also be harmful for health and vegetation. Indeed, there is uncertainty regarding whether there exists a threshold value below which ozone has no effect (Royal Society Report, 2008). Daily ozone values from hourly measurements vary largely and a relatively long record of data is needed to establish patterns in ozone levels responsible for adverse effects on human health and vegetation. Ozone exposure levels in Ireland are among the lowest in Europe and the results cannot be compared quantitatively with the results from other countries where, in general, ozone levels are much higher. This work contains novel information on ozone concentration levels, such as exceedances, target values and trends for protection of human health; and AOT40 levels and trends relevant to protection of vegetation and forests.

Three years average of diurnal variation during two time periods about a decade apart (1996-1998 and 2007-2009) for four measurement sites have shown a very clear picture...
of change in ozone level at the different sites, as indicated in Figure 3.1. The sites which are most influenced by local ozone production and loss and are isolated from the rest of the troposphere during night time e.g. low altitude inland sites, have shown a significant decrease in day time peak ozone concentration in about a 11-year period. The Cork-Glashaboy site (Figure 3.1 (c)) has shown a similar reduction in night-time as well. Opposite change were noticed for sites which have stronger influence on free troposphere and Atlantic air-masses like the moderately high altitude site of Monaghan and the coastal site of Mace Head but these positive changes are not as pronounced as the negative changes in inland isolated sites.

Accumulated ozone above a threshold level of 40 ppb is calculated for vegetation and forest for May to July and April to September respectively (Figures 3.2 and 3.3). The corresponding species are supposedly most sensitive during these months with growing season and highest exposure levels. AOT40 level for almost all sites were found to be within the critical levels set by CEC (2008) legislation. A 11-year running average for four sites showed different trends depending on the location of sites. Sites like Cork-Glashaboy and Lough Navar have shown a strong negative trend for AOT40 (for both vegetation and forest) while Mace Head has shown a positive trend. The Monaghan site which is at a relatively high altitude and not completely isolated from the planetary boundary layer and night time mixing taking place does not show any significant trend. These trends are an important indicator as to the likelihood of Ireland meeting the CEC’s (2008) target and long-term objective values for the protection of vegetation.

Similar results are obtained for maximum daily 8-hour running mean exceedances, with respect to protection of human health. Exceedances above 120 µg/m³ remain well within the set critical limit of 25 exceedances per year. The number of peak ozone episodes with concentration above 100 µg/m³ in prevailing Atlantic marine air-masses observed at Mace Head seems to be increasing. Marine air-masses, when transported to mainland stations can contribute positively to observed values at those stations, which may well lead to a reduction in the probability of decreases in the no. of episodes (above 100 µg/m³) in sites like Lough Navar and Cork-Glashaboy which have recorded a significant negative trend in the number of episodes between 80 and 100 µg/m³. The Monaghan site has not shown any significant trend in the no. of episodes between these limits (80 - 100
µg/m³ and 100 – 120 µg/m³). Overall, with the exception of the Mace Head site, ozone measurement records at Irish sites show a downward negative trend in peak values that affect human health and vegetation and probably indicates the effect of a decline in ozone precursor emissions at local level.

In a recent study conducted by Lefohn et al. (2010) for many monitoring sites in US, they found two most common trends in ozone exposure. The first is a continuous negative trending for some sites over a 29-year period and the second is a shift from negative to no trend status. They also found that a very few sites exhibit statistically significant increases in the exposure indices. These results may be qualitatively comparable to our findings for Ireland and an indication of the positive impact of emission control measures undertaken by some countries. As per European Environmental Agency Report (EEA, 2009), ozone observations for the whole of Europe matches well with modelled results based on decreasing precursor emissions but regional differences still exist. The influence of changing (increasing or decreasing) precursor emissions on regional ozone concentrations is also reported in several other studies (Tanimoto et al., 2009; Wang et al., 2009, Chan and Vet, 2009). All of these studies have indicated a significant influence of precursor levels (either locally produced or transported) on ozone concentration. In addition, there is also recognition (EEA, 2007; Wilson et al, 2012) that meteorological variability could be partially masking the effect of reduction in ozone precursor emissions on ozone levels.
4. Assessment of the effects of climate change on ozone using a regional climate model

4.1 Introduction

Future air quality levels are influenced by a large number of factors. One of the most important contributing factors to future air quality is the impact of a changing climate which can affect air quality in a number of ways. Warmer climate could negatively influence air quality by increasing stagnation events which lead to significant build-up of pollutants and increasing the temperature-dependent emission rates of biogenic pollutants e.g. isoprene (Andersson and Engardt, 2010). In contrast, changing temperature could positively affect air quality by inhibiting the condensation of semi-volatile compounds (e.g. ammonium nitrate and some organics), inducing more frequent summer rains causing more wash-out and thus decreasing atmospheric pollution concentrations and increased solar radiation would enhance light-dependent dry deposition of ozone to vegetative and oceanic surface, reducing ozone concentrations (Andersson and Engardt, 2010, Coleman et al., 2011). Within this context, it is essential that Europe has high resolution predictive capability with regard to air quality parameters. The focus of this study centres on regional projections of future levels of gaseous air quality pollutants with particular reference to future ozone levels. As a tropospheric pollutant, ozone is a major contributor to poor air quality. The scale of ozone pollution is considered regional due to the local emission of ozone precursors, but it is also a global pollutant, with background ozone levels influencing local air-quality due to long range inter-continental transport (Jenkin, 2008).

