<table>
<thead>
<tr>
<th>Title</th>
<th>Regional Scale Modelling of Boundary Layer Ozone and Influences of Climate Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Coleman, Mary</td>
</tr>
<tr>
<td>Publication Date</td>
<td>2013-02-20</td>
</tr>
<tr>
<td>Item record</td>
<td><a href="http://hdl.handle.net/10379/3278">http://hdl.handle.net/10379/3278</a></td>
</tr>
</tbody>
</table>
Regional Scale Modelling of Boundary Layer Ozone and Influences of Climate Change

A thesis submitted for the degree of

Doctor of Philosophy

to the

School of Physics

National University of Ireland Galway
July 2012

by Mary Coleman

Under the Supervision of

Prof. Colin D. O’Dowd
“The grand aim of all science is to cover the greatest number of empirical facts by logical deduction from the smallest number of hypotheses or axioms.”

Albert Einstein
Contents

Acknowledgements v

Abstract vii

Introduction 1

1.1 Climate . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 2
  1.1.1 Climate impacts of Greenhouse Gases . . . . . . . . . . . . . . 3
  1.1.2 Climate Impacts of Atmospheric Aerosols . . . . . . . . . . . . 4
1.2 Ozone . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 5
  1.2.1 Chemical properties of Ozone and Atmospheric Cleansing . . . 6
  1.2.2 Health Impacts of Ozone . . . . . . . . . . . . . . . . . . . . . 6
  1.2.3 Ozone Trends and Regulation . . . . . . . . . . . . . . . . . . 7
  1.2.4 Current Regulation of Ground-level Ozone . . . . . . . . . . . . 9
  1.2.5 Future Trends of Ozone as determined by Emission Scenarios . 10
  1.2.6 Sources and Sinks of Tropospheric Ozone . . . . . . . . . . . . 13
  1.2.7 The Tropospheric Ozone Budget . . . . . . . . . . . . . . . . . 22

Questions Addressed in the Thesis 25

Review of Papers 28

Conclusions and Outlook 36

Bibliography 41

Appendices 53
A Dry Deposition Parameterisation of Wesely (1989) . . . . . . . . . . . 54
A1 Derivation of $R_a$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 54
A2 Derivation of $R_b$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 57
A3 Derivation of $R_c$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 61
A4  Calculation of Deposition Velocity ...................... 62
B  Ozone dry deposition parameterisation of Fairall et al. (2007) .... 63
B1  Ocean surface transfer velocity from fundamentals ........ 65

Papers 68

Paper I: Regional-Scale Ozone Deposition to North-East Atlantic Waters ....................................................... 70
Paper II: Photochemical Impact on Ozone Fluxes in Coastal Waters 87
Paper III: Assessment of changing meteorology and emissions on air quality using a regional climate model: Impact on Ozone 94
Acknowledgements

I acknowledge the EPA for their financial support of this research project which was carried out in the Centre for Climate and Air Pollution Studies at the School of Physics in the National University of Ireland, Galway.

I’d like to express my gratitude to the members of the group for the opportunity to work beside and learn from esteemed and outstanding scientists. Not least, I’d like to acknowledge my supervisor Prof. Colin O Dowd for steering my research and for generously sharing his abundant knowledge. Also, thanks to Prof. S.G. Jennings for his generosity of time and advice throughout the duration of this work.

Thanks to Dr. Mark Lang and the School of Physics for providing support and facilities.

I am deeply grateful to the members of the modelling group, Dr. Saji Varghesse and Dr. Robert Flanagan for sharing their technical expertise. Thanks also to Dr. Baerbel Langmann for her generosity of time and information.

I also thank my fellow students, whose company made my experience throughout this work much more enjoyable. I especially thank Ciaran Monahan for his tireless generosity and making available the resource of his technological agility. Thanks also to Ann and Aditya for advice and discussion on topics vast and eclectic.

I wish to thank Dr. Indie Olbert and Dr. Tomasz Dabrowski for making available their data and also to Alastair McKinstry for support with computational issues.

Thanks to Dr. Mairead Hurley and Michael Coleman for sharing their time and expertise in technical language.
I'd like to thank my parents for their most welcome support which enabled me to complete this work. Míle buchas freisin do Pháidín, Rosie agus Cuan a chabhraigh liom an meon caoi a choimeád le linn an saothair seo.
Abstract

Regional Scale Modelling of Boundary Layer Ozone and Influences of Climate Change

by Mary Coleman

Ozone is a major air quality parameter, a key player in atmospheric chemistry and instrumental in greenhouse gas forcing. Consequently, the subject of ozone pollution warrants significant consideration in the construction of efficient pollution control measures. Ozone is a powerful oxidising agent, and has a complex chemistry with nonlinear relationships between precursors and ozone formation. In order to make any worthwhile predictions about the future of ozone levels their consequences for the earth’s climate, models must have the ability to simulate accurately ozone transport, chemistry and long term trends accurately.

Existing climate models have not been able to reproduce the rising trends in background ozone levels that have been observed at remote marine sites. This calls into question the ability of such models to predict future ozone trends. Background ozone levels are influenced by the hemispheric transport of ozone and relevant removal processes during such transport. One such removal process is the dry deposition of ozone to the ocean surface.

Although the downward flux of ozone to land surfaces exceeds the downward flux to water by an order of magnitude, the dry deposition of ozone to water surfaces is a sizeable removal process for tropospheric ozone given that two thirds of the earth’s surface is covered by water. The mechanisms involved in the deposition process are not entirely understood, current knowledge on dry deposition being unable to account for some elevated flux measurements. The enhancement of ozone deposition due to reactions between ozone and organic matter has been identified as a possible mechanism accelerating the rate of dry deposition, but the kinetics of
sea-surface reactions between ozone and organic matter are still relatively unknown, as is the effect of these reactions on deposition rates of ozone to the ocean. This thesis advances the current knowledge of processes governing the dry deposition of ozone to the ocean and investigates the effects of emission mitigation and changing meteorology on air quality with respect to tropospheric ozone levels using regional climate model, REMOTE.

Results show that although modelled boundary layer ozone levels are relatively insensitive to the rate of ozone deposition, an upward flux of iodine compounds occurs as a consequence of marine ozone deposition. This flux is sensitive to the deposition rate and was quantified as being of potential global significance. Further results indicate a photoenhancement of reactions influencing ozone deposition which may bridge the gap between observed elevated flux measurements and flux magnitudes accounted for by current theory. Finally, the effect of changing precursor emissions and changing meteorology on future ozone pollution levels was investigated. Results suggest that over the European mainland, future ozone levels will be predominantly driven by emissions whereas in the clean marine environment of the North East Atlantic, changing meteorology will predominate in determining future ozone levels.

Keywords: Ozone, marine dry deposition, air quality, climate
Introduction

“There’s so much pollution in the air now that if it weren’t for our lungs there’d be no place to put it all.”

Robert Orben

The earth’s atmosphere is a complex, dynamic system of gases, comprising mostly nitrogen, oxygen, noble gases and small but highly variable quantities of trace gases. Pollutants in the earth’s atmosphere exist as gases or as liquid or solid particles suspended in the air, in concentrations significant enough to adversely affect life on earth, the natural environment or man-made structures.

The lifetime of pollutants in the atmosphere varies from minutes to days (aerosol particles) or from seconds to millenia (gas molecules). During the time period in which a pollutant resides in the atmosphere, it can be transported over sizeable distances and may undergo a number of physical and chemical changes while interacting with other atmospheric components via homogenous or heterogeneous processes, possibly forming secondary pollutants. In this way, pollutants have the capacity to alter significantly the chemical properties of the atmospheric system.

The Oxford dictionary describes pollution as the presence in, or introduction into the environment of a substance which has harmful or poisonous effects. It can be argued that the earth’s atmosphere has been “polluted” since the formation of the planet as a result of natural occurrences such as volcanic activity, biomass burning, and dust storms. Since the industrial revolution, anthropogenic activities have caused a phenomenal increase in atmospheric air pollution levels, to the extent of forcing global climate.
1.1 Climate

Climate refers to the long-term behaviour of the weather over time scales of decades to centuries. The climate system of the earth has always been in a state of flux, changing according to cyclical patterns determined by natural forcings. The time scales of identified climate cycles range from decades to millions of years and the cycles often overlap: therefore, climate cycles and patterns are difficult to identify. Factors inducing climate change include variations in solar radiation output, deviations in the planetary orbit and motion of tectonic plates. Tectonic plate activity causes variation in the topographical profile of the earth’s surface and alters ocean circulation patterns - a critical determining factor in the global climate. Further, tectonic activity could alter the global carbon cycle by exposing calcium-silicate rocks at the surface of the earth. During the weathering process, atmospheric $CO_2$ reacts with calcium-silicate in the presence of water thus sequestering the $CO_2$ (Goosse et al., 2010).

Generally speaking, the most fundamental variable in defining climate is global annual mean surface temperature. Since the formation of the planet, the earth has been oscillating between climate states. The earth’s climate state today is a cold period, with global temperatures nearly 15°C lower than temperatures of warmer climate states (Scotese, 2002). The present scientific consensus is that anthropogenic activity and consequent air pollution is the most likely cause of the rapid rise in global average temperature observed over the past three decades (IPCC, 2007), whereas the temperature rise in the earlier part of the 20th century is more likely to be attributable to natural forcings or unforced natural variability. This theory is supported by model studies conducted by Meehl et al. (2004) in which global warming in the latter part of the century cannot be simulated without considering anthropogenic climate forcing, whereas the global warming in the early 20th century can be simulated considering only natural forcing in the model.

Global temperature adjusts so as to balance incoming solar energy and emission of heat-energy to space. Of all the solar radiation that reaches the earth’s surface, roughly 30% is reflected back to space due to scattering by clouds, air molecules, atmospheric aerosols and the surface of the planet. The remaining 70% of the radiation is absorbed by the earth.

Of the energy reflected, around 70% is lost to clouds, 12% is lost at the surface,
and the rest is scattered. In order to maintain a stable climate, the energy absorbed by the earth must eventually be reradiated back out to space by the climate system. This is achieved through emission of longwave radiation by the planetary surface. Of the energy absorbed by the earth, atmospheric constituents absorb around 30% (Ramanthan, 1987). Much of the longwave radiation emitted from the planetary surface is trapped in the atmosphere by naturally occurring greenhouse gases and re-radiated in all directions. This is known as the natural greenhouse effect. This effect has been augmented in recent years by an increase in greenhouse gases due to anthropogenic activities, causing an elevation in global temperatures (see Section 1.1.1). The greenhouse effect renders the effective radiating temperature of the earth-atmosphere system lower than the actual surface temperature, thus maintaining the delicate solar radiation balance of the planet, while enabling the planet to maintain an average surface temperature of around 15°C.

Any perturbations to the delicate energy balance may affect the amount of energy reaching the earth or the radiation lost to space and could thus induce change in the climate. *Radiative Forcing* refers to a perturbation to the energy balance of the earth which is of sufficient magnitude to potentially alter the global surface temperature. The IPCC (Intergovernmental Panel on Climate Change) defines radiative forcing as the change in net irradiance at the tropopause after allowing for stratospheric temperatures to re-adjust to radiative equilibrium, whilst the surface and tropospheric temperatures and state remain fixed at the unperturbed values (Ramaswamy, 2001). The Earth’s radiation balance could be affected by altering the energy-absorbing or energy-scattering properties of the atmosphere.

It has long since been established that the increase in atmospheric greenhouse gas and aerosol concentrations since the beginning of the industrial revolution are consequences of anthropogenic activities (Roeckner et al., 2006), and the change in the atmospheric components have been sufficiently significant as to cause a major radiative forcing of the Earth’s climate (Ramaswamy, 2001).

### 1.1.1 Climate impacts of Greenhouse Gases

The IPCC Third Assessment Report (IPCC, 2001) states that most of the global warming observed in the latter half of the 20th century is likely to be as a direct consequence of elevated atmospheric greenhouse gas levels caused by anthropogenic activity.
Since the 1820s, scientists have been aware of the *natural greenhouse effect* (Fourier, 1824), whereby infrared radiation reflected off the planetary surface is absorbed by atmospheric *greenhouse gases* (water vapour ($H_2O$), carbon dioxide($CO_2$), methane ($CH_4$), ozone ($O_3$) and nitrous oxide($N_2O$)) which trap and re-radiate the radiation omni-directionally, transferring energy back to the planetary surface and the lower atmosphere thus elevating the surface temperature of the earth. The term “greenhouse gas” refers to an atmospheric trace gas with the ability to absorb and re-radiate infrared radiation. The *enhanced greenhouse effect* refers to the augmentation of the greenhouse effect due to the increased concentrations in the earth’s atmosphere of anthropogenically sourced long-life greenhouse gases since the dawn of the industrial era. The IPCC fourth assessment report (IPCC, 2007) states that the increase in the mean annual planetary temperature since the middle of the 20th century is likely to be a direct consequence of increases in anthropogenic greenhouse gas concentrations.

Water vapour is responsible for most of the greenhouse effect. Human activities do not hugely influence the atmospheric content of water vapour, but other greenhouse gases have anthropogenic as well as natural sources. Although $CH_4$ is 80 times more effective than $CO_2$ as a greenhouse gas, $CO_2$ is the trace gas that contributes most significantly to the greenhouse effect. This is due to its abundance in the atmosphere (average concentration of 390ppmv) and its long atmospheric lifetime (estimated at 200 years (Seinfeld and Pandis, 1997)). Tropospheric ozone is also a significant greenhouse gas and is 25% as effective as $CO_2$ in absorption of incoming solar UV radiation and reflected long wave IR radiation (IPCC, 2001).

### 1.1.2 Climate Impacts of Atmospheric Aerosols

In addition to greenhouse gases, atmospheric aerosols also affect the global energy balance. Greenhouse gases act only on the longwave radiation reflected from the earth’s surface, but aerosols can act on incoming solar radiation as well as reflected long wave radiation, thus influencing both sides of the planetary energy balance.

Aerosols have the capacity to scatter and absorb incoming solar radiation. Aerosols of diameters less than 1µm scatter incoming radiation particularly efficiently (Seinfeld and Pandis, 1997). In addition to absorption and scattering effects,
aerosols can alter properties of clouds, such as albedo and lifetime. The combination of these scattering and cloud-altering effects can lead to a phenomenon known as global dimming (Roderick and Farquhar, 2002) whereby atmospheric aerosols reduce the global direct irradiance at the Earth’s surface, causing a global cooling effect.