Many modelling studies have been performed to investigate the effect of changing climate and emissions on future ozone trends over the United States (Bell et al., 2007, Jiang et al., 2008, Lam et al., 2011). Recently, Wild et al. (2011) evaluated the effect of changing emission patterns on surface ozone concentrations in four major global regions: North America, Europe, South Asia and East Asia, evaluating changes in surface ozone concentrations in the selected regions due to changing emission scenarios by 2050. Changes in surface ozone could be attributed to changes in individual sources, with uncertainties quantified according to spread of results from the different models.
Trends in global ozone have been previously investigated: Johnson et al., (2001) simulated global ozone up to 2100 using a coupled global model, but the future of regional trends was not addressed. Using the same coupled global model, Stevenson et al., (2005) assessed the effect of climate on global ozone up to 2030 using the current legislation emission (CLE) emission scenario (Cofala et al., 2007). The CLE scenario reflected 2005 perspectives of individual states on future economic development, but in light of more stringent pollution control strategies to be enforced in the future, and recent changes in global economics, the CLE scenario does not now represent most likely future emissions: from the most recent EU legislation, the European Commission now aims to reduce domestic emissions by 80-95% by 2050 in order to keep global warming below 2°C by the next century (Roadmap2050, 2011).

In this study, the regional influence of the changing climate and emissions on ozone over Europe and the North East Atlantic is assessed using the regional climate REMOTE (REgional climate MOdel with Tracer Extension) (Varghese et al., 2011). Annual simulations were run for time-slice years 2006, 2030, 2050 and 2100, using the RCP6.0 emission scenarios and driven by boundary conditions from the ECHAM5-HAM global circulation model (GCM) coupled to the MPIOM–HAMMOC ocean model run using the A1B emission scenario from the IPCC SRES. In order to be totally consistent, global model forcing data run with RCP6.0 emissions would have been preferential, but RCP data were not available for ECHAM5. However, reports show that the radiative forcing occurring by models using RCP6.0 emissions correlate very well up to 2100 with radiative forcing simulated using the SRES A1B emissions (Van Vuuren et al., 2009), and this gives a good degree of confidence that the use of the A1B forced global boundary conditions serves our purpose in investigating effects of climate-chemistry feedbacks for regional-scale RCP6.0 emissions.

Further simulations were performed with 2006 meteorology, but with future emissions for January and August of the time slice years to enable assessment of isolated effect of emissions on future air quality. With the ECHAM5-HAM–MPIOM-HAMMOC model results predicting a 5 degree global temperature increase by 2100, the changing climate could have significant effect on air quality in the coming century.
The primary aim of this study is the elucidation of regional-scale effects of changing climate and emissions on air quality over Europe in the coming century. In contrast to the study of Wild, et al., (2011), the effect of changing climate is considered in these model results. In addition, simulations are performed for 2100, allowing for more long-term predictions of air-quality trends over Europe. Finally, use of a robust regional model enables identification of localised regional air quality trends in different domains within Europe, allowing for underpinning of meteorological processes in different environments (e.g. from clean marine to polluted continental European). The focus of the study is on ozone pollution whilst the effect of climate change on future particulate matter levels will be the subject of a companion paper. Seasonal ozone trends are investigated for the time-slice simulation years, as well as monthly means, extremes and exceedences.

4.2. Methodology

4.2.1 Emission storyline

The emission storyline utilised in this study was chosen from the representative concentration pathways (RCP) emission scenarios which were developed for the Intergovernmental Panel on Climate Change (IPCC) 5th Assessment Report Climate Model Intercomparison Project (CMIP5) (Moss et al., 2010). Emission scenarios of the IPCC Special Report on Emission Scenarios (IPCC SRES) used in previous assessment reports (Nakicenovic et al., 2000) were based on future narratives of socio-economic scenarios and focused on greenhouse gas emissions to explore the long-term climatic effects of emissions. These scenarios do not include future projections of particulate matter emissions; their use is limited in predicting future air quality. RCP emission scenarios were developed by first establishing some radiative forcing trajectories that could be established from any number of economic, technological, demographic, policy and institutional scenarios. Researchers then identified specific emission scenarios from available scientific literature as plausible pathways to reach each predefined forcing trajectory. This emission scenario reflects only one of a number of possible emission scenarios that could result in the specific forcing trajectory chosen, hence the term
“representative” concentration pathways. The RCPs are intended for use in climate-change related research and are compatible with a range of stabilization, mitigation and baseline emission scenarios available in current scientific literature (Moss et al., 2007). The RCP pathway chosen for this study is a stabilisation pathway in which radiative forcing peaks at approximately 6 Wm$^{-2}$ at 2100 and stabilises thereafter. In this stabilisation pathway, global emissions are set to rise until mitigation takes effect (around 2050), after which time emissions decrease resulting in improved air quality (Moss, et al., 2007).

4.2.2 Model Overview

The online climate-chemistry/aerosol model REMOTE is a regional climate three-dimensional model which predicts the physical, photochemical and aerosol characteristics of the model atmosphere at every model time step (Varghese, et al., 2011). The dynamical core of the model is based on the EUROPA model, the former regional weather forecast system of the German Weather Service (Majewski, 1971).