SO$_2$ emitted from industrial sources oxidises to form sulphate (SO$_4^{2-}$), which constitutes much of these light-scattering aerosols (Seinfeld and Pandis, 1997). Biomass burning and fossil fuel combustion are also prominent sources of atmospheric aerosols, mostly in the form of organic matter and soot. Soot refers to the internally mixed agglomerates that are formed when black carbon (BC) and particulate organic matter (POM) are co-emitted (Roeckner et al., 2006). Because of its size and composition, BC can absorb as well as scatter radiation, but the absorption properties of soot can be considerably greater than those of BC, depending on the chemical properties and mixing state of the soot (Jacobson, 2001). Mineral dust is also present in the atmosphere: this occurs where winds pass over and entrain soil, a process that is enhanced by anthropogenic soil disruption and land use change. Mineral dust can also absorb radiation as well as scatter it. The scattering effect of mineral dust dominates over the absorbing effect in the visible part of the spectrum, which leads to an overall cooling effect, whereas in the infra-red spectrum, mineral dust absorbs radiation, leading mineral dust to behave as a greenhouse gas (Seinfeld and Pandis, 1997).

As stated above, aerosols can considerably alter the properties of clouds. Modelling studies have shown that the observed global mean annual temperature increase of 0.3 - 0.6 °C from the mid 19th Century to the present cannot be explained solely by greenhouse gas effects; that the inclusion of aerosol-forcing in climate models is necessary to simulate observed temperature patterns (Wigley and Raper, 1992; Engardt and Rohde, 1993; Santer et al., 1993, 1995; Mitchell et al., 1995).

1.2 Ozone

The stratosphere houses approximately 90% of atmospheric ozone (Newman, 2003) where a high concentration of ozone forms the stratospheric ozone layer. This ozone layer absorbs harmful UV rays, preventing them from travelling to the earth’s surface. Ozone mixing ratios in the stratosphere ozone levels are as high as 10,000 parts per billion, or ppb (Seinfeld and Pandis, 1997), whereas tropospheric mixing ratios
are relatively small, of the order of a few tens of ppb. In the troposphere, ozone is one of the main constituents of photochemical smog, a toxic pollutant and is instrumental in greenhouse gas forcing. Radiative forcing of tropospheric ozone is roughly 25% that of CO$_2$ (IPCC, 2001) (US-EPA, 2003). Currently, stratospheric ozone levels are depleting, whilst tropospheric ozone levels are on the rise (WMO, 1986), causing much consternation for global authorities and the scientific community.

1.2.1 Chemical properties of Ozone and Atmospheric Cleansing

The ozone molecule was discovered in the mid 19th century by German-Swiss chemist, Christian Friedrich Schönbein in the laboratory and since then, it has been the subject of much scientific research. Physically, ozone is a pale-blue gas with a distinctive, pungent odour, caused by ions which are formed during the rapid chemical changes associated with ozone. Ozone owes its name to its distinctive odour (ozein being the Greek for the verb ”to smell”). The ozone molecule consists of three oxygen atoms. It has a bent C$_2v$ symmetry, with a distance of 1.27 Å and an angle of 116.8° between the oxygen atoms. The molecule is formed with one single and one double bond. These bonds blend to form a resonance structure with 1.5 bonds between each pair of oxygen atoms. It is a powerful, reactive oxidant that is very unstable at high temperatures. Ozone heavily influences the oxidising capacity of the atmosphere as the dominant precursor to the ubiquitous hydroxyl radical which acts as an atmospheric cleansing agent by determining the lifetime of important atmospheric trace gases (Seinfeld and Pandis, 1997). Specifically, the photodegradation of ozone can produce excited oxygen atoms that can only be returned to ground state by collision with another atmospheric species, most often colliding with nitrogen or oxygen molecules, thus removing these trace gases from the atmosphere. Occasionally, the excited oxygen atom collides with a water molecule to produce two OH radicals. This reaction is the only tropospheric gas-phase reaction known to break the double hydrogen bound in water molecules (Seinfeld and Pandis, 1997).

1.2.2 Health Impacts of Ozone

In the stratosphere, the zone of high ozone concentration at altitudes 15-30 km above the earth’s surface is known as the ”Ozone layer”. Within the ozone layer, ozone mixing ratios range between 3000 and 5000ppb. The high concentration of ozone molecules filter out solar ultra violet (UV) rays which are harmful to human
life. UV rays can cause sunburn and eye damage, and some UV rays are sufficiently energetic as to break DNA bonds which can result in cell damage and lead to further complications including skin cancer (Newman, 2003). The role played by stratospheric ozone is therefore beneficial to life on earth.

In the troposphere, however, ozone is hazardous to human life even in very low concentrations. (US-EPA, 2003). Ozone levels in Ireland are monitored by the EPA because human exposure to high concentrations can induce of chest pains, nausea and coughing whereas long term exposure can reduce lung capacity and exacerbate heart disease, emphysema, bronchitis and asthma. The current WHO guidelines recommend an eight-hour mean ozone mixing ratio limit of 50ppb. The limit has recently been lowered from 60ppb, based on recent studies linking ozone concentrations to daily mortality. Obviously, the negative impact of ozone upon health is a function of ozone concentration and time of exposure. In mixing ratios less than 50 ppb, ozone poses no health risk. When the mixing ratios excess 50ppb, ozone causes mild respiratory irritation in humans and some damage to vegetation. The impact increases with increasing mixing ratios of ozone, with possible lung damage casued at mixing ratios in excess of 80ppb. At mixing ratios exceeding 150ppb, ozone becomes a serious health hazard (Air Quality Ontario, 2010)

1.2.3 Ozone Trends and Regulation

In the last few decades, a simultaneous increase in tropospheric ozone and decrease in stratospheric ozone has been found. This is a cause for concern considering the respective positive and negative roles played by ozone in the stratosphere and the troposphere. In the troposphere, the rising ozone levels have a negative impact because of ozone’s toxicity and its role in global warming. Volz and Kley (1988) found by analyzing measurements made from 1876 to 1910 that mean ozone mixing ratios for this period were around 10ppb compared to modern-day ratios of between 20 and 45 ppb. This rise in levels of tropospheric ozone can be attributed to an increase in anthropogenic emissions of ozone precursors (NOx and non-methane hydrocarbon) since the industrial revolution.

To investigate intercontinental transport of air pollution in the Northern Hemisphere, the United Nations Economic Commission for Europe (UNECE) established the Task Force on Hemispheric Transport of Air Pollution (TF HTAP). A comprehensive report was issued by the TF HTAP in which extensive research into the
intercontinental transport of air pollution was conducted with a view to reviewing pollution protocols. The report for ozone and particulate matter was produced by Dentener et al. (2010). Among its conclusions were that mid-latitudinal ozone levels increased by a factor of two or more during the latter half of the 20th century. This trend was attributed to increases in anthropogenic emissions. The effect of emission mitigation to date was observed by the TF HTAP, where the ozone increase in the Northern Hemisphere have decelerated, whereas the increase of ozone levels has accelerated in regions downwind of eastern Asia, where mitigation policies have yet to take effect. The report also shows that hemispherically transported ozone can influence local ozone levels, especially in remote clean-air environments, where the transported ozone can be sufficiently large to induce air quality exceedances, in spite of very low local emissions.

An example of one such remote site where ozone levels are influenced by hemispheric transport is the Mace Head research site located on the western coast of Ireland. Air measured at Mace Head represents air advected from the Atlantic to Europe in the marine planetary boundary layer (MPBL). Tripathi et al. (2010) analysed data from various measurement sites around Ireland from 1988 to 2007. Findings from this study indicate decreasing ozone levels at all sites, except for the clean-marine site at Mace Head which exhibits a rising trend or 0.16 ppb per year. The negative trends in the rural and urban measurement sites were attributed to decreasing severity in photochemical production, as postulated by Jenkin (2008) as a factor governing local ozone concentrations.

Rising ozone concentrations observed at Mace Head represent a rising background ozone level. The findings of Tripathi et al. (2010) indicate that background ozone levels heavily influence local ozone pollution levels in Ireland. Derwent et al. (2007) also observed an increasing trend in background ozone levels at Mace Head from 1987 to 2007. For this time period, ozone levels were observed to rise 0.31 ppb per year on average, with higher increases in the spring months. This trend is significantly more pronounced than that observed by Tripathi et al. (2010), most likely due to the decrease in ozone precursor levels in North America and Europe (Tripathi et al., 2010). Derwent et al. (2007) postulated several possible explanations for the rising background ozone levels observed at Mace Head, including increased anthropogenic emissions of ozone precursors, sporadic biomass burning events and perturbations in lower-stratospheric ozone concentrations (as argued by Ordóñez et al. (2007)). Simmonds et al. (2004) observed an increasing trend in ozone levels
at Mace Head of the order of 0.5 to 0.8 ppb per year. The results of Simmonds et al. (2004) correlate well with the rising trend in ozone levels observed by Jaffe et al. (2003) in California. However, Simmonds et al. (2004) observed a larger trend in the winter months than in summer months and the reverse was observed by Jaffe et al. (2003). This was explained by Simmonds et al. (2004) as being due to differing winter weather systems in the two regions, which would affect air-sea exchange and consequently influence background ozone levels.

To date, model studies have not been able to reproduce the rising trend in background ozone concentrations as observed at Mace Head (Jonson et al., 2006; Wild et al., 2012). In fact, Dentener et al. (2010) found that although global models perform adequately in simulating pollutant transport, both global and regional models fail to reproduce historical trends. This highlights a gap in the current understanding of processes governing ozone transport and removal mechanisms and it calls into question the ability of current models to predict future ozone trends. However, the models prove to be useful tools in predicting future ozone trends in response to changing emissions. This topic has been the subject of many recent model studies (Wild et al., 2012; Stevenson et al., 2005; Johnson et al., 2001).

1.2.4 Current Regulation of Ground-level Ozone

The discovery of the negative impact of ozone on human health and vegetation during the latter half of the 20th century (Haagen-Smit, 1952) motivated the formulation of ozone pollution mitigation policies in a range of countries across the globe. Initial control measures focused on limiting emissions of ozone precursors and diminishing peak ozone levels that were most damaging to health and vegetation (Chameides et al., 2007). Currently, the World Health Organisation (WHO) issues a guideline air quality limit of 50ppb $O_3$ as a daily 8-hourly mean, above which levels are hazardous to human health. This limit was chosen based on epidemiological studies and evidence from human exposure cases. On a more regional scale, the UNECE set an 8-hourly mean $O_3$ limit of 60ppb as the critical level for human health defined by the Gothenburg Protocol over the domain pertaining to the European Monitoring and Evaluation Programme (EMEP). As an indicator of air quality, UNECE sets AOT40 limits, where an AOT40 is defined as the sum of mean hourly mixing ratios in excess of 40 ppb for during daylight hours ($AOT40 = \Sigma(x_i - 40)$ ppb, where $x_i =$ hourly mean ozone concentration). To prevent loss of vegetative crops as a result of $O_3$ exposure, UNECE set AOT40 limits of 3000 ppb.
hour over a typical three month growing season for sensitive arable crops and an AOT40 limit of 5000 ppb hour over a growing season for young trees. AOT40 measures the overall exposure to ozone mixing ratios over the relevant daylight period. The European Union (EU) Directive on Ambient Air and Clean Air for Europe (CAFE, 2008) has set similar air quality limits for 2010. To protect human health, ozone levels are not to exceed 60 ppb as a daily 8-hourly mean more than 25 days per year averaged over three years at any given site. Long term objectives of the CAFE directive are to set an absolute exceedance limit of 60ppb for the protection of human health. For the protection of vegetation, AOT40 levels are limited to 9000 ppb hours from May to July, averaged over 5 years. Again, the long term objective of the CAFE directive is to set an AOT40 limit of 3000 ppb hour from May to July.

Within the EU, the Information Threshold, whereby the public are to be informed of elevated ozone levels is set as an hourly mean of 90ppb and in the event of hourly ozone levels exceeding 120 ppb, a public alert is to be issued informing the public of a health threat.

As of 2011, the CAFE directive ozone air quality standards are incorporated into Irish law (SI 180, 2011).

1.2.5 Future Trends of Ozone as determined by Emission Scenarios

From model studies, it has been shown that the effect of changing emission scenarios on future ozone levels is determined by the particular future emission scenario used in simulations. Emission scenarios used in the current Intergovermental Panel on Climate Change (IPCC) 5th Assessment Report Climate Model Intercomparison Project (CMIP5) are the representative concentration pathways (RCP) scenarios. These RCP 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. Each emission scenario reflects only one of a number of possible emission scenarios that could result in the specific forcing trajectory chosen, hence the word “representative” in the term RCP. 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 sci-
Emission scenarios used in previous IPCC assessment reports were derived by the IPCC Special Report on Emission Scenarios (SRES). These scenarios were developed by first establishing future narratives of socio-economic development scenarios. These scenarios focused on greenhouse gas emissions with no projections of future aerosol pollutant trends and so their main value is in the investigation of the long-term effect of emissions on climate as opposed to air quality.

Model Studies

Using a coupled global model, Stevenson et al. (2005) assessed the effect of climate on global ozone concentrations up to the year 2030 using the current legislation emission (CLE) scenario (Cofala et al., 2007; Dentener et al., 2005). The CLE scenario reflected 2005 perspectives of individual states on future economic development, but in the 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).

As part of the Atmospheric Composition Change European Network of Excellence (ACCENT) PhotoComp intercomparison, the role of ozone precursors in determining future global trends up to 2030 was investigated using 26 different global models (Dentener et al., 2006). Three emission scenarios were used to reflect the range of possible emissions in the future. Summertime ozone concentrations for 2040-2050 and 2090-2100 have recently been simulated using the regional climate model RegCM3 (run with IPCC A1B emission scenario) (Katragkou et al., 2011). Results of this study showed an increase in summertime ozone mixing ratio of under 1 ppb between the 1990s and the 2040s, but by the 2090s the summertime increase of over Europe is predicted to be as high as 6.2 ppb. The study finds that the change in biogenic emissions and change in meteorology (temperature and radiation) have comparable effects on simulated ozone levels. Recently, Wild et al. (2012) investigated the effect of changing emission patterns on surface ozone concentrations in four major global regions: North America, Europe, South Asia and East Asia. By using results from 14 global models, a parameterisation was generated to assess the changes in surface ozone concentrations occurring in response to changes
in precursor emissions and atmospheric methane. This parameterisation was then employed to evaluate changes in surface ozone concentrations in the selected regions brought about by a range of future emission scenarios (both SRES and RCP) by 2050. Using the emission-response parameterisation, changes in surface ozone could be attributed to changes in individual sources, with uncertainties quantified according to spread of results from the different models. Results from this study show the range of predicted future ozone levels to be determined by the emission scenario used, with the SRES A2 scenario suggesting an $O_3$ increase of 7.7ppb over Europe by 2050 whereas the RCP 2.6 scenario suggested a reduction in $O_3$ of 4.7ppb over Europe by 2050. With the SRES A1B scenario, a 4.6ppb rise in surface ozone is predicted over Europe by 2050, whereas using the RCP 6.0 scenario, a 2.0 decrease in surface ozone is predicted within the same time period.