4.2.3 Chemical Mechanism

Photochemical production and loss in REMOTE is determined by the RADM II chemical scheme (Stockwell et al., 1990) by 163 chemical reactions in the gas phase including a wide range of photolysis rates and hydrocarbon degradation reactions. In the aqueous phase, sulphate production is determined, depending on pH via oxidation by H$_2$O$_2$, O$_3$, methylhydrogenperoxide, peroxyacetic acid and is catalysed by Fe$^{3+}$ and Mn$^{2+}$. Calculation of cloud water pH is by iteratively solving a continuously-maintained ion balance (Walcek and Taylor, 1986). A full description of the aerosol modules within REMOTE will be included in the companion publication of this paper (Martin et al., 2012) and in Varghese et al., (2011).
4.2.4 Oceanic ozone dry deposition scheme

Dry deposition to the ocean is a significant loss mechanism for tropospheric ozone, representing approximately a third of global ozone loss via dry deposition (Ganzeveld et al., 2009). An advanced ozone dry deposition scheme has been incorporated into REMOTE, replacing the general gaseous deposition scheme of Wesely (1989) to explicitly simulate chemical and turbulent enhancement of ozone deposition to the ocean (Fairall et al., 2007). Chemical enhancement of dry deposition is particularly significant for a weakly soluble yet highly volatile gas such as ozone. The scheme has been advanced to include a sea-surface temperature dependent expression for ozone solubility and diffusivity, as well as a temperature and salinity dependent reaction rate between ozone and iodide (Coleman et al., 2010). The scheme was further adapted to parameterise organic reactions between ozone and dissolved organic matter (DOM), as well as a solar enhancement of ozone-DOM reactivity (Coleman et al., 2011). The enhancement of ozone deposition to iodide-enriched waters has been well documented (Chang et al., 2004), with reaction rates established for waters of varying temperatures and ionic molarities (Magi et al., 1997).

4.2.5 Model Set Up

Numerical simulations are carried out with the REMOTE model for the domain (Figure 4.1) comprising Europe and North East Atlantic with horizontal resolution of 0.5° (~50 km), 81×91 grid points. The model domain covers an area from 10° W to 30° E at the southern boundary of about 30° N and from 40° W to 60° E in the north at about 70° N. Within the primary domain, three sub-domains were selected for trend analysis – namely, a North East Atlantic marine sub-domain representing background air entering into Europe but not influenced by local emissions; a continental central (mainland) European domain expected to be predominantly influenced by local emissions; and thirdly, a hybrid domain (specifically Ireland), expected to be influenced by both marine trends and local emissions. Simulations were performed for 2006, 2030, 2050 and 2100. The regional
climate model is applied with a time step of 300s. Nineteen vertical layers of increasing thickness between the Earth's surface and the 10 hPa pressure level using terrain following hybrid pressure sigma coordinates are used in the model. The prognostic equations are written on an Arakawa-C-grid (Mesinger and Arakawa, 1976). The height of the lowest layer with prognostic trace species concentration is approximately 40 m, dependent on surface pressure.

REMOTE is initialised at the first time step using the down-scaled meteorological analysis data from the coupled ECHAM5-HAM – MPIOM–HAMMOC model (Kloster et al., 2007) which are updated at the lateral boundaries every 6 hours and used for nudging the model in the boundary zone of 8 grid cells. Monthly mean values (January and August) for temperature difference of future simulated years compared to 2006 are shown in Figure 6b whilst the equivalent data for clear sky shortwave radiation are included in supporting information. Trace species concentrations are initialised for each simulated month using the monthly mean output of the ECHAM5-HAM–MPIOM-HAMMOC model and the same data set is used at the lateral boundaries for the monthly simulation. Future anthropogenic emissions of SO$_x$, NO$_x$, NH$_3$, CO, VOC's and PM$_{2.5}$ are taken from the RCP6.0 emission scenario.

NO$_x$ emissions are split into NO (96%) and NO2 (4%) emissions. Total VOC emissions are split into VOC classes (Memmesheimer et al., 1981). With respect to primary anthropogenic aerosol emissions, number mean radius and number concentration of the respective size mode is related to the mass concentration (Stier et al., 2005).
Chemical speciation of PM2.5 emissions into POC (primary organic carbon) and BC is based on Andersson-Skold and Simpson, (2001).

In addition to anthropogenic emissions, terrestrial biogenic terpene and isoprene emissions from forests are included (Guenther, et al., 1993). Marine isoprene was calculated using isoprene water concentrations correlated to chlorophyll whilst sea-air isoprene fluxes were then calculated using the wind-speed dependent flux parameterisation of Wanninkhof, (1992) normalised for the diffusivity of isoprene (Antila et al., 2010).

For gaseous compounds other than ozone, dry deposition fluxes are determined following Wesely, (1989). Ocean chlorophyll fields are taken from satellite observations for 2006, and taken as output from global ocean model MPI-OM run under the IPCC A1B scenario for subsequent simulation years. Ocean DOM and nitrate fields were taken from the model output, with oceanic iodide fields computed from the nitrate fields using the anti-correlation from Campos et al., (1999), as done in previous model studies (Ganzeveld, et al., 2009).

4.3 Results and Discussion
4.3.1 Model validation

Simulated mixing ratios for the Irish domain for 2006 were compared with in situ ozone measurements taken at Mace Head, Galway throughout 2006 (Figure 4.2). The seasonal trend agrees well, with root mean square error (RMSE) of 2.52 and deviation of just 0.39 ppb between observed and simulated annual mean. Use of the chemically enhanced ozone dry deposition scheme improves correlation between observed and simulated ozone seasonal trends which gives a RMSE of 2.59 ppb and a difference between observed and simulated annual means of 1.07ppb compared to simulation results using the scheme of Wesely, (1989).
Figure 4.2 Comparison between seasonal trend in observed and modelled ozone concentrations (ppb) at Mace Head
Figure 4.3 shows the monthly mean ozone mixing ratios (ppb) for January, April, August and November, 2006, 2030, 2050 and 2100 within the REMOTE model domain, and