To study the effect of changing anthropogenic emissions on surface-level ozone budgets, a comprehensive understanding of the tropospheric sources and sinks of ozone in the troposphere is required.

The major tropospheric source of surface ozone is the photochemical production via oxidation of precursors ($NO_x$ and $VOCs$) and influx of stratospheric ozone also accounts for a minor tropospheric ozone source. Distribution of ozone within the troposphere is highly dependent on boundary layer processes. Entrainment from the free-troposphere has previously been flagged as influencing elevated surface ozone measurents in the US and Europe (Kley et al., 1994) and surface ozone concentrations in Europe have been correlated with wind speeds, indicating increase in ozone concentrations due to increased entrainment (Davies et al., 1992).

The planetary boundary layer (PBL) refers to the lowest part of the atmosphere, whose behaviour is directly influenced by its contact with the planetary surface and air movement is influenced by surface drag. In a marine environment, the PBL is influenced by the ocean and is termed the Marine Boundary Layer (MBL). Large quantities of heat, moisture and momentum are transferred between the ocean and the atmosphere through the MBL, primarily through turbulent transfer (Fairall et al., 1996). In a study of ozone budgets in the MBL, Heikes et al. (1996) estimated the entrainment flux of ozone from the free troposphere as $11 \pm 10 \times 10^{10} \text{ molecules cm}^{-2} \text{s}^{-1}$ whereas the destruction of ozone within the MBL was estimated as $6 \pm 2 \times 10^{10} \text{ molecules cm}^{-2} \text{s}^{-1}$, the majority of destruction due to photochemistry with $1.7 \pm 0.22 \times 10^{10} \text{ molecules cm}^{-2} \text{s}^{-1}$ deposited directly to the sea surface. Previous studies have shown that destruction of ozone within the MBL is mediated by entrainment of ozone-rich air from the free troposphere (Liu et al., 1983).
In the following section, the dominant sources and sinks of surface level ozone are discussed, but the downward vertical transport of ozone from the tree troposphere to the boundary layer is not discussed. However, the distribution of ozone within the troposphere is considered according to boundary layer theory.

1.2.6 Sources and Sinks of Tropospheric Ozone

Ozone is brought into the troposphere by two main processes: transportation from the stratosphere and photochemical production. The quantity of ozone transported from the stratosphere can be estimated using the OH radical as an indicator of ozone concentrations (Jacob, 1999). The dominant source of OH in the atmosphere is from photolysis of ozone (Seinfeld and Pandis, 1997). The global stratosphere-troposphere flux of ozone is estimated as $1 - 2 \times 10^{13} \text{molO}_3\text{yr}^{-1}$. This rate is in the same range as global annual cross-tropopause ozone flux estimates from model studies, estimated to range between $300 - 1400 \text{TgO}_3\text{yr}^{-1}$ (IPCC, 2001). As each $O_3$ molecule can produce a maximum of two OH molecules, the maximum production rate of OH from stratospherically-sourced ozone is $2 - 4 \times 10^{13} \text{molOHyr}^{-1}$. This OH production rate is a factor of 2.5 to 5 too low to account for global OH concentrations and so, there must be an in-situ tropospheric $O_3$ source to supplement stratosphere-originated ozone. However, from these figures, it can be concluded that cross-tropopause ozone flux accounts for 20 to 40% of tropospheric ozone concentrations.

Ozone transported from Stratosphere

Stratosphere-tropopause exchange (STE) occurs primarily in the tropopause folds and cut-off lows that are generated due to baroclinic disturbances in the meandering jet stream that are associated with mesoscale complexes and thunderstorms. During these events, sections of stratospheric air intrude into the tropospheric region and mix irreversibly within the troposphere (Roelofs et al., 2003). STE is more significant in the northern hemisphere, with estimated downward flux of $3 - 8 \times 10^8$ molecules $cm^{-2}s^{-1}$, whereas estimated STE in the southern hemisphere is roughly half this magnitude (Crutzen, 1995). In addition to tropopause folding, ozone is transported from the stratosphere to the troposphere over a longer time period by a global-scale meridional circulation mechanism: Brewster-Dobson circulation (BDC). BDC describes the transport of trace gases from the tropics to the poles (Brewer, 1949; Dobson, 1956), during which ozone is transported from the upper stratosphere to the lower stratosphere. Vertical transport of tropospheric air into the stratosphere
occurs initially in the tropics as a consequence of deep cumulus convection and then moves towards the poles in the stratosphere (Seinfeld and Pandis, 1997). To conserve mass, air must eventually be transported back down to the troposphere. The breaking of planetary waves in the extra-tropics disturb the general zonal air flow to form a midlatitudinal “surf zone” which facilitates the vertical transport of tropospheric air (Weber et al., 2011; Seinfeld and Pandis, 1997). The air rises in a vertical column analogous to a “tropical pipe” whereby tropical air is vertically advected upward, with relatively little mixing with midlatitudinal stratospheric air (Seinfeld and Pandis, 1997). However, some mixing of the upwardly advected air does occur in the midlatitudes. As the air rises in the tropical pipe, photochemical ozone production takes place in the upper stratosphere. As the air ascends towards the upper stratosphere, the circulation pattern bends towards the mid-latitudes, carrying the ozone-rich air downwards from the stratospheric tropics to the mid to high latitudes in the lower stratosphere (Newman, 2003). The timescale of transport of stratospheric ozone to the troposphere via BDC is slow compared to ozone transported by tropopause folding events. Furthermore, BDC is subject to seasonal variation with ascending air in the northern hemisphere moving at rates of $17 \text{ mday}^{-1}$ in the summer and $26 \text{ mday}^{-1}$ in the winter (Boering et al., 1996). The timescale of transport of equatorial stratospheric air to the lower polar stratosphere is of the order of a few years (Waugh and Hall, 2002), with transport more effective in the winter hemisphere (Chipperfield and Jones, 1999).

**Photochemical Ozone Production**

The formation of ozone requires availability of atomic oxygen to bond with an oxygen molecule. In the stratosphere, atomic oxygen is produced by the Chapman Mechanism, whereby molecular oxygen is split by high energy UV rays, allowing the formation of ozone molecules. As the majority of UV radiation is filtered out in the stratosphere, there is another mechanism responsible for *in situ* production of tropospheric ozone.

Following the emergence of urban photochemical smog in Los Angeles in the 1940s and the identification of ozone as its main constituent in the 1950s (Haagen-Smit, 1952), this hitherto unknown form of air pollution sparked research interest. In pioneering research, Haagen-Smit (1953) postulated a free radical chain reaction involving $NO_x$ and organic compounds as the mechanism responsible for tropospheric $O_3$ production; $NO_x$ compounds were identified as catalysts in the production process but the species resposible for oxidation of the organic compounds was unknown.
Nearly twenty years later, Levy (1971) identified the hydroxyl radical (OH) as the principle oxidising agent of the troposphere, with production of the hydroxyl radical initiated by reactions of photoexcited atomic oxygen with water vapour. It is now understood that tropospheric ozone production occurs via hydroxy radical chain reaction with the two major precursors being volatile organic compounds (VOCs) and NO\textsubscript{x}, the latter behaving as a catalyst.

**Tropospheric photochemical \( O_3 \) production**

The principal *in situ* source of tropospheric ozone is photochemical production via the methane oxidation chain, although ozone production can also be intialised by oxidation of carbon monoxide. Methane (\( CH_4 \)) is the most plentiful hydrocarbon in the atmosphere. A naturally occurring gas, it is emitted as a by-product of enteric fermentation (Seinfeld and Pandis, 1997). Methane is the dominant component of natural gas, widely used as fuel. As mentioned in section 1.2.1, photodegradation of ozone forms an excited oxygen atom which forms a pair of hydroxyl radicals on collision with a water molecule. When methane is oxidised by the hydroxyl radical, a chain reaction is initiated which generates organic peroxy radicals (\( HO_2 \)), and eventually yields nitrogen dioxide (\( NO_2 \)). An abbreviated pathway of the methane oxidation chain (omitting non-stable intermediate species) is shown below.

\[
\begin{align*}
OH + CH_4 + O_2 &\rightarrow H_2O + CH_3O_2 \quad (1.1) \\
CH_3O_2 + NO &\rightarrow CH_3O + NO_2 \quad (1.2) \\
CH_3O + O_2 &\rightarrow HCHO + HO_2 \quad (1.3) \\
HO_2 + NO &\rightarrow OH + NO_2 \quad (1.4)
\end{align*}
\]

Ozone formation is initiated by photo-dissociation of \( NO_2 \), which photolyses at wavelengths readily available in the troposphere.

\[
\begin{align*}
2(NO_2 + h\nu &\rightarrow NO + O) \quad (1.5) \\
2(O + O_2 + M &\rightarrow O_3 + M) \quad (1.6)
\end{align*}
\]

The net yield of this reaction chain can be summarised as follows:

\[
CH_4 + 4O_2 + 2h\nu \rightarrow HCHO + 2O_3 + H_2O \quad (1.7)
\]
**Photochemical Ozone destruction**

The main tropospheric sink, which accounts for around 75% of ozone loss (Seinfeld and Pandis, 1997), is ozone photolysis. It is only when the excited oxygen atom collides with a water molecule that two hydroxyl radicals are generated, and the oxygen atom does not recombine with an oxygen molecule to reform ozone.

This reaction chain is dependent on the water vapour concentration, and so is most effective in low latitudes and altitudes due to the intense radiation and high humidity in these regions. The higher the water vapour concentration, the more ozone molecules that are destroyed following photolysis. In the lower troposphere, as many as 0.2 molecules of OH are produced for every ozone molecule photolysed, the remainder reverting back to ozone. Naturally, the photochemical destruction of ozone has a diurnal variability.

Further, ozone destruction depends on the availability of atmospheric water vapour and local ozone destruction rates vary with atmospheric humidity accordingly. The photolytic lifetime of an $O_3$ molecule in the troposphere is estimated as 11 days (Seinfeld and Pandis, 1997).

**Dry Deposition of Ozone**

Dry deposition refers to the removal of gases and particles at air-surface interfaces in the absence of precipitation, as a result of air motion (Jacobson, 2005). The gas species or particle is removed from the air because it either sticks to or reacts with the surface.

In the case of particles, the gradual downward gravitation of a particle towards the earth is called *sedimentation* (Jacobson, 2005). Sedimentation of small particles is a very slow process because of the small mass and small gravitational force on the particles but sedimentation of large molecular particles (sea spray, rain and cloud droplets and dust) is of significant consequence to atmospheric processes. In the case of gases, although they also undergo sedimentation, their masses are generally so small as to have negligible downward velocities and so their downward deposition is dependent on other factors, such as atmospheric turbulence levels, the physical and chemical attributes of the species and the type of terrain to which the species is being deposited.
The rate at which a gaseous species is deposited is parameterised by a \emph{deposition velocity}, or $v_d$ which is computed as the reciprocal of the sum of the resistance encountered by the species on its journey to the earth’s surface.

In calculating $v_d$, it is assumed that the dry deposition flux ($F$) is proportional to species concentration ($C$) at some reference height.

$$F = -v_d C$$ \hfill (1.8)

The use of single parameter to define such a complicated process as dry deposition means that all the microphysical and chemical complexities are contained in a single parameter, thus simplifying computations. However, this renders specification of $v_d$ difficult.

Turbulent transfer dominates the downwards transport of the gaseous species through the atmosphere. Approaching the air-surface interface, viscous layers adjacent to earthly obstacles form a thin layer of stagnant air which impedes deposition of gases due to supression of turbulent motions and within this layer, transport of the gaseous species is dependent on molecular diffusion. Generally, the turbulent transport exceeds molecular transport by several orders of magnitude, but the turbulent motion cannot penetrate into the air-earth interface because the turbulence is attenuated in the interfacial viscous layer (Jähne et al., 1987).

This phenomenon has given rise to conceptual models of gas-transfer in which the boundary layers on either side of the interface are divided into two sub-layers: the outer layer in which turbulent transfer dominates, and the inner sublayer in which molecular transfer dominates. The inner layer is known as the quasi-laminar sublayer and is dependent both on the intensity of initial atmospheric turbulent motion and on the diffusion coefficient of the gas species. In the case of gas species being deposited to a water-body, the molecular diffusivity of gas in air exceeds the molecular diffusivity of gas in water by four orders of magnitude, and the transport of weakly soluble gases in water is determined solely by the mass boundary layer in the water (Liss and Slinn, 1983), which is of the order of 0.1mm in thickness.

Once the species has undergone turbulent transfer through the atmosphere and diffusive transport through the quasi laminar sublayer, the final stage involved in dry deposition involves adherence of the species to the earthly surface. These three steps of dry deposition are schematically represented for the case of ozone being
deposited to a water surface in Figure 1.1.

To compute the overall transfer rate of dry deposition, \( v_d \), dry deposition has been empirically represented as a three step process where \( v_d \) is parameterised as the inverse sum of a series of resistances (Wesely and Hicks, 1977; Walcek et al., 1986). This concept arose by analogy to an electrical circuit: layers through which the species flow can be organised into regions with explicit “resistances” to the gaseous transfer, analogous to electrical resistance to the flow of electrons (Wesely and Hicks, 1977). The three “resistance layers” in the case of dry deposition are aerodynamic resistance \( (R_a) \), resistance to molecular diffusion in the laminar sublayer \( (R_b) \) and surface resistance \( (R_c) \). The reciprocal of each resistance yields a specific transfer speed, a measure of the rate of transfer of the species during the respective processes. The flux of a species during one of the steps can be calculated as follows

\[
F_i = Cv = \frac{C}{R_i}
\]

(1.9)

where \( v \) and \( R \) respectively denote the transfer rate and corresponding resistance during the step in question. Using the Resistance Approach deposition velocity...
can be calculated as the reciprocal as the sum of all three resistances:

\[
v_d = \frac{1}{R_a + R_b + R_c}
\] (1.10)

The dry deposition of ozone represents a major sink for surface layer ozone, comprising roughly 22% of the total removal of tropospheric ozone (Table 1.2). Parameters influencing surface deposition include land use category, vegetation type, plant species, leaf area index, greenness (indicated by normalised difference in vegetation index), plant structure, exposed soil and soil acidity. Over land, the uptake of ozone by vegetation is a major sink for surface level ozone. The rate at which ozone is taken up by vegetation is governed by diurnal and seasonal cycles in plant activity, as well as physical properties of the vegetation. The presence of water films on vegetation surface also affects deposition rate, the water rendering the plant surface more resistant to ozone deposition.