4.3.2 Monthly mean values and future trends

Figure 4.3 shows the monthly mean ozone mixing ratios (ppb) for January, April, August and November, 2006, 2030, 2050 and 2100 within the REMOTE model domain, and
changing patterns in ozone mixing ratios are apparent. For all months except January, ozone levels decrease as the century progresses, owing to decreasing emissions of ozone precursors. Low insolation in polluted areas can facilitate ozone destruction by NO\textsubscript{x} titration and this effect of reducing NO\textsubscript{x} emissions during winter months can increase ozone (Wilde et al., 2003). However, given the relatively coarse vertical resolution of the model used in this study it is difficult to attribute any future wintertime ozone increases to this effect presently. This warrants further investigation and will be a focus of future studies. The rise in ozone concentrations in January is consistent with those of Wild, et al., (2011) pointing to a 2 ppb reduction by 2050 under RCP 6.0. Their study estimated regionally averaged changes in surface O\textsubscript{3} due to changes in emissions using a parameterisation derived from the results of 14 different model studies in which the effect of precursor concentrations on simulated ozone levels is quantified. The parameterisation was then applied to future emissions scenarios and the resulting ozone mixing ratios evaluated with the uncertainty between models with each model using its own best estimate of 2001 meteorology and emissions. The effect of emissions on future ozone is elucidated and individual effects of changing particular atmospheric precursors by the establishment of continental-scale source-receptor relationships. For these precursors these source-receptor relationships are assumed to be linearly additive over the range of emission perturbation studied.

Figure 4.4 Simulated trends in annual and summer-time ozone (May to August) means (ppb) over representative sub domains and full REMOTE model domain for 2006 – 2100.
Annual means are shown by solid lines and summer-time means are shown by dotted lines.

The work presented here attempts to quantify changes on a more regional level as well as distinguishing between climate change and air quality under a particular emission storyline. Figure 4.4 shows the annual and summer-time (May to August) pollutant mixing ratio means over select domains. A general decrease in summer-time ozone levels is observed for all domains, with the most pronounced decrease of more than 8 ppb occurring over Europe during summer, governed by anthropogenic emissions. In the RCP6.0 emission scenario, emissions do not decline significantly until after 2050 when mitigation policies take effect. This is evident from the trend of mean annual ozone concentrations over Europe, which increases before stabilising and finally drops slightly between 2050 and 2100.

4.3.3 Ozone deposition

The decrease in ozone levels by the year 2100 is apparent in all domains, the main decrease occurring in the summer months. The influence of the seasonal variation of ozone concentrations over the ocean on ozone levels in Ireland is apparent by comparing trends in the North East Atlantic and Ireland: large decreases in mean ozone levels occur in the summer months for all years. This is also correlated with organic enhancement of marine deposition velocity. The annual dip in ozone concentrations in the North East Atlantic coincides with maximum ozone deposition velocities, which in turn corresponds to maximum primary productivity in the ocean as well as maximum solar enhancement of ozone-DOC reactions that accelerate ozone uptake at the ocean. Figure 4.5 shows the ocean productivity and ozone deposition velocity for the simulation years under investigation. From Figure 4.5a, ocean productivity is set to decrease between now and 2100 with a consequential decrease in ozone deposition velocity (Figure 4.5b). However, this indicates that the dry deposition process is not the determining factor in governing ozone concentrations over water bodies because a decrease in deposition velocity does not lead to an increase in ozone concentrations. Thus, other factors (to be discussed later) dominate the ozone budget over the ocean.
4.3.4 Effect of both changing climate and emissions on future ozone levels

Figure 4.6a depicts the monthly mean surface ozone mixing ratios simulated for January and August 2006 and 2100, with an additional plot of ozone mixing ratios simulated using 2006 climatology (including natural emissions) and 2100 RCP6.0 anthropogenic emissions. From Figure 4.6a the simulated change in ozone mixing ratios for the coming century can be attributed to either changing emissions or climate change. It can be seen that changing emission patterns over the century account for a large degree of simulated change in surface ozone concentration. Percentage changes in surface ozone simulated over the model domain and for the regions illustrated in Figure 4.1 are quantified in Table 4.1.
Figure 4.5 (a) Ozone Deposition velocity (cm s$^{-1}$) in North East Atlantic  
(b) Monthly Mean DOM (µM Phosphorous) concentrations in North East Atlantic

Included for comparison purposes in Table 4.1 are the equivalent values for NO$_2$ and SO$_2$. These values indicate that the effect of changing emissions is by far the most important parameter in determining future concentrations of these gases. The importance of climate in future SO$_2$ levels is more variable than with NO$_2$ due to the oceanic source of SO$_2$ from the oxidation of dimethylsulphide. Although the primary focus of this paper is on future trends in ozone, supplementary information is provided on future SO$_2$ and NO$_2$ levels in supplementary data.

2006 emissions and meteorology  
2100 emissions and meteorology  
2006 meteorology, RCP 2100
Figure 4.6a Impact of changing RCP6.0 on simulated ozone concentrations (ppb) for 2006.

From *Bell, et al.*, (2007), increasing temperature was found to account for an average increase in ozone of 4.8ppb over the United States by 2050, with ozone increases as high as 9.6 ppb. This climate-driven ozone rise was counteracted by projected reductions in emissions, leading to overall reduction in surface ozone levels of -4 to -15% by 2050. Generally, changes in emission patterns were found to dominate over changing climate in
determining future ozone trends (Jacob and Winner, 2009, Tagaris et al., 2007, Zhang et al., 2008), except for regions in which biogenic emissions are strongly influential on local ozone levels (Lam, et al., 2011). Monthly mean values (January and August) for temperature difference of future simulated years compared to 2006 are shown in Figure 4.6b. From Table 4.1, it can be seen that the changing emissions dominate the future trends in surface ozone, except in the North East Atlantic – a region representative of clean marine air influenced by hemispheric transport. The effect of climate on future ozone concentrations is regionally variable, but generally it causes an increase in surface ozone in January and a decrease in surface ozone in August. Climate-change induced decrease in surface ozone over oceans occurs due to increased photo-destruction of ozone, and due to the NO$_x$-poor marine environment, this is not compensated for by increased photochemical ozone production.
Table 4.1 Regional simulated percentage changes in surface ozone, NO\textsubscript{2} and SO\textsubscript{2} between 2006 and 2100 for January and August due to combined a) changing anthropogenic emissions and climatology, b) changing anthropogenic emissions and changing climate.

<table>
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<th>Europe</th>
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<td>August</td>
<td>January</td>
<td>August</td>
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Over Eastern Europe and parts of Scandinavia, climate change causes a reduction in ozone concentrations. This is most likely due to increased biogenic VOC emissions, which decrease surface ozone by two chemical pathways: firstly, by sequestering NO\textsubscript{x} as isoprene nitrates, thus suppressing O\textsubscript{3} formation, and secondly, by direct ozonolysis of isoprene (Fiore et al., 2005). Further, increased solar radiation could enhance dry deposition rates, resulting in considerable decreases in surface ozone depletion over vegetative regions (Andersson and Engardt, 2010).

Regional analysis of seasonal trends in surface ozone was performed over the model domain and subdomains marked in Figure 4.1. Monthly mean ozone mixing ratios with 2006 climatology and future RCP6.0 anthropogenic emission projections are shown in Figure 4.7. The decrease in ozone levels by the year 2100 is apparent in all domains, with a prominent summer time decrease. The influence of the seasonal variation of ozone mixing ratios over the ocean on ozone levels in Ireland is apparent. In the North East Atlantic, the changing emissions do not change surface ozone trends, with the decrease in 2100 levels attributable to changing climate.
Over the European sub domain, the seasonal variation in ozone mixing ratio is markedly different to those over Ireland and the Atlantic regions. From Table 4.1, and by comparison of seasonal trends with the monthly means generated using 2006 meteorology and future RCP emissions, mixing ratios can be predominantly attributed to the effect of anthropogenic emissions. Over the entire model domain, the seasonal cycle is driven by a combination of emissions and climatology. The pattern of climatological depletion of ozone over the oceans by 2100 influences the model domain, indicated by the prominent dip in 2100 ozone levels in July (seasonal peak of photo-destruction). By 2100, mean summer-time ozone mixing ratios over the whole domain are simulated to be as low as 27 ppb.
4.3.5 Variances, exceedences and extreme events

The variance is a statistical measure of the range of ozone concentrations. Figure 4.8 shows the monthly variance in ozone concentrations for representative months over the four time-slice years. It can be seen that most extreme events occur in the summertime months, because ozone production is at its maximum in warm, high pressure weather. Extreme ozone events are predicted to significantly diminish in frequency by 2100.

In Figure 4.9, the effect of emissions and climate on ozone variance is investigated. Simulations of 2006 using 2100 emissions compared with standard runs illustrate clearly that the variance in future ozone levels is predominantly driven by emissions as opposed to climatology. As well as understanding changes in variance it is important to quantify the relative change in exceedences.

The Ambient Air Quality and Cleaner Air for Europe (CAFE) Directive (2008/50/EC) was published in May 2008. It replaced the Framework Directive and the first, second and third Daughter Directive and has an air quality limit of 60 ppb (120 µg/m3) ozone. Daily 8 hour means are not to exceed this value more than 25 times per annum. To relate the simulated ozone mixing ratios to these air quality guidelines, annual exceedences of 60 ppb are shown in Figure 4.10. The values presented here are
Figure 4.8 Monthly variance of ozone concentrations (ppbv^2) for months of January, April, August and November simulated for time slice years 2006, 2030, 2050 and 2100.

instantaneous 6-hourly outputs, so they do not correlate exactly to the 8-hourly means specified in the legislation with instantaneous values being more extreme than the time averaged values. From Figure 4.10, some extreme ozone mixing ratios in 2030 cause a significant number of 60 ppb exceedences. On analysis of model output, this is due to advection of northern ozone-rich air following a large ozone pollution event, causing some high ozone mixing ratios on particular days. Otherwise, exceedences of 60 ppb ozone limit will be practically zero by 2100 over the mid-western European domain. Over the mainland European domain there is a significant reduction in the number of exceedences across the domain although there are still a significant number of exceedences in southern Europe by 2100.
Figure 4.9 Impact of changing RCP6.0 on simulated ozone variance (ppbv²) for 2006.

To assess the future of extreme ozone events both in Ireland, as a domain influenced by both background marine and local anthropogenic emissions, and mainland Europe as a region mainly influenced by local emissions, simulated monthly maximum ozone mixing ratios are shown in Figure 4.11. In Ireland, the seasonal cycle in 2006 to 2050 has a pronounced peak in summer time months. The aforementioned advection patterns in summer 2030 cause extreme ozone mixing ratios, but by 2100 when emission controls have taken effect, extreme ozone mixing ratios fall below the 60 ppb limit all year round. Comparing the seasonal cycles to monthly means of emission control simulations,
Figure 4.10 Simulated annual number of exceedences of the current European CAFÉ Directive air quality limit of 60ppb as 8 hourly mean ozone mixing ratios for 2006, 2030, 2050 and 2100 over Europe.