In current dry deposition parameterisations (Wesely, 1989; Ganzeveld and Lelieveld, 1995), surface resistance to ozone depositions is calculated as a series of smaller resistances (cuticle resistance, mesophyll resistance, leaf cuticle resistance etc.). These resistances are estimated based on field measurement studies and parameters such as solar radiation, air temperature are used to parameterise plant activity. Obviously, the surface resistance is defined based on land-use category and season. Ozone deposition velocities to land surfaces exceed those to water bodies by an order of magnitude (Ganzeveld and Lelieveld, 1995). This occurs due to significantly larger surface resistance over water compared to land because of smaller roughness length over the ocean. The rate of ozone transfer over sea water increases with increasing sea roughness (Galbally and Roy, 1980). However, as 70% of the globe is water-covered, dry deposition of ozone to the ocean is still a sizeable sink for tropospheric ozone. The total loss of tropospheric ozone due to dry deposition is estimated as \( 8 \times 10^{10} \) molecules \( \text{cm}^{-2} \text{s}^{-1} \) (Galbally and Roy, 1980) or a loss of 600-1000 Tg year\(^{-1} \) (Fairall et al., 2007; Ganzeveld et al., 2009).

Dry deposition of ozone is dependent on the particular characteristics of the ozone molecule. Ozone is a weakly soluble gas and so transfer of ozone to water surfaces is limited by its weak solubility. The dry deposition of ozone to the ocean is a complex process involving a number of processes: physical, chemical and biologi-
cal. The parameterisation of these processes has been hindered by a sparsity of field studies measuring deposition rate of ozone to the sea surface. During the deposition of ozone to a water surface, $R_c$ dominates over the other resistances (Lenschow et al., 1982) and so is the determining parameter in quantifying the deposition rate of ozone. Table 1.1 displays the wide range of $R_c$ and $V_d$ values obtained to date from *in-situ* measurements and from model studies.

A parameterisation widely-used in modelling the dry deposition of ozone is that of Wesely (1989); a model developed for a range of trace gases being deposited. This parameterisation uses the three-step resistance model as described above and its methodology for computing the deposition velocity of ozone to water is described in detail in Appendix A. The parameterisation computes deposition velocities for a number of different terrain types. At the time of the construction of the parameterisation, the processes involved in surface transfer were not generally quantified, and so $R_c$ was assigned a fixed value based on available field measurements. In the Wesely (1989) parameterisation, $R_c = 2000 \text{sm}^{-1}$ was chosen based on laboratory measurements of Galbally and Roy (1980) and field measurements of Wesely et al. (1981). As $R_c$ is the determining resistance in the case of ozone deposition to the ocean (Lenschow et al., 1982), setting $R_c$ to this constant value in a gaseous dry deposition parameterisation will yield ozone deposition velocities to ocean surface of $v_d \approx 0.05 \text{cms}^{-1}$, regardless of atmospheric and water conditions.

From Table 1.1, it can be seen that ozone velocities measured directly at sea vary over an order of magnitude ($0.01 \rightarrow 0.17 \text{ cms}^{-1}$) and it is well documented that atmospheric and water surface turbulence enhance ozone uptake at the sea surface (Tiefenau and Fabian, 1972; Fairall et al., 2007; Gallagher et al., 2001), as does the presence of ozone reactants in the sea surface layer (Garland et al., 1980; Schwartz, 1992; Chang et al., 2004; Fairall et al., 2007). Therefore, it is apparent that to accurately estimate the amount of ozone deposited to the sea surface, a more advanced dry deposition model is required.

A significantly more advanced parameterisation was developed by Fairall et al. (2007). This parameterisation is an extension of the theoretically robust gas-transfer parameterisation of Fairall et al. (2000), but tailored for the specific case of ozone deposition to the ocean. The original gas-transfer parameterisation accounts for increased gaseous deposition at high windspeeds due to generation of whitecap bubbles. This does not apply to ozone, however due to the small penetration depth of
ozone into seawater (of the order of \( \mu m \)). Based on integration of the turbulent-molecular transport equation in the ocean, the scheme encompasses more advanced turbulent, molecular and chemical mechanisms than previous parameterisations, such as those of Garland et al. (1980), Schwartz (1992) and Chang et al. (2004), allowing for significant sea surface transfer of ozone in the case of high turbulence or high chemical reactivity. Previous parameterisations assumed all reactions occurred in the molecular sublayer, whereas this advanced parameterisation allows for reactions to occur within the bulk water due to turbulent driving.

This advancement of chemical mechanism is especially pertinent to ozone, due to its weakly soluble yet highly reactive nature. A detailed description of the mathematical composition of the parameterisation is given in Appendix B. \( R_c \) is explicitly computed considering the effects diffusion, solubility, reactivity and turbulence. Chemical destruction can occur either within the molecular sublayer (in the case of high ocean reactivity towards ozone), or within the bulk water. In the case of ozone reacting in the bulk water, the effect of turbulence on deposition becomes significant.

Chemical reactivity of ozone in the ocean is characterised by first order loss rate, \( a(\text{s}^{-1}) \). Within this parameterisation, the mass budget equation is solved for the case where at the surface, the ozone flux equals the air-side flux and where the ozone concentration tends to zero deep in the ocean. The budget equation is arranged so as to take to form of Bessel’s differential equation, the solution of which are modified Bessel functions (as used to solve Laplace’s equation). This solution of the budget equation allows the extent of the turbulent enhancement of surface transfer to be governed by the reactivity term. In the case of low oceanic reactivity (\( a < 100\text{s}^{-1} \)) not all ozone reacts within the molecular sublayer and the effect of turbulent diffusion on \( R_c \) becomes significant. In the case of high oceanic reactivity, all the gas is assumed to react within the molecular sublayer and the expression for \( R_c \) reduces to the case in which all ozone is destroyed within the molecular sublayer. Effectively, this means that in conditions of high turbulence, the transfer velocity has a much weaker dependence on reactivity. It was found that the transition between a strong-reaction regime and a weak reaction regime occurs for reactivity values of \( 10^3 \text{s}^{-1} \).

Further, reproduction of typical observed ozone deposition velocities such as those observed by Gallagher et al. (2001) would require \( a = 10^3 \text{s}^{-1} \).

A sensitivity test (Fairall et al., 2007) confirmed that observed deposition velocities may be due to the presence of a thin surfactant layer on the water surface, as
previously postulated (Schwartz, 1992). The parameterisation was used to compute transfer velocities using meteorological measurements taken during a field campaign on NOAA ship \textit{Ronald H. Brown} off the coast of New Hampshire in July and August 2004. Simulated $V_d$ ranged between $0.01 \rightarrow 0.12\text{cms}^{-1}$ with median value of $0.044\text{cms}^{-1}$, in the same range as previous observations (Fairall et al., 2006). This value yields a boundary layer removal timescale of 1 day.

The biggest unknown in this parameterisation is the scaling of the chemical reactions. Iodide was identified by Chang et al. (2004) as the reactant most significant in ozone removal at the sea surface and Schwartz (1992) suggested that owing to the short penetration depth of ozone (around $1\mu m$), significant chemical destruction of ozone may be occurring due to organic species residing in the sea surface. Recent work by Clifford et al. (2008), Reeser et al. (2009b) and Martino et al. (2012) confirm the influence of organic matter on ozone deposition. The concentration of organic reactants in the sea surface is highly seasonally dependent, and so it is essential that the chemical reactivity of ozone in seawater be scaled accordingly. Fairall et al. (2007) set the reactivity to a constant value of $1000\text{s}^{-1}$. This value is chosen to yield deposition velocities close to observations and cannot be justified by knowledge of reactant oceanic concentrations and reaction kinetics to date. A major aim of this study is to resolve this issue and adequately parameterise chemical reactions pertinent to ozone and identify reactants facilitating ozone uptake at the water surface.

1.2.7 The Tropospheric Ozone Budget

The role of $NO_x$ in generating tropospheric $O_3$

The hydroperoxyl radical ($HO_2$) is created in the atmosphere when carbon monoxide ($CO$) reacts with the hydroxyl radical in the presence of $O_2$.

$$CO + OH + O_2 \rightarrow CO_2 + HO_2$$

The fate of the $HO_2$ radical is decreed by the atmospheric level of $NO$. When $NO$ is readily available, it reacts with the $HO_2$ radical, forming $NO_2$ and the hydroxyl radical.

$$HO_2 + NO \rightarrow NO_2 + OH$$
Table 1.1: Summary of measured water surface resistances and transfer velocities of ozone

<table>
<thead>
<tr>
<th>Models</th>
<th>Details</th>
<th>$R_c$ ($\text{sm}^{-1}$)</th>
<th>$v_d$ ($\text{cms}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chang et al. (1987)</td>
<td>Based on observations</td>
<td>2000</td>
<td>0.05</td>
</tr>
<tr>
<td>Wesely (1989)</td>
<td>Based on observations</td>
<td>2000</td>
<td>0.05</td>
</tr>
<tr>
<td>Ganzeveld and Lelieveld (1995)</td>
<td>Based on observations</td>
<td>2000</td>
<td>0.05</td>
</tr>
<tr>
<td>Chang et al. (2004)</td>
<td>$R_c$ comprised of parallel turbulent (empirical) and chemical resistances</td>
<td>6250</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1282</td>
<td>0.078</td>
</tr>
<tr>
<td>Fairall et al. (2007)</td>
<td>$R_c$ derived from fundamental principles</td>
<td>10000</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>833</td>
<td>0.12</td>
</tr>
<tr>
<td>Ganzeveld et al. (2009)</td>
<td>Global model study using parameterization of Fairall et al. (2007)</td>
<td>5000</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1111</td>
<td>0.09</td>
</tr>
<tr>
<td>Oh et al. (2008)</td>
<td>Regional model study using parameterization of Chang et al. (2004)</td>
<td>2000</td>
<td>0.016</td>
</tr>
</tbody>
</table>

**Lab Studies**

<table>
<thead>
<tr>
<th>Models</th>
<th>Details</th>
<th>$R_c$ ($\text{sm}^{-1}$)</th>
<th>$v_d$ ($\text{cms}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldaz (1969)</td>
<td>Wind Tunnel Measurements</td>
<td>2400</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3400</td>
<td>0.03</td>
</tr>
<tr>
<td>Garland and Penkett (1976)</td>
<td>Wind Tunnel &amp; box decay Seawater</td>
<td>2400</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3400</td>
<td>0.03</td>
</tr>
<tr>
<td>Galbally and Roy (1980)</td>
<td>Chamber decay method</td>
<td>1100</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4000</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>In situ chamber method Seawater</td>
<td>1200</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4400</td>
<td>0.02</td>
</tr>
<tr>
<td>Garland et al. (1980)</td>
<td>Stop flow apparatus Seawater</td>
<td>3200</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1900</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Seawater + I</td>
<td>3400</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>740</td>
<td>0.14</td>
</tr>
<tr>
<td>McKay et al. (1992)</td>
<td>Chamber measurements Seawater</td>
<td>6600</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330</td>
<td>0.03</td>
</tr>
<tr>
<td>Martino et al. (2012)</td>
<td>Chamber measurements Seawater + I</td>
<td>10000</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6600</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Measurements**

<table>
<thead>
<tr>
<th>Models</th>
<th>Details</th>
<th>$R_c$ ($\text{sm}^{-1}$)</th>
<th>$v_d$ ($\text{cms}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tiefenau and Fabian (1972)</td>
<td>Gradient method</td>
<td>650</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1250</td>
<td>0.08</td>
</tr>
<tr>
<td>Wesely et al. (1981)</td>
<td>Eddy Correlation Fresh water</td>
<td>9000</td>
<td>0.01</td>
</tr>
<tr>
<td>Lenschow et al. (1982)</td>
<td>Aircraft measurements Seawater</td>
<td>1690</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1890</td>
<td>0.05</td>
</tr>
<tr>
<td>Kawa and Pearson (1989)</td>
<td>Aircraft Eddy Correlation Seawater</td>
<td>4190</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1890</td>
<td>0.05</td>
</tr>
<tr>
<td>Heikes et al. (1996)</td>
<td>Airframe measurements &amp; budget equation</td>
<td>3333</td>
<td>0.03</td>
</tr>
<tr>
<td>Gallagher et al. (2001)</td>
<td>Eddy correlation Seawater</td>
<td>1000</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>588</td>
<td>0.17</td>
</tr>
<tr>
<td>Helmig et al. (2012)</td>
<td>Eddy correlation (ship) Seawater</td>
<td>10000</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2941</td>
<td>0.034</td>
</tr>
</tbody>
</table>
As $NO_2$ and the hydroxyl radical are both instrumental in ozone production via the methane oxidation chain, this reaction leads to ozone formation. In the event of a low supply of atmospheric $NO$, the $HO_2$ radical would then react with an ozone molecule, leading to ozone destruction:

$$HO_2 + O_3 \rightarrow OH + 2O_2$$ (1.13)

Whether $HO_2$ leads to the creation or destruction of $O_3$ depends on the availability of $NO$ in relation to local $O_3$ concentrations, and the rate constants of reactions 1.12 and 1.13.

**VOC to $NO_x$ ratio**

The ratio of volatile organic carbon $VOC$ compound concentration to $NO_x$ concentration in the atmosphere also affects ozone formation in the atmosphere. This is because the $VOC$s compete with $NO_x$ for the $OH$ radical. When the $VOC$ concentration exceeds the $NO_x$ concentration by a factor smaller than 5.5, the atmosphere can be said to be $NO_x$-saturated. The nitrogen oxide then becomes oxidised by the $OH$ radical, so removing $OH$ from the active $VOC$ oxidation cycle. This retards ozone formation and so ozone decreases with increasing $NO_x$. In a different regime, when the $VOC$ concentration exceeds the $NO_x$ concentration by a factor greater than 5.5, ozone production in the troposphere is sensitive to $NO_x$ concentration, and the $VOC$ reacts with the hydroxyl radical, and so new radicals are generated by the process outlined above. In this regime, ozone production is correlated with $NO_x$ concentrations and varies very little with $VOC$ concentrations. Finally, if the

| Table 1.2: Estimates of main sources and sinks of ozone in the troposphere, reproduced from Wang et al. (1998) and Stevenson et al. (2006) |
|-----------------|-----------------|-----------------|-----------------|
|                 | Wang et al. (1998) | Stevenson et al. (2006) |
| **Average Global Source** | $Tg/year^{-1}$ | $Tg/year^{-1}$ |
| Stratosphere    | 400             | 550             |
| Photochemical Production | 4100           | 5100           |
| **TOTAL**       | 4500            | 5650            |
| **Average Global Sink** |               |                 |
| Dry Deposition  | 820             | 1000            |
| Photochemical Destruction | 3680           | 4650           |
| **TOTAL**       | 4500            | 5650            |
environment is very poor in $NO_x$ (as is the case over the ocean), peroxy radical - peroxy radical reactions become significant, resulting in a depletion of oxidising radicals and inhibiting production of ozone. This competition between $NO_x$ and VOCs for oxidation by the $OH$ radical is especially pertinent for urban areas with high emissions of these relevant species.

Table 1.2 displays a basic estimation of the dominant global tropospheric ozone sources and sinks taken from two separate model studies. In the first study of Wang et al. (1998), the budget applies up to a height of 150 mbar (around 14km) whereas the budget presented by Stevenson et al. (2006) represents a multimodel ensemble study. Photochemical production is the dominant source of ozone in the troposphere, photochemical removal being the dominant sink. With this in mind, dry deposition of ozone is still a sizeable sink for tropospheric ozone. As mentioned in the previous section, entrainment from the free troposphere plays a role in replenishing surface ozone levels following PBL destruction. The rate of ozone entrainment can be crudely quantified in assuming a typical entrainment velocity of $0.4 cms^{-1}$ (Faloona et al., 2005). From ozone profiles taken at Valentia, Ireland, the ozone concentration difference was evaluated across the PBL as 10 ppb. From these values, entrainment flux was evaluated across the PBL as roughly 1300 Tg per year. This is roughly double the amount of global ozone lost through dry deposition to the ocean, assuming oceanic ozone deposition velocity of $0.05 cms^{-1}$ (Wesely, 1989) and ambient ozone concentration of 35 ppb.

Within regional climate model REMOTE (REgional climate MOdel with Tracer Extension Langmann et al. (2008); Varghese et al. (2011)), the various processes affecting boundary layer ozone levels are parameterised. Photochemical ozone production and destruction is simulated within the RADMII chemical mechanism (Stockwell et al., 1990) which simulates atmospheric chemistry, including all reactions pertinent to ozone. Vertical and horizontal advection are simulated using the Smolarkiewitz scheme (Smolarkiewitz, 1983). Convective cloud transfer, including shallow convection, mid-level convection and deep convection is parameterised after Tiedtke (1989), accounting for entrainment and detrainment during vertical transport. Vertical turbulent diffusion is parameterised after Mellor and Yamada (1974) and mixing length is computed after Blackadar (1962), within which stability functions of Louis (1979) are applied. The model is constrained using species concentrations obtained from a global model. This study uses REMOTE to assess a number of questions pertaining to simulating boundary layer ozone budgets outlined in the next section.
Questions Addressed in the Thesis

There is a number of questions pertaining to boundary level ozone values that this thesis aims to explore:

1. Biological Impact on Oceanic ozone Deposition

The most recent research into ozone deposition shows that organic matter residing in the sea surface enhances the deposition of ozone to the ocean at least as significantly as oceanic iodide (Martino et al., 2012). As of yet, all the mechanisms involved have not been identified. The wide range of measured ozone deposition values tabulated in Table 1.2.6 is not explained by the current state-of-the art knowledge of oceanic dry deposition. However, work as part of this thesis shows that consideration of reactions between ozone and sea surface dissolved organic matter (DOM) may bridge the gap between ozone deposition measurements and theory. Further, results that have come to light as part of this work indicate there may be a hitherto unaccounted for photo-enhancement of ozone-organic matter reactions that may have a considerable impact on oceanic deposition rates.

Considering the declining trend in oceanic productivity occurring due to climatic change, the biological impacts on oceanic ozone deposition is an extremely current topic. This work seeks insight into the effect of changing ocean productivity on simulated ozone levels by using an organically-enhanced deposition scheme to simulate ozone flux to water surfaces within REMOTE.

2. Impact of Ozone Deposition to Aerosol Halogen Precur-
sors

The most up-to-date studies on halogen formation have identified formation of halogen precursors that occur as a consequent of sea-surface reactions that occur following sea-surface uptake of ozone. Martino et al. (2009) identify the release of volatile
organic iodine vapours (VOIs) following water-side reactions of ozone and dissolved organic carbon and iodide. An alternative mechanism whereby ozone reacts with chlorophyll resulting in eventual halogen release from the sea surface was proposed by Reeser et al. (2009a). This mechanism is enhanced by radiation and gives weight to the theory of photo-enhanced reactions between ozone and organic matter in the sea surface.

The release of halogens at the sea surface has significant biogeochemical consequence due to the role played by halogens in particle formation and growth. Once formed, marine aerosols can act as cloud condensation nuclei (CCN) and are instrumental in aerosol forcing. Using REMOTE, the total ozone-deposition driven iodine flux can be quantitatively estimated.

3. The Impacts of future emissions and Climate Change on Ozone

The final and most robust subject addressed by this thesis is the impacts of changing emissions and changing climate on future surface layer ozone levels. Ozone is a major air quality parameter and the response of surface ozone levels to changes in meteorology and emission patterns is of significant interest to pollution-control policy makers. Current European air quality legislation dictates that ozone levels of 60ppb taken over an 8 hour mean are not to be exceeded more than 25 times per annum. In order to assess the future of air quality, it is necessary to predict likely changes in surface ozone over the coming decades.

Previous model studies have been performed to assess the future of ozone pollution under specific emission scenarios. Most recently, Wild et al. (2012) simulated changes in surface ozone occurring as a response to changing emission scenarios on continental scales. This thesis differs from the work of Wild et al. (2012) in that the effect of meteorological changes on future surface ozone levels are also considered, thus enabling attribution of changes in surface ozone to either meteorological or emission changes.

The effect of a changing meteorology on surface ozone levels is difficult to predict; changing meteorological patterns can influence pollution either positively or negatively. The increased temperature predicted in the coming decades could increase occurrences of high-pressure stagnation events, thus exacerbating pollution events.
Conversely, increasing temperature may also stimulate more frequent rainfall, thus causing more pollution \emph{wash out}.

This thesis aims to investigate the effects of changing meteorology and emissions on surface ozone; both on a continental scale and also in regional subdomains, thus linking emission pattern changes and meteorological changes to specific environments and highlighting local effects.

For this thesis, simulations were performed for the RCP 6.0 emission scenario: a medium high emission scenario which assumes radiative forcing peaks at $6.0 \, Wm^{-2}$ and stabilises from 2150. The RCP datasets will be used in CMIP5 Coupled Model Intercomparison Project which aims to produce results for analysis in the IPCC Fifth Assessment Report (AR5). Consequently, results in relation to RCP datasets are most relevant in terms of global pollution mitigation strategies.
Review of Papers

Three papers derived from this study, summarised below, deal with the regional climate modelling of surface level ozone. The first two papers relate to the dry deposition of ozone to the ocean, utilising the advanced oceanic dry deposition parameterisation of Fairall et al. (2007) within regional climate model REMOTE. Paper I investigates the sensitivity of REMOTE results to sea-surface reactant concentrations using a monthly simulation. In Paper II, a new photochemical sink for ozone deposition is identified by comparing in situ ozone flux measurements to the Fairall et al. (2007) box-model results. In Paper III, large-scale annual simulations were performed with REMOTE to analyse the effect of a changing climate on ozone concentrations in 2030, 2050 and 2100, with baseline simulations performed for 2006.

Paper I

Regional-scale Ozone Deposition to North-East Atlantic Waters

*Advances in Meteorology*

Volume 2010, Article ID 243701, doi:10.11.56/2010/243701

Monthly simulations were performed using REMOTE for a period of high biological activity (June 2003). Simulation results using the advanced turbulent-chemical ozone deposition parameterisation of Fairall et al. (2007) were compared to results obtained using the highly-parameterised Wesely (1989) dry deposition scheme. The sensitivity of the Fairall et al. (2007) deposition scheme to key parameters affecting ozone deposition (sea surface temperature, solubility, diffusivity) was investigated and the sensitivity of REMOTE results to varying oceanic iodide concentrations was assessed.

The Fairall et al. (2007) parameterisation was extended to account for reactions
between ozone and sea surface organics, with chlorophyll used as a proxy for organic matter. This was achieved by using a factor for maximum enhancement of ozone deposition to the ocean identified by Clifford et al. (2008), applying this factor the event of a regional maximum chlorophyll value and scaling back linearly. REMOTE results using this organically-enhanced mechanistic version of the Fairall et al. (2007) were compared to results using the Wesely (1989) deposition scheme.

A potentially globally significant upward iodine flux that occurs as a consequence to ozone uptake at the sea surface is discussed and the upper limit of this flux was quantified. The flux was estimated to be in the range of 2.5 to 500 M molec $cm^{-2}s^{-1}$. This amounts to an additional flux of 27 to 5400 M molec $cm^{-3}$ of iodine vapours per day in the boundary layer. Acting as condensable vapours, these iodine oxides lead to new particle formation, having considerable potential for nucleation and particle growth (O’Dowd and Hoffmann, 2005). Findings of this paper show that REMOTE simulated monthly mean surface ozone levels are not sensitive to sea surface iodide levels, but in evaluation of the ozone deposition-driven iodine flux, surface iodide level is a critical parameter. The result indicates that within REMOTE, monthly mean surface ozone concentrations are independent of deposition velocity below a certain threshold value, above which the deposition velocity becomes a viable sink for MBL ozone. However, the upward iodine flux is evaluated from ozone deposition velocity, which is highly dependent on surface reactant concentrations.

Further, the paper shows that although the inclusion of the advanced mechanistic parameterisation of Fairall et al. (2007) in REMOTE does not result in simulated ozone levels significantly different to those obtained using the highly parameterised Wesely (1989) deposition scheme, the mechanistic scheme performs markedly better when tested against in situ measurements at Mace Head.

Finally, simulated results using the organically-enhanced mechanistic version of the Fairall et al. (2007) parameterisation were very similar to results obtained when chemical reactivity ($A_{oz}$) in the parameterisation was set to constant 1000$s^{-1}$; this being the reactivity value chosen by Fairall et al. (2007) to yield model results consistent with observations. Without considering the organic enhancement of ozone deposition, iodide is the only reactant hitherto identified in literature as capable of influencing ozone deposition. However, realistic oceanic iodide concentrations alone cannot theoretically explain ozone reactivity, which is typically of the order of 1000$s^{-1}$. Therefore, results of this study indicate that the previously observed
The discrepancy between measured and modelled ozone fluxes may be corrected by consideration of organic chemical enhancement of ozone deposition.

**The contribution of the author to this work includes amending the original Fairall et al. (2007) ozone deposition scheme to account for varying salinity and temperature, sensitivity testing of the amended scheme, implementation of the box model parameterisation into the three-dimensional regional climate model REMOTE, running the monthly simulations within REMOTE with the various dry deposition mechanisms, analysis of REMOTE output, comparison of model output to measurements, development and production of figures for manuscript and preparation of the manuscript text.**

**Paper II**

**Photochemical Impact on Ozone Fluxes in Coastal Waters**

*Advances in Meteorology*


Volume 2012, Article ID 943785, doi:10.1155/2012/943785

In this paper, *in situ* ozone gradient flux measurements taken at Mace Head were compared to box model results of Fairall et al. (2007).

A large part of the work involved extending the Fairall et al. (2007) deposition scheme to include reactions between ozone and DOM based on experimental work (Martino et al., 2012). The experimental results were scaled to the theory of Fairall et al. (2007) to yield a first order reaction rate between ozone and DOM. This is a significant improvement on the organic enhancement of deposition velocity used in Paper I which enhances deposition velocity linearly according to oceanic chlorophyll concentration.

By comparing Mace Head flux measurements to model output, a photochemical enhancement of ozone deposition was identified which renders the deposition rate of ozone to the ocean more sensitive to the organic content of the ocean than previous theory suggests.
A rising trend has been observed in background ozone levels in various stations, worldwide (Tripathi et al., 2010; Derwent et al., 2007; Jaffe et al., 2003). Changes in patterns of ozone deposition to the ocean may be influencing surface ozone levels during hemispheric transport and knowing that ocean primary productivity is in decline as a result of changing climate (Boyce et al., 2010; Gregg et al., 2005), it is feasible that trend of rising background ozone levels may be coupled to the trend of decreasing oceanic organic matter content.

This matter has yet to be explored and is one of the questions raised during this thesis. It is a matter of potential global significance to marine boundary layer ozone budgets and so warrants further investigation.

*For this paper, the author further developed the ozone deposition parameterisation to include the organic chemical ozone sink. The author carried out the modelling side of the work by running simulations and comparing box model results to the in situ flux measurements. Manuscript was written by the author with exception of initial drafts of the measurement methods section. Figures 2 and 3 were also developed and produced by the author.*

**Paper III**

**Assessment of changing meteorology and emissions on air quality using a regional climate model: Part 1-Impact on Ozone**

*Atmospheric Environment*


2013, Volume 69, pages 198-210

This paper presents annual simulations executed using REMOTE in order to assess potential changes in surface ozone levels in the years 2030, 2050 and 2100 occurring as a result in changes in meteorology and emissions. This study focuses on emission scenario RCP 6.0: a medium-high prediction which predicts stabilisation in radiative forcing to occur by 2150. The most recent study investigating future ozone trends focuses on the response of surface ozone levels to changing emission patterns (Wild et al., 2012) whereas in this work, the effect of changing meteorology has also been considered.
Meteorological data was procured from long term climate simulations performed on the global circulation model ECHAM5 including the HAM aerosol scheme, coupled to the MPI ocean model with the HAMOCC ocean carbon cycle - ECHAM5-HAM - MPI-OM HAMMOC (Stier et al., 2006; Wetzel et al., 2006), emissions prescribed according to the A1B scenario. It has been shown that radiative forcing simulated using the A1B scenario correlates very well with up to 2100 with radiative forcing simulated using the RCP6.0 emissions, confirming that the two emission pathways correspond in terms of meteorology. This validates our use of A1B-derived future-boundary data in conjunction with RCP6.0 emission scenario for the model domain. Although no long-term climate simulations were performed in this study, the changing meteorology of the time slice years are representative of climate change as simulated using ECHAM5-HAM MPI-OM HAMMOC.