It is noted that the extreme ozone mixing ratios are not only determined by emissions, but are significantly influenced by climatology. Monthly exceedences for January and August simulated with the emission control runs are shown in Supporting Information given in Appendix IV. From *Air Quality Ontario*, (2010), ozone poses no human health risks for mixing ratios less than 50 ppb, but mild irritation and some vegetation damage commences at mixing ratios 51-80 ppb, with an increasing risk at concentrations in excess of 81 ppb and becomes a serious health hazard at concentrations exceeding 150 ppb. From Figure 4.11, simulated Irish ozone levels never reach hazardous levels and are significantly decreased by 2100, but over the mainland European boxed region, monthly maximum ozone concentrations are in the health-risk range (80+ ppb) for all simulated years. Extreme climate events rather than emissions cause the high ozone concentrations in Europe, for August 2050 and 2100.
Figure 4.11 Simulated ozone monthly maxima (ppb) in Ireland and Europe for time-slice years 2006, 2030, 2050 and 2100.
4.4 Conclusions

Model evaluation of the seasonal cycle of ozone mixing ratios with measurements made at the Mace Head atmospheric research station show good agreement for the 2006 reference year. Future simulations for 2006, 2030, 2050 and 2100 indicate that ozone levels are set to decrease under the RCP.6 emission storyline. There is a large degree of temporal variability in ozone seasonal cycles over the model domain which has been elucidated by interrogating a series of sub-domains. The use of a higher resolution scale allows identification of more specific processes responsible for changes in air quality in regions including over Ireland and over clean marine air where ozone levels over the Irish domain are very closely linked to North Eastern Atlantic. The reduction in European ozone concentrations are most significant after 2050 when the most significant changes in emissions due to mitigation policies occur. Peak reductions of more than 8 ppb are observed during summertime over mainland Europe by 2100. An analysis of the ozone variance suggests that the reduction in emissions under the RCP6.0 scenario will lead to a significant decrease in extreme ozone events. Exceedences over Ireland are simulated to decrease considerably by 2100 and the most extreme simulated ozone levels over Ireland would not pose a health risk. Over the mainland European sub-domain, however, simulated monthly maximum ozone levels are always in the hazardous category.
5. Appendices

Appendix I: The algorithm used for trajectories clustering

The algorithm used here is a non-hierarchical clustering algorithm, based on the work of Mattis (2002) and Dorling et al., (1992). It was implemented in C. It starts with a certain number of clusters, and then decreases the number of clusters by merging two clusters at a time. After each merging step, centroids are recalculated, and trajectories are reassigned if necessary.

Thirty synthetic trajectories (initialisers I) are created, to start the clustering procedure. The initialisers I are trajectories arriving at the final destination in a straight line, from 30 different directions. Every trajectory T is assigned to its closest initialiser I. In this way, thirty groups/clusters of trajectories are formed. At the end of this step, the initialisers I are no longer needed, they only served as an initial assignment of the trajectories to groups.

As a metric, the distance between two trajectories (e.g. trajectory T and initialiser I) is calculated as the distance between the two trajectories on the surface of the earth, averaged over all time steps. The distance between two points is calculated as the real distance (as the crow flies).

For each group, a centroid C is calculated. The centroid is a ‘trajectory’ that is derived from the trajectories in this group. It describes this group. It is calculated by averaging the latitude and longitude values for all the members of this group, for each time step. For each trajectory, it is tested if it is in the group with the centroid it is closest to. If a trajectory is closer to a centroid of a different group, the trajectory is reassigned to this other group. Once all trajectories have been reassigned (if necessary), the centroids are recalculated for the new groups.

This step - reassignment of trajectories and recalculation of centroids - is repeated, until no further reassignments are necessary. The mean distance of all trajectories from their centroid is calculated, for this clustering, noting the number of groups/clusters at this step (initially 30).
Then those two groups with closest centroids are merged, forming a new group of trajectories. The number of groups/clusters thus decreases by one. This process is repeated until all trajectories end up in one group/cluster.

The algorithm can be summarized as follows:
1. The creation of 30 group/cluster initializers I
2. Every trajectory T is assigned to the closest initializer I
3. For each group, a centroid C is calculated
4. For each T: check if it is in the right group, otherwise reassign; recalculate centroids. Repeat 4 until no reassignments are necessary
5. Mean distance (for T from its C) for this clustering is calculated and noted as a function of the number of clusters
6. Merge two groups with closest centroids
7. Repeat 4 – 6 until all T are in one group

**Number of groups/clusters**

To determine the optimum number of clusters, the relative change in overall mean distance calculated for each number of clusters – step 5 of the algorithm – is plotted as a function of the number of clusters. The overall mean distance usually increases slightly with decreasing number of clusters. However, if there is a strong increase in overall mean distance, this is an indication that two clusters have been merged that are dissimilar. The number of clusters just before this merging is then a good choice.

**Appendix II: A Seasonal Trend Decomposition (STD) procedure for analysis of time series**

A time series can be decomposed into seasonal, trend, and remaining components (Cleveland et al., 1990), in order to assess a trend of longer term data. These components can be considered to be multiplied to give the original series or added to give the original series. Depending on the approach of series modeling they are called a multiplicative or an additive model. In this work, the additive model is used for the decomposition and the series can be expressed as:

\[(\text{Series})_t = (\text{Trend})_t + (\text{Seasonal})_t + (\text{Error})_t\], where \(t\) is the point of time.
For decomposition of a time series, the commercial software MINITAB is used for this analysis. The data are first seasonally adjusted and then a linear trend line is fitted on this seasonally adjusted series using least squares linear regression. To adjust the series seasonally, the seasonal indices are first calculated for each month from smoothed series. The series is smoothed with a central moving average procedure of the order of the length of seasonal cycle. The moving average is then subtracted from the original data to obtain raw seasonal values. Medians of the corresponding time periods (time periods 12 months apart) of this raw seasonal cycle are then adjusted to give their average as zero. These adjusted medians are called seasonal indices and are used to adjust the data seasonally. This is called a seasonal trend decomposition (STD) procedure and the representative model of the time series is called a STD model.