A determining factor of future ozone concentrations which was not considered in these experiments is the effect of future land-use changes. The effect of future land-use change on meteorology varies with location and emission scenario, as shown by study of Feddema et al. (2005) in which agricultural expansion into forested areas cause a rise in temperature in the Amazon and cooling of the upper air column and nearby waters whereas in the mid-latitudes, agricultural expansion induces an overall cooling effect. The potential effects of land-use change on surface ozone are complex and non-linear.

Land-use change making way for agricultural activity would have a bearing on both the $NO_x$ and VOC burden. $NO_x$ is emitted from certain vegetative species, as are VOCs. Deforestation would reduce the amount of isoprene emissions due to a reduction in source vegetation. However, a warmer climate would increase vegetation density and increase the rate of isoprene emissions (Wu et al., 2012). Isoprene concentrations are correlated with ozone concentrations in low $NO_x$ environments, but anti-correlated with ozone concentrations in polluted regions. Further, urbanisation of rural land would reduce agriculturally-derived emissions, but cause an increase in transport and industrial emission of ozone precursors. On a more physical level, land use change could change the dry deposition due to changes in surface resistance to ozone deposition. As mentioned before, the effect of land-use change on surface ozone is complex and highly non-linear. Sanderson et al. (2003) found the effect of landuse change to reduce the severity of rise in global ozone mixing ratios projected under the SRES A2 scenario.
This study is restricted to analysis of effect of changing meteorology and emissions on ambient surface ozone concentrations and results are to be interpreted with this in mind.

Additional simulations were carried out using 2006 meteorology but changing emissions, isolating the effect of emissions and enabling apportionment of climate-induced change in future ozone levels.

Performance of the model was validated against annual cycles of 2006 surface ozone measurements taken at EMEP stations at Mace Head in Ireland, Tustervatn in Norway, Neuglobsow in Germany and Schausinland in Germany. A good correlation was found between modelled and measured seasonal cycles, especially in regions unaffected by anthropogenic activities. This result validates the use of REMOTE in determining long term ozone trends.

Future surface ozone levels were investigated over the European domain, but more regional effects were elucidated by also performing analysis for three subdomains; the North East Atlantic which is representative of a clean marine environment relatively unaffected by anthropogenic emissions, a central European region which is highly affected by anthropogenic activities and the Irish land mass which is influenced by the background ozone levels and local emissions. Analysis on these regional scales enabled identification of different responses of ozone to emissions and climate change, depending on the environment. In each of these subdomains, changes in surface ozone levels were attributed to either changing emissions or changing meteorology between 2006 and 2100 for representative months of January and August.

Over the European region bounded by the model domain, it was found that predicted future changes in surface ozone were dominated by changes in emissions with the exception of clean marine regions, as in the case of the North East Atlantic where future changes in ozone levels are predicted to be determined by meteorology changes. Using the RCP6.0 emission scenario, ozone levels are predicted to decrease by 2.0 ppb over Europe by 2100. The predicted fall in ozone concentration is attributed primarily to reduced emissions of ozone precursors. However, in periods of low insolation (winter months), the effect of reduced \( NO_x \) emissions was to increase ozone pollution due to reduced removal of ozone via \( NO_x \) titration. The effect of the changing meteorology is to decrease ozone in the summer months, most likely due to a temperature-driven increase in water vapour concentration which plays a role in ozone destruction.
In terms of modelling the future of ozone in terms of current air-quality indicators, a significant reduction in extreme ozone pollution events is shown in simulation results. The most extreme surface ozone levels simulated over Ireland falling well below the health-risk limit. It was also found that ozone pollution events are not only dependent on anthropogenic emissions, but are influenced by meteorology, with future extreme pollution events simulated over Europe in 2050 and 2100 despite significant reduction of ozone precursor emissions.

Considering the use of the RCP emission scenarios in the coming IPCC 5th Assessment report, results from this study are of considerable significance in evaluating the worth of emission control legislation in the light of likely meteorological changes in the coming century.

For this paper, the author downscaled 6-hourly meteorological data from the global climate model for use as initial and boundary conditions. Data was tested for a number of main parameters to ensure compatibility between model parameters. Emission data was obtained from the RCP database and compiled, converted and interpolated so as to be compatible with REMOTE. Again, data was tested and graphed to ensure no errors had occurred. In order to set up a pseudo-coupled regional climate model, monthly data was taken from the MPI-OM ocean model and interpolated for use as monthly input in REMOTE. Chemical boundary conditions were also procured from the ECHAM5-HAMMOC model and prepared in the same way.

The author ran all simulations on the high-performance computing system Stokes run by the Irish Centre for High-End Computing. Each monthly simulation was run in parallel, allowing for speedy execution of the tasks.

The author validated model performance by comparing model output of annual ozone cycle with in situ measurements at four separate EMEP locations.

All analysis was carried out by the author, including writing analysis scripts and writing scripts for preparation of graphs in GRADS soft-
ware. The author wrote the initial draft of complete paper and produced all figures and tables with the exception of Figure 6.
Conclusions and Outlook

Because of the high oxidising capacity of ozone and the non-linearity inherent in ozone chemistry, modelling of tropospheric ozone pollution is complex and relevant processes must be adequately parameterised in climate models. The significance of ozone fluxes to the ocean as a removal mechanism for MBL ozone has been in question for a number of decades and during this study, the mechanisms involved in the dry deposition of ozone to the ocean were investigated.

Several advances were made on the ozone parameterisation of Fairall et al. (2007). These include modelling the effect of salinity, sea surface temperature and sea surface iodide and organic concentrations on ozone deposition and evaluating a first order reaction rate between ozone and DOM was evaluated from laboratory experiments. The extended deposition scheme was then incorporated into the REMOTE model. The REMOTE model was then used to run annual simulations for base year 2006 and time-slice years 2030, 2050 and 2100 with scaled-down meteorological data from the ECHAM5-HAM MPIOM HAMMOC coupled model. From model results, the effects of climate change and changing RCP 6.0 emissions on future surface level ozone was quantified.

Key results from the annual simulation show that over Europe, future ozone levels are set to decrease, correlated with the decrease in ozone precursor emissions as determined by the RCP6.0 emission scenario. This reduction becomes most significant after 2050, when the effect of pollution mitigation kicks in over Europe. Due to the photochemical nature of tropospheric ozone production, simulated reductions are more pronounced in the summer, with a summertime reduction of 8ppb simulated over the model domain between 2006 and 2100. Results also show a reduction in future extreme pollution events under the RCP 6.0 scenario and the most extreme ozone levels simulated over Ireland in 2100 fall beneath the health-risk threshold.
It is noted that the use of time-slice years to evaluate the effect of climate change on a surface pollutant gives a questionable indication of future trends because the inter-annual variability between meteorological parameters has been neglected in the regional model simulations. Full investigation of the effects of climate change on boundary level ozone pollution would require long term (decadal) simulations to be performed on the regional model. However, on analysis of the meteorological output from regional climate model REMO (sister-model to REMOTE) as part of ENSEMBLES regional climate model validation project, deviation between surface temperature trend derived using each year between 2006 and 2100 compared to trend derived using only time slice years 2006, 2030, 2050 and 2100 was less than 10%. This gives a degree of confidence to the time-slice method.

In terms of the influence of the dry depositional sink on boundary level ozone budgets, results show that although advancement of the ozone deposition scheme improved model performance in simulating ozone concentrations when compared to in situ measurements, the overall impact on modelled ozone concentrations was insignificant compared to results obtained using the highly parameterised Wesely (1989) deposition scheme. This indicates that the dry depositional flux of ozone is not a critical parameter in the simulation of surface ozone levels within the REMOTE set up and other processes dominate in regulating of ozone budgets.

However, a significant controlling factor in this is the application of lateral boundary conditions to the domain of REMOTE which spans Europe and a section of the North East Atlantic. Boundary conditions significantly influence the ozone levels simulated in the North East Atlantic region and because of this, REMOTE is not an optimal tool to investigate the effect of advancing the ozone deposition scheme on simulated ozone levels in this region. Hence, the question of the effect of including the explicit oceanic deposition parameterisation on simulated ozone concentrations remains somewhat open. In order to fully assess the effect of the more explicit oceanic deposition scheme, simulations would need to be performed on global models, or regional models with domains covering a larger area of ocean. Simulations on this alternative spatial scale would also be required to assess the effect of changing ocean productivity on ozone deposition and whether this is of importance to long range transport of ozone and long term ozone trends (the question raised in Paper II, *Photochemical Impact on Ozone Fluxes in Coastal Waters*). Another question that remains open, is to what extent the boundary conditions influence simulation results. To make a crude attempt at quantifying the influence of boundary
conditions on simulated surface ozone concentrations, simulations were performed firstly with original boundary conditions, then increasing and decreasing the initial and boundary conditions by 50%. Simulated results were then averaged over the domain and over a boxed 1000km by 1000km region in the North East Atlantic. Results indicated that after the ten days, a 50% change in initial and boundary conditions altered the simulated ozone concentration by 35% over the entire model domain, but when focusing on the North East Atlantic region, the effect of altering the emissions was 47%. Despite the uncertainties presented by the influence of the boundary conditions on the simulation results and the subsequent inconclusiveness on the impact of the enhanced deposition model on simulated ozone concentrations, the work culminated in some significant results.

1. Further developing the Fairall et al. (2007) ozone deposition scheme

The development of the scheme to account for varied ozone deposition to waters of different salinity and temperatures is a further advancement of the dry deposition scheme which allows for more accurate application of the dry deposition theory to oceanic flux measurements, thus aiding investigation into as yet unidentified processes pertinent to ozone deposition. Further, the quantification of the reactions between ozone and DOC supported well established claims that this chemical sink may bridge the gap between observed ozone fluxes and theory. Uncovering a photodependence of the organic enhancement to ozone deposition is a new finding, and one that requires further study. To understand fully the mechanisms involved, more laboratory studies are required for the accurate determination of ozone-DOM reaction kinetics. Further, the distribution of the reactants in the surface layer may be significant, as may be the effect of multiple reactants in the microlayer on the ozone reactions.

2. Quantifying the upward iodine flux following ozone deposition

Despite the insensitivity of ambient ozone levels to ozone deposition flux in REMOTE, accurate deposition fluxes are required to evaluate subsequent iodine release. This ozone deposition driven halogen source is thought to drive new particle formation in the marine environment which is obviously of significant global importance. Hence, explicit representation of ozone deposition to the ocean in climate
models is vital in evaluating future climate scenarios and the interaction between air
quality and climate in particular. Preliminary studies have coupled the ozone driven
iodine emissions to particle formation within the REMOTE model, with interesting
results. The enhancement to the yield of nucleation mode particles as a result of
ozone deposition to DOM enriched ocean surfaces is simulated to be of the order
$1 \times 10^6 Nm^{-3}$ and further studies are required to quantify this particle formation
mechanism in relation to DMS-derived particles.
Bibliography


H. Goosse, P. Barriot, W. Lefebvre, M. Loutre, and Zunz. Introduction to climate

W. W. Gregg, N. W. Casey, and C. R. McClain. Recent trends in global ocean


U. Hogstrom. Non-dimensional wind and temperature profiles in the atmospheric

IPCC. IPCC third assessment report, climate change 2001: The scientific basis:

IPCC. Climate change 2007: the physical science basis. contribution of working
group i to the fourth assessment report of the intergovernmental panel on climate

D. Jacob. *Introduction to Atmospheric Chemistry*. Princeton University Press,

M. Z. Jacobson. Strong radiative heating due to the mixing state of black carbon


Appendix
A Dry Deposition Parameterisation of Wesely (1989)

The dry deposition parameterisation of Wesely (1989) is used in regional-scaled numerical models. It calculates deposition velocity for the range of gases used in acid deposition models by scaling the effective Henry’s law constants and chemical reactivities of the various gases to representative gases of SO$_2$ (highly soluble yet weakly reacting gas) and O$_3$ (weakly soluble yet highly reactive gas).

Derivation of the deposition velocity is divided into three steps, involving calculation of $R_a$, $R_b$ and $R_c$.

A1 Derivation of $R_a$

The mechanism involved in transport of the species through the atmosphere is turbulent transfer and it is the measure of atmospheric turbulence that determines $R_a$. Turbulence can be characterised by the kinetic energy of the turbulent velocity components (Liss and Slinn, 1983). Mean air flow is generated, driven by horizontal pressure gradients. Due to friction at the terrain surface, a shear flow (flow with a vertically changing wind vector) is produced which then converts the mean flow energy to turbulent kinetic energy.

The ambient density stratification strongly influences the turbulent intensity. The atmosphere is said to be stably stratified when ambient temperature increases or only slightly decreases with altitude, causing conditions in which a vertically-displaced particle of air decelerates and returns to its initial position, turbulent motions suppressed by friction-induced vertical motions which oppose the density stratification. A stable atmosphere inhibits cloud formation and leads to accumulation of pollution in the boundary layer (BL). The atmosphere is unstably stratified when ambient temperatures decrease with altitude, causing buoyant acceleration of a vertically displaced air parcel, thus enhancing vertical motions which receive energy from the density stratification. The intensity of turbulence is also dependent on surface roughness length, $z_{0,m}$ which refers to the height above a surface at which the logarithmic profile of windspeed versus altitude extrapolates to zero wind-speed. $z_{0,m}$ thus gives a measure of vertical turbulence generated due to horizontal wind flow at the terrain surface (Jacobson, 2005).

Turbulence has a diurnal cycle, with large turbulence intensity over a well-mixed layer in the daytime, leading to large atmospheric species transfer. Nocturnal turbulence is reduced due to stable stratification, effectively reducing potential for
atmospheric species transfer. Generally, $R_a$ is computed using gradient-transport theory and mass-transfer/momentum transfer similarity theory. On the assumption that turbulent transport of the species in the BL can be expressed in terms of an eddy diffusivity, $K$ multiplied by a concentration gradient, the vertical turbulent flux of species $i$ with concentration $C_i$ is described by the following expression:

$$F_i = K \frac{\partial C_i}{\partial z}$$

(A1)

Eddy diffusivity, $K$ is computed using similarity theory. Similarity theory refers to a method whereby variables are combined to form a dimensionless group. Empirical values for each parameter in the dimensionless group are then obtained experimentally. Then, an empirical expression for the dimensionless group is derived as a function of one or more of the component parameters (Jacobson, 2005). On repetition of the experiment, it is generally found that equations obtained from later experiments are similar to those obtained from the initial experiments. Thus giving rise to the term “similarity theory”. The relationship between the empirically derived equation and the dimensionless group is described as a similarity relationship. Application of similarity theory in the surface layer is described as Monin-Obukhov Similarity Theory (MOST) or surface-layer theory. MOST is employed in estimation of eddy diffusivities for momentum ($K_M$) and heat ($K_T$):

$$K_m = \frac{\kappa u_* z}{\phi_M(\varsigma)}$$

(A2)

$$K_T = \frac{\kappa u_* z}{\phi_T(\varsigma)}$$

(A3)

In these expressions for turbulent eddy diffusivities, $u_*$ is the friction velocity; a measure of the surface layer vertical momentum flux.

$$u_* = \sqrt{(\overline{w'v'})} = \left[ (\overline{w'u'})^2 + (\overline{w'v'})^2 \right]^{1/4} = \sqrt{\frac{|\tau_z|}{\rho_a}}$$

(A4)

where $u'$, $v'$ and $w'$ denote the fluctuating components of velocity in, respectively, the horizontal mean wind direction, the horizontal perpendicular to mean wind direction and the vertical direction. $\tau_z$ describes the vertical turbulent flux of horizontal momentum. $\kappa$ is the von Karman constant, a dimensionless constant describing the logarithmic velocity profile of a turbulent fluid flow near a boundary with a no-slip
condition \(^1\). \(\kappa\) relates to \(u_*\) by the following expression:

\[
u(z) = \frac{u_* \ln \frac{z}{z_{0,m}}}{\kappa}
\]  

(A5)

where where \(u(z)\) denotes the mean flow velocity at height \(z\), and \(z_{0,m}\) is the aforementioned roughness length, at which height \(u\) extrapolates to zero. \(\kappa\) is know to have a value between 0.35 and 0.43 (Hogstrom, 1988) and a value of 0.4 is assumed in many numerical models. Charnock’s formula is commonly used to relate \(z_{0,m}\) to \(u_*\):

\[
z_{0,m} = 0.015 \frac{u_*^2}{g}
\]  

(A6)

In equation A2 and A3 above, \(\phi_M\) and \(\phi_T\) are dimensionless momentum and temperature profile functions, derived using MOST. Integrating equation A1, the expression for aerodynamical species flux across the surface layer (from surface roughness length \(z_{0,m}\) to reference height, \(z\)), \(F_i\) can be rewritten as follows:

\[
F_i = \Delta C_i \int_{z_{0,m}}^z \phi(\varsigma) \kappa u_* z \, dz
\]  

(A7)

\(\Delta C_i\) refers to the concentration gradient over the surface layer, varying from surface roughness length to reference height, \(z\). \(\phi(\varsigma)\) denotes either \(\phi_M\) or \(\phi_T\), depending on which is most suitable to correspond to the species profile function. By comparison with equation 1.9, an expression for aerodynamic resistance, \(R_a\) can be written as follows:

\[
R_a = \int_{z_{0,m}}^z \frac{\phi(\varsigma)}{\kappa u_* z} \, dz
\]  

(A8)

Integrating over the relevant heights:

\[
R_a = \frac{1}{\kappa u_*} \ln \left( \frac{z}{z_{0,m}} \right)
\]  

(A9)

As mentioned above, the turbulence of the atmosphere is highly dependent on atmospheric stability. Therefore, this expression for \(R_a\) holds only for neutral conditions (when the dimensionless scaling parameter used in MOST \(\varsigma = z/L = 0\) where \(z\) is the reference height and \(L\) is the Monin-Obukhov length (MOL)). The MOL is a length scale proportional to the height above the surface above which buoyancy produced turbulence begins to dominate over shear turbulence (Jacobson, 2005).

\(^1\)From Wikipedia
The MOL is effectively a measure of stability in the surface layer.

\[ MOL = \frac{-\rho \dot{c}_p T_0 u_*^3}{\kappa g \bar{q}_3} \]  \hspace{1cm} (A10)

where \( \rho \) is air density, \( \dot{c}_p \) is the heat capacity of air under constant pressure, \( T_0 \) is surface temperature and \( \bar{q}_3 \) is the vertical mean turbulent heat flux. In an atmosphere of neutral stability, the temperature gradient within the mixed layer is not pronounced enough to allow unrestrained convection (as in an unstable atmosphere); nor is the temperature gradient weak enough to prevent all convection (as in a stable atmospheric environment). Vertical mixing occurs in a neutrally stratified atmosphere, but convective acceleration of air parcels does not. When the atmosphere is in a state of either stable or unstable stratification, obviously the expression for \( R_a \) above must be corrected for stability. This is achieved by way of a diabatic correction term \( \Psi \).

\[ R_a = \frac{1}{\kappa u_*} \left[ \ln \left( \frac{z}{z_{0,m}} \right) - \Psi \left( \frac{z}{MOL} \right) \right] \]  \hspace{1cm} (A11)

The diabatic correction is calculated as a function of the dimensionless MOST scaling factor \( \varsigma = z/MOL \) which considers atmospheric stability and estimated effects of buoyancy-induced alterations to the flux-gradient relationships. Calculation of \( \Psi \) is described in Wesely and Hicks (1977).

### A2 Derivation of \( R_b \)

There exists a thin layer of stagnant air (the quasi-laminar sublayer) adjacent to the earth’s surface within which the downward movement of a gas species is dependent on molecular diffusion. Adhering to the resistance model for dry deposition, the next step in calculating dry deposition velocity involves estimating the resistance to diffusion across the quasilaminar sublayer, which is determined by the molecular properties of the gas and the characteristics of the earthly surface (Seinfeld and Pandis, 1997). As the turbulent flow has a much greater mixing efficiency than molecular transfer, weak gradients are produced away from the interface, whereas strong gradients are produced in the near-surface regions where the turbulent flows are suppressed due to the viscosity of the quasi-laminar layer. The stagnant air is formed by multiple viscous layers adjacent to the earth’s surface and consequently, the depth of the layer varies with turbulent shear stresses adjacent to the boundary and is dependent on the shape and smoothness of the surface. For example, the
quasi-laminar sublayer may exist only at intermittent stages on a plant leaf, which is in constant motion. Using the resistance-approach model for computation of dry deposition rate, the quasi-laminar sublayer is assumed to exist.

The flux across the quasi-laminar sublayer at the surface is defined using a dimensionless transfer coefficient, \( B \). Under steady-state conditions, it is assumed that the flux \( F_i \) of gas species \( C_i \) across the quasi-laminar sublayer is equal to that across the surface layer. By convention, \( B \) is parameterised using the measure of turbulence, \( u_* \).

\[
F_i = B u_* \Delta C_i
\]  

(A12)

where \( C_i \) denotes the concentration difference of gas \( i \) across the layer. Resistance to the quasi-laminar sublayer flux, \( R_b \) is therefore given by:

\[
R_b = \frac{1}{B u_*}
\]  

(A13)

(Seinfeld and Pandis, 1997). To quantify \( R_b \), transfer coefficient \( B \) is expressed in terms of a surface transfer function Particles diffuse via Brownian motion, whereby continuous collisions between particles suspended within the fluid cause the particles to drift in a seemingly random motion (Seinfeld and Pandis, 1997). Diffusivity of a particle can be estimated from the Stokes-Einstein Equation

\[
D = \frac{k_B T}{3\pi \mu D_p}
\]  

(A14)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \mu \) refers to the viscosity of the gas and \( D_p \) is the particle diameter. Gases diffuse via molecular diffusion; diffusion that occurs due to the thermal properties of the molecules. The rate at which a gas diffuses across the quasi-laminar sublayer, and consequently \( B \), is dependent on the small-scale molecular characteristics of the gas in question: the temperature, the viscosity of the fluid and the mass of the gas molecules. The molecular diffusion coefficient of a gas \( i \) in air is given by the following expression (Chapman and Cowling, 1970; Davis, 1983):

\[
D_i = \frac{5}{16N_A d_i^2 \rho_a} \sqrt{\frac{RT m_a}{2\pi \left( \frac{m_i + m_a}{m_i} \right)}}
\]  

(A15)

where \( N_A \) is Avogadro’s number, \( d_i \) is the collision diameter of a gas molecule of species \( i \), \( R \) is the gas constant, \( T \) is the temperature, \( m_a \) and \( m_i \) are the molecular weights of air and gas species \( i \), respectively. The dynamic viscosity of air, \( \eta_a \) is
quantified by:

\[ \eta_a = \frac{5}{16N_A d_i^2} \sqrt{\frac{RT_m}{\pi}} \]  

(A16)

and the kinetic viscosity, or vorticity of air, \( \nu_a \) is defined as the ratio of the momentum diffusivity:

\[ \nu_a = \frac{\eta_a}{\rho_a} \]  

(A17)

Vorticity measures the tendency of the fluid to 'curl up' or to spin. If the species in question is air, diffusion coefficient \( D_i \) can be expressed as \( \nu_a \) and equation A15 can be simplified to expression A17.

For gas species \( i \), the molecular diffusivity is characterised by the dimensionless Schmidt number, \( Sc_i \)

\[ Sc_i = \frac{\nu_a}{D_i} \]  

(A18)

The Schmidt number of a gas species is the ratio between the kinematic viscosity of the fluid in which the species resides (air in this case), and the molecular diffusion coefficient of the gas in question. At an interfacial surface, a continuum fluid flow must stop, and so the surface is a source of vorticity for the fluid. The generated vorticity diffuses into the fluid, while simultaneously the trace gas molecules diffuse towards the surface. Near a surface, the Schmidt number gives a measure of the relative thicknesses of the viscous and diffusion boundary layers (see figure A1, reproduced from Liss and Slinn (1983) which represents the diffusion of a gas molecule in a water droplet). For \( Sc_i \approx 1 \), as for gases with low molecular weight, the thicknesses of the two layers are roughly equivalent.

For \( Sc_i \gg 1 \) (as in the case of ozone), the diffusion layer is very thin, and so the density gradients are large, and the diffusive flux does not decrease linearly with particle size as \( D_i \) decreases, but instead decreases with \( D_i^{2/3} (Sc_i^{-2/3}) \) in the case of a rigid surface, or as \( D_i^{1/2} (Sc_i^{-1/2}) \) in the case of a free surface (Jähne et al., 1987; Ledwell, 1982, 1984; Esdorn and Mersmann, 1984; Coantic, 1986). In this case, the viscous boundary layer \( \nu_a \) is thicker than the particle diffusion layer (D). The larger the gradients, the larger the flux of particles.

If the Schmidt number characterises the diffusive flux of a gas species due to the molecular diffusion of the species, the Prandtl number characterises the diffusive flux of a gas species due to thermal properties of the gas. The Prandtl number is proportional to the ratio of the dynamic viscosity of air to its thermal conductivity \( (\kappa_a) \):

\[ Pr = \frac{\eta_a c_{p,m}}{\kappa_a} = \frac{\nu_a}{D_h} \]  

(A19)
Figure A1: Schematic representation of Schmidt number
where $c_{p,m}$ is the specific heat capacity for moist air at constant volume and $D_h$ is the molecular thermal diffusion coefficient, expressed as

$$D_h = \frac{\kappa_a}{\rho_a c_{p,m}}$$  \hspace{1cm} (A20)

(Pruppacher and Klett, 1997). From Wesely and Hicks (1977), the dimensionless transfer coefficient $B$ can be expressed in terms of the Schmidt and Prandtl numbers, thus accounting for molecular and thermal diffusion across the laminar sublayer, respectively:

$$B = \frac{\kappa}{\ln(z_{0,m}/z_0)(Sc_i/Pr)^{2/3}}$$  \hspace{1cm} (A21)

where $z_0$ is a roughness length specific to the gas in question. $\ln(z_{0,m}/z_0)$ was estimated as having a value of 2 for vegetated areas using both wind tunnel data (Garratt and Hicks, 1973) and the profile method, (Shepherd, 1974). Resistance to gaseous transfer across the quasi-laminar sublayer can therefore be written as follows:

$$R_b = \frac{2(Sc_i/Pr)^{2/3}}{\kappa u_*}$$  \hspace{1cm} (A22)

### A3 Derivation of $R_c$

$R_c$ parameterises the resistance to gas uptake at the earth’s surface. It is governed by the physical and chemical properties of the gas as well as the properties of the terrain to which the gas is being deposited, making $R_c$ the most difficult of the three resistances to parameterise. Generally, $R_c$ is computed as the combined resistance of all transfer pathways instrumental in the surface uptake of the trace gas (Ganzeveld and Lelieveld, 1995). Within the schemes, some of the component resistances of $R_c$ are assigned using data tables of field measurements while others are scaled to vary with some governing parameters (solar radiation, surface temperature, Henry’s constant, diffusivity etc.) In the Wesely (1989) gaseous deposition parameterisation, the component resistances for various gas species are scaled to measured resistance values of $SO_2$, which represents a highly soluble, yet weakly reacting gas and to $O_3$, which represents a weakly soluble, yet highly reactive gas.

In this parameterisation, the surface resistance of ozone to water is set to a constant $2000 \text{ sm}^{-1}$, regardless of atmospheric and water conditions. This value was chosen based on the limited number of field studies available at the time, namely the labo-
ratory measurements of Galbally and Roy (1980) and field measurements of Wesely et al. (1981).