Appendix III: Auto-Regressive Integrated Moving Average (ARIMA) model

An autoregressive model is used to understand a time series and predict future values. The value of the variable in question at any point of time in a time series, say \(X_t\), depends on the past history and can be expressed in terms of one or more prior values and corresponding white noise or random shocks. The number to which we go back to and represent the present value is called the order of autoregressive model. In a linear autoregressive model, the dependence of \(X_t\) on its past values and error terms are supposed to be linear and here we consider a linear model. In mathematical terms, an autoregressive model for a time series \(X_t\) can be expressed as:

\[
X_t = \sum_{i=1}^{p} \phi_i X_{t-i} + \epsilon_t + c
\]  
(A1)

where \(\phi\) are the parameters of the model to be calculated, \(c\) is a constant (often omitted for simplicity of the model), and \(\epsilon\) is the error terms or random shocks with zero mean. For a first order autoregression, the series can be expressed as a linear function of the previous value.

\[
X_t = \phi X_{t-1} + \epsilon_t
\]  
(A2)
The parameter $\varphi$ can be calculated using various methods and the most commonly used method is a linear least squares technique. So autoregression is simply a linear regression of the current value against previous value(s).

Another approach to represent a term in a time series or predict future values is to represent it in the terms of moving averages. Here a term of the series is represented in terms of the mean of the series and error terms of a past number of values. The number here is called the order of the moving average model. Mathematically, a $q$-order moving average model of a time series $X_t$ can be expressed as:

$$X_t = \mu + \varepsilon_t + \sum_{i=1}^{q} \theta_i \varepsilon_{t-i}$$

where $\theta$‘s are parameters, $\mu$ is the mean of the series and $\varepsilon_t$ are error terms. For the first order moving average, the series becomes:

$$X_t = \theta \varepsilon_{t-1} + \mu + \varepsilon_t$$

(A4)

Comparing the above two different model equations (A1) and (A4), it is clear that the moving average model is the linear regression of the current value against random shocks of the preceding value(s). The difference between the two approaches is that in a moving average model, the random shocks of prior values are propagated to the future values of the time series.

To identify a possible model for a time series, the plots of an autocorrelation function (ACF) and partial autocorrelation function (PACF) for the series are useful methods. They can also be used to identify the periodicity or seasonality in the time series if present. Autocorrelation plots are also useful in identifying non-stationarity in the data and in that case, initial differencing steps are required to make the data stationary. Sometimes both the autoregressive (AR) and moving average (MA) terms are used to model the time series. The approach to identify the model, if one or both models are needed, is called Box-Jenkins approach (Box and Jenkins, 1970) to model a time series. If both terms are used to model a time series, then the model is called the autoregressive moving average model or ARMA model and a term in the time series is dependent on the past history as well as on the past error terms. In case of a non-stationary time series, if a differencing term is used to make the series stationary, the model is called an
autoregressive integrated moving average (ARIMA) model. The above approach is used to identify the model using commercial statistical software SPSS for time series of ground ozone data.

ARIMA analysis does not give a direct explanation for the time series but the model fitted data give an idea of trend and seasonal variation. For ARIMA analysis, various tests need to be performed to check what kind of model fits best the data series: whether it is a moving average or regression or a mixture of both. Note that the ARIMA predicted time series for the surface ozone monthly mean values starts at the 13\textsuperscript{th} month and is explained in the following paragraph as an example for Rathmines time series analysis. More details of the ARIMA procedure and relevant references are given by Junker et al., (2004).

First transformation of the time series (e.g. for Rathmines) is an order of seasonal differencing: the new series starts at the series index number 13 with the value equal to the value at series index number 13 minus the value at series index number 1. The new series has a lesser number of points (12 less) than the original series. Autocorrelation function (ACF) and partial autocorrelation function (PACF) analysis of the new series shows that the best fit model has a non-seasonal moving average (MA) of first order and a seasonal MA of first order. This means that the value of surface ozone at a particular month is a function of its value at the preceding 12\textsuperscript{th} month (because of seasonal differencing) and a function of the fluctuations in the present month and preceding month (both because of the presence of first order of the non-seasonal MA), 12\textsuperscript{th} preceding month, and the 13\textsuperscript{th} preceding months (for the presence of first order of seasonal MA). The main difference between ARIMA and STD approaches and their treatment of the time series is outlined in the following points:

1. STD uses smoothing technique to decompose time series into trend and seasonal components and ARIMA looks for any correlation in the time series – seasonal or non-seasonal.

2. STD is useful in time series with a constant trend and seasonal pattern whereas ARIMA can be used for any kind of time series with or without a trend or seasonal pattern.
3. STD model is independent of the original time series whereas ARIMA model is represented as a function of the original time series.

4. STD is useful in trend analysis and long range forecasting whereas ARIMA is more useful in modeling patterns that are not easily detected in plotted data or STD models.

Besides these differences both models can be used to model a time series with a constant trend and seasonal pattern and they are used here for monthly mean ozone time series. ARIMA treats seasonal fluctuations (particularly for exceptional values of surface ozone such as during spring of 2003) as seasonal variations and next year’s values are correlated with these exceptional values. But in the STD approach, high peak values in 2003 are adjusted (when data are de-seasoned) in a way that most of their values are attributed to the error terms, leaving the series with less seasonal variation. This makes sense when there are large annual variations and particularly seasonal variations of ground level ozone. But this comes with a cost: part of the seasonal adjustment (de-seasoning) goes towards the trend part and the de-seasoned series show a stronger trend. This competition between seasonality and trend effects by two modeling approaches might be smoothed if the length of the series is longer, giving more importance to a continuous and a longer record of surface ozone at a site.

**Appendix IV: Supporting Information relating to Section 4 of the Report**

Monthly mean and monthly maximum NO$_2$ and SO$_2$ concentrations over three sub-domain regions of the North East Atlantic, Ireland and Europe and over the primary REMOTE domain, (as shown in Figure 4.1) are shown below [Figures A.2, A.3, A.4, A.5, A.6, and A.7] for years 2006, 2030, 2050 and 2100. Also shown are simulated trends of annual and summer-time means of NO$_2$ and SO$_2$ concentrations [Figure A.1]. In addition, difference in clear sky net surface radiation (W m$^{-2}$) for months of January and August for years 2006, 2030, 2050 and 2100 compared to the base year of 2006 are shown [Figure A.8].
Figure A.1: Simulated trends in annual and summer-time (May to August) means of a) NO$_2$ (ppb) and b) SO$_2$ (ppb) concentrations over select regions over the period 2006 – 2100. Annual means are shown by solid lines and summer-time means are shown by dotted lines.
Figure A.2: Monthly mean NO$_2$ (ppb) concentrations for 2006, 2030, 2050 and 2100, in boxed regions illustrated in Figure 4.1 and over the model domain.

Figure A.3: Monthly maximum NO$_2$ (ppb) concentrations simulated over Ireland and over the whole domain for each simulated year.
**Figure A.4:** Monthly mean SO$_2$ concentrations for 2006, 2030, 2050 and 2100, in boxed regions illustrated in Figure 4.1 and over the model domain.

**Figure A.5:** Monthly maximum SO$_2$ (ppb) concentrations simulated over Ireland and over the whole domain for each simulated year.
Figure A.6: Simulated monthly mean NO₂ (ppb) mixing ratios for January, April, August and November for simulation years 2006, 2030, 2050 and 2100.
Figure A.7: Monthly mean simulated SO$_2$ (ppb) mixing ratios over the model domain for years 2006, 2030, 2050 and 2100.

2030-2006  2050-2006  2100-2006
Figure A.8: Difference in clear sky net surface solar radiation (W/m²) for January and August 2030, 2050 and 2100 compared to the base year of 2006.
6. References


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Fowler, D., Smith, R. I. and Weston, K.J., 1994, Quantifying the spatial distribution of surface ozone exposure at the 1 km _ 1 km scale in J. Fuhrer and B. Achermann (eds), Critical levels for ozone: A UNECE workshop report, Schriftreihe der Les Cahiers de la FAC Liebefeld 16, Liebefeld-Bern, Switzerland: 196-205.


2557–2566.


ozone for protection of human health, vegetation and forest in Ireland, submitted for publication.


### 7. Acronyms

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<th>Acronym</th>
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<td>ACCENT</td>
<td>Atmospheric Composition Change: The European Network</td>
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<td>ACF</td>
<td>AutoCorrelation Function</td>
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<td>AOT40</td>
<td>Yearly accumulated Ozone above a Threshold of 40 ppb</td>
</tr>
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<td>ARIMA</td>
<td>AutoRegressive Integrated Moving Average</td>
</tr>
<tr>
<td>ARMA</td>
<td>AutoRegressive Moving Average</td>
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<td>CAFÉ</td>
<td>Clean Air For Europe</td>
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<td>CLRTAP</td>
<td>Convention on Long-Range Transboundary Air Pollution</td>
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<td>COST</td>
<td>Cooperation in Science and Technology</td>
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<td>Department for Environment Food and Rural Affairs</td>
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<td>ECMWF</td>
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<td>EESC</td>
<td>Equivalent Effective Stratospheric Chlorine</td>
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<td>GAW</td>
<td>Global Atmosphere Watch</td>
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<td>HYSPLIT</td>
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<td>INSCON</td>
<td>INternational SCience CONsultants</td>
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<td>MATCH</td>
<td>Determination of Stratospheric Polar Ozone Losses</td>
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<td>MBL</td>
<td>Marine Boundary Layer</td>
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Table 3.1. Exceedances of 8 hour running average values and trends for different ozone concentration ranges [>120; 100-120; 80-100 and > 80 µg m\(^{-3}\)] for the 8 ozone monitoring sites, over the years from 1994 to 2009. Trend values shown in the last column have a unit of days / year.

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|           |      | 7 | 14 | 14 | 4 | 3 | 7 | 6 | 7 | 1 | 8 | 4 | 2 | 1 | 2 | 5 | 1 | -0.6 ± 0.2 |
| 100-120  |      | 70 | 41 | 41 | 32 | 23 | 65 | 47 | 38 | 46 | 53 | 57 | 81 | 35 | 21 | 50 | 14 | -0.8 ± 0.9 |
| 80-100   |      | 78 | 63 | 63 | 39 | 27 | 72 | 55 | 48 | 47 | 63 | 61 | 85 | 42 | 24 | 58 | 15 | -1.5 ± 1.0 |
| >80      |      | 78 | 63 | 63 | 39 | 27 | 72 | 55 | 48 | 47 | 63 | 61 | 85 | 42 | 24 | 58 | 15 | -1.5 ± 1.0 |