**A4 Calculation of Deposition Velocity**

As stated in the main text, deposition velocity is computed as the reciprocal of the sum of resistances. However, as $R_c$ is the determining resistance in the case of ozone deposition to the ocean (Lenschow et al., 1982), setting $R_c$ to a constant value of 2000 $sm^{-1}$ in a gaseous dry deposition parameterisation will yield ozone deposition velocities to ocean surface of $v_d \approx 0.05cms^{-1}$. 
Ozone dry deposition parameterisation of Fairall et al. (2007)

From first principles, integration of the budget equation for mass conservation of a chemical \( X \) in water over vertical height \( z \) (Fairall et al., 2000) yields:

\[
\frac{\partial X_w}{\partial t} + U \cdot \nabla X_w = - \frac{\partial \left[ w' x' w - D_{xw} \frac{\partial X_w}{\partial z} \right]}{dz} - aX_w
\]  

(B1)

where \( z \) is the distance from the air-sea interface, \( U \) is the mean horizontal flow, \( w' x' w \) is the turbulent flux, \( D_{xw} \) is the molecular diffusivity of species \( X \) in the water, and \( aX_w \) is the loss rate in the water due to chemical reactions. Chemical reactivity term \( a \) is equivalent to the \( \lambda \) term used in previous parameterisations (Garland et al., 1980; Chang et al., 2004). Representing the turbulent flux using eddy diffusion coefficient, \( w' x' w = -K \frac{\partial X_w}{\partial z} \), the above equation can be rewritten:

\[
\frac{\partial X_w}{\partial t} + U \cdot \nabla X_w = - \frac{\partial \left[ - (D_{xw} + K(z)) \frac{\partial X_w}{\partial z} \right]}{dz} - aX_w
\]  

(B2)

The flux of species \( x \) into the water phases can be deduced by integrating the mass conservation equation over height \( z \). It is assumed that reactant concentration is constant with respect to \( z \).

\[
F_{xw} = - \left[ D_{xw} + K(z) \right] \frac{\partial X_w}{\partial z} + a \int_0^z X_w(z)dz
\]  

(B3)

This flux expression comprises three components: the diffusive flux (\( F_{xD} \)), the turbulent flux (\( F_{xT} \)) and a third flux, associated with the concentration gradient of the gas species as it penetrates into the water depth and reacts. By assuming the case of a non reactive gas (\( a = 0 \)) where

\[
F_{xw} = \left[ D_{xw} + K(z) \right] \frac{\partial X_w}{\partial z}
\]  

(B4)

and then matching the gas fluxes at the air and sea sides of the interfaces, an expression for a general flux term can be derived:

\[
F_{xa} = \frac{X_a/\alpha_x - X_a}{(R_a + R_b) + (\alpha_x V_{xw})^{-1}}
\]  

(B5)

where \( X_w \) and \( X_a \) are the water phase and air phase gas concentrations respectively, \( V_{xw} \) is the surface transfer of ozone and \( \alpha \) is the dimensionless solubility of the gas.
This flux expression can be applied to a reacting gas. In the case of a reacting gas, it can be assumed that the gas concentration falls to zero in the bulk water, so $X_w \rightarrow 0$. From this, it follows that:

$$\frac{1}{R_c} = \alpha_x V_{xw} = \frac{\alpha F_{xw}}{X_{ws}}$$  \hspace{1cm} (B6)

$$V_{dx} = \frac{1}{R_a + R_b + R_c}$$  \hspace{1cm} (B7)

Within this robust parameterisation, the turbulent component of ozone deposition is treated using standard MOST (Fairall et al., 2000). Within the molecular sublayer, transport is influenced by chemical reactions. In the case of the molecular sublayer at the air-water interface, both fluids display almost linear height/depth dependence of vertical turbulence. This occurs due to increased fluid viscosity at the interface and subsequent dissipation of the turbulent eddies: the smaller the turbulent eddy, the more intense the dissipation. This results in a turbulent micro-scale:

$$\delta u \approx \frac{10\nu}{u_*}$$  \hspace{1cm} (B8)

$\nu =$kinematic viscosity, $u_*$=friction velocity, where turbulent fluctuations smaller than $\delta u$ are exponentially attenuated.

Because of this attenuation of small boundary-side turbulent eddies, ozone approaching the ocean surface from the air is initially transported away from the boundary interface by molecular diffusion.

The time taken for random molecular transport over the turbulent microscale is defined as

$$t_D \approx \frac{\delta^2}{D_x}$$  \hspace{1cm} (B9)

$D_x$ being the molecular diffusivity of the gas. Characterising the time-scale of a chemical reaction for species X with in the fluid using the chemical reactivity term $a$, akin to first order loss rate used by Chang et al. (2004) and Garland et al. (1980), gives:

$$t_D = \frac{1}{a}$$  \hspace{1cm} (B10)

Disregarding the effects of turbulence, completion of the reaction occurs by the time the species has traversed distance $\delta$:

$$\delta = \left(\frac{D_x}{a}\right)^{1/2}$$  \hspace{1cm} (B11)
δ_u is generally about a millimetre in depth and assuming molecular diffusivity is of the order of \(10^{-9} \text{m}^2 \text{s}^{-1}\) (Johnson and Davis, 2006; Wilke and Chang, 1955), from this analysis it can be presumed the effect of turbulent driving of ozone into the bulk layer need not be considered for for reactions with \(a > 100 \text{s}^{-1}\). For \(a\) values exceeding 100\(\text{s}^{-1}\), \(\delta << \delta_u\) and so the effect of turbulent diffusion is negligible.

**B1 Ocean surface transfer velocity from fundamentals**

When reactivity is high, ozone reacts so quickly that the profile of the gas within the molecular sublayer becomes negligible. Applying this to the mass conservation equation gives:

\[
F_{xs} = D_x \frac{\delta^2[X]}{\delta z^2} - a[X] = 0
\]  

(B12)

where \(a\) is the aforementioned first order loss rate due to chemical reactions. Assuming ozone concentration exceeds the reactant concentration in the water, a first order reaction rate can be applied. By combining this with Fick’s first law of diffusion, \(R_c\) (Equation B6) can then be estimated by the following expression:

\[
R_c = \frac{1}{\sqrt{aD_x}}
\]  

(B13)

Surface transfer is defined as:

\[
V_{xw} = \frac{F_{xs}}{X_s} = \sqrt{aD_x}
\]  

(B14)

In considering turbulent enhancement of surface transfer, eddy diffusivity must be accounted for in formulations. Fairall et al. (2000) derive the following expression using surface layer similarity scaling:

\[
K(z) = \kappa u_* z
\]  

(B15)

Here, \(u_*\) denotes the friction velocity in the water surface layer. Now, the mass conservation equation is written as follows:

\[
\frac{\partial}{\partial z} \left[ (D_x/\kappa u_* + z) \frac{\partial X}{\partial z} \right] - \frac{a}{\kappa u_*} X = 0
\]  

(B16)

Let \(y^2 = (D_x/\kappa u_* + z)\), and solutions of Equation B16 are modified Bessel functions
of zero order (Geernaert et al., 1998).

\[ X = A I_0(\xi) + B K_0(\xi) \]  
(B17)

\[ \xi^2 = \frac{4a}{\kappa u_s} \left( z + \frac{D_x}{\kappa u_s} \right) \]  
(B18)

\( I_0 \) and \( K_0 \) being modified zero-order Bessel functions (Abramowitz and Stuegun, 1964). \( A \) and \( B \) are obtained by constraining the boundaries. Assuming chemical reactivity is uniform within the water, boundary conditions are defined at the air-sea interface \(( z = 0 )\), and infinitely deep in the ocean \(( z = \infty )\).

At the surface, the sum of turbulent and diffusive flux of species \( X \) can be expressed as follows:

\[ F_{xs} = - \left[ D_x + K(z) \right] \frac{\partial X}{\partial z} \]  
(B19)

Infinitely deep in the ocean, ozone concentration tends to zero, as all of it will have been destroyed by reaction. As \( I_0 \) increases with depth, from Equation B17 \( A \) can be assumed to be 0. Equation B17 can then be rewritten as:

\[ X = B K_0(\xi) \]  
(B20)

The mixing component of the flux, \( F_{xM} \) (the sum of diffusive and turbulent fluxes) can now be expressed as follows:

\[ F_{xM} = - \left( D_x + \kappa u_s \right) \frac{\partial X}{\partial z} = -B \left( D_x + \kappa u_s \right) \frac{\partial K_0(\xi)}{\partial z} \]  
(B21)

Using the recurrence relation of Bessel functions whereby \( \frac{\partial K_0}{\partial \xi} = -K_1 \) (note: differs to expression quoted in original Fairall et al. (2007) paper), mixing flux can be expressed in terms of variable \( \xi \):

\[ F_{xM} = B \frac{\kappa u_s}{2} \xi K_1(\xi) \]  
(B22)

By applying this expression for ozone concentration to the surface boundary condition, \( F_{xM} = F_{xs} \), an expression for \( B \) can be evaluated:

\[ B = \frac{2F_{xs}/\kappa u_s}{\xi_0 K_1(\xi)} \]  
(B23)

\[ \xi_0 = \frac{2}{\kappa u_s} \sqrt{a D_x} \]  
(B24)

Applying this expression for \( B \) to Equation B20, a depth-dependent expression for
ozone concentration within the water is obtained.

\[ X(z) = \frac{2F_{xs}/\kappa u_*}{\xi_0 K_1(\xi_0)} \]  

Combining Equation B22 with the expression for B, an expression is obtained for the mixing flux throughout the mixing depth:

\[ F_{xM}(z) = F_{xs} \frac{\xi K_1(\xi)}{\xi_0 K_1(\xi_0)} \]  

This expression defines how the mixing flux declines as the gas is absorbed balanced by chemical destruction of the ozone. Applying the expressions for the ozone profile and mixing flux to the total water flux, as described in Equation B3 gives:

\[ F_{xw} = \left[ \xi K_1(\xi) + \int_{\xi_0}^{\xi} \xi K_0(\xi) d\xi \right] \frac{F_{xs}}{\xi_0 K_1(\xi_0)} \]  

In this expression, the first term defines turbulent and diffusive transport, whereas the second defines chemical loss. As \( z \to \infty \), the transfer term tends to zero and total flux is now only dependent on the chemical term:

\[ F_{xs} = a \int_{0}^{\infty} \frac{X(z)dz}{\xi K_1(\xi)} = \frac{\kappa u_*}{2} B \int_{0}^{\infty} \frac{K_1(\xi_0)}{K_0(\xi_0)} B_{00}(\xi) \]  

By once again employing the use of the recurrence property of Bessel functions, this expression can be used to relate the surface flux to \( B \). The surface transfer velocity is obtained by applying the gas concentration profile (Equation B25) to the fundamental \( V_d - \) flux relationship (Equation 1.8):

\[ V_{xw} = \frac{F_{xs}}{X(z)} = \frac{\kappa u_* \xi_0 K_1(\xi_0)}{2K_0(\xi)} = \sqrt{aD_x} \frac{K_1(\xi_0)}{K_0(\xi_0)} \]  

In the case of a highly reactive gas, \( a \) will be large, so the limit of \( \frac{K_1}{K_0} \) will tend to 1. This yields the same expression for \( V_{xw} \) as in the case of no turbulence (Equation B14, previously defined by Garland et al. (1980)). Further, in the molecular sublayer, the concentration of ozone tends to zero as \( z > \frac{D_x}{\kappa u_*} \) (when the turbulent eddy diffusivity exceeds the molecular diffusivity).

\[ V_{xw} \to -\frac{\kappa u_*}{2} \ln \left( \frac{2}{\kappa u_* \sqrt{aD_x}} \right) \]  

With low reactivity values, the profile of \( Z \) is linear in the diffusion sublayer, logarith-
mic in the bulk, and approaches zero for $z \neq \frac{\kappa u_*}{4a} = \delta_T$ where $\delta_T$ can be described as the chemo-turbulent diffusive scale. The transition between the strongly and weakly reacting occurs for $\xi_0 \neq 1$ which translates to reactivity $a_{\text{crit}} = \frac{(\kappa u_*)^2}{4D_x}$. It is notable that the dimensionless parameter $\xi_0$ is the ratio between $\delta_T$ and the chemomolecular diffusive scale $\delta$ defined in Equation B11. For typical oceanic conditions, $a_{\text{crit}} = 10^3 \text{s}^{-1}$. 
Paper I
Research Article

Regional-Scale Ozone Deposition to North-East Atlantic Waters

L. Coleman, S. Varghese, O. P. Tripathi, S. G. Jennings, and C. D. O’Dowd

School of Physics and Centre for Climate and Air Pollution Studies, National University of Ireland, Galway, Ireland

Correspondence should be addressed to L. Coleman, colin.odowd@nuigalway.ie

Received 15 February 2010; Revised 28 May 2010; Accepted 16 July 2010

Academic Editor: Elisabetta Vignati

Copyright © 2010 L. Coleman et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A regional climate model is used to evaluate dry deposition of ozone over the North East Atlantic. Results are presented for a deposition scheme accounting for turbulent and chemical enhancement of oceanic ozone deposition and a second non-chemical, parameterised gaseous dry deposition scheme. The first deposition scheme was constrained to account for sea-surface ozone-iodide reactions and the sensitivity of modelled ozone concentrations to oceanic iodide concentration was investigated. Simulations were also performed using nominal reaction rate derived from in-situ ozone deposition measurements and using a preliminary representation of organic chemistry. Results show insensitivity of ambient ozone concentrations modelled by the chemical-enhanced scheme to oceanic iodide concentrations, and iodide reactions alone cannot account for observed deposition velocities. Consequently, we suggest a missing chemical sink due to reactions of ozone with organic matter at the air-sea interface. Ozone loss rates are estimated to be in the range of 0.5–6 ppb per day. A potentially significant ozone-driven flux of iodine to the atmosphere is estimated to be in the range of 2.5–500 M molec cm\(^{-2}\) s\(^{-1}\), leading to a mixing-layer enhancement of organo-iodine concentrations of 0.1–22.0 ppt, with an average increase in the N.E. Atlantic of around 4 ppt per day.

1. Introduction

Ozone plays a key role in atmospheric chemistry, absorbing harmful UV rays in the stratosphere whilst simultaneously acting as a greenhouse gas (radiative forcing of tropospheric ozone is around 25% that of CO\(_2\) [1]), and acting as a harmful pollutant in the troposphere [2–4]. Influencing the oxidising capacity of the atmosphere as a powerful oxidising agent, it is the dominant precursor to the ubiquitous hydroxyl radical which acts as an atmospheric cleansing agent by determining the lifetime of important atmospheric trace gases. It is vital, therefore, that tropospheric ozone concentrations are realistically simulated in modelling both air pollution and chemistry-climate interactions.

600–1000 Tg O\(_3\) year\(^{-1}\) is removed from the troposphere via dry deposition [5]. The deposition of ozone to water surfaces is small compared to deposition to land [6]: typically, the rate of dry deposition of ozone to the continent is nearly six times faster than the dry deposition rate of ozone to the ocean [7]. However, considering 70% of the globe has ocean coverage, the loss of marine boundary layer ozone via oceanic dry deposition still represents a significant sink for the global ozone budget. Obtaining an accurate prediction of ozone flux to the sea is imperative not only in predicting ambient ozone concentrations, but also because of the biogeochemical consequences of ozone reactions in the sea surface.

For example, recent work [8, 9] has shown that ozonation of iodide in the sea surface can result in the formation of reactive organoiodine products that result in iodocarbon emissions from the sea surface. These iodocarbons photodissociate rapidly form iodine atoms which are known to catalytically destroy ozone [10], resulting in further reduction of marine boundary layer ozone levels. Also, ozonation of iodine atoms results in formation of iodine oxide (IO) radicals which have the potential to lead to new marine aerosol formation [11]. This newly discovered mechanism could have significant biogeochemical consequences, in terms of the feedback mechanism in halogen-mediated ozone destruction, the halogen source in coastal areas which
could account for the hitherto unexplained elevated levels of IO observed at Cape Verde [12], and the subsequent formation of new particles which could influence the solar radiation budget.

There is still major uncertainty regarding the amount of ozone lost to the ocean by dry deposition [13]. The dry deposition of ozone to the ocean involves a number of complex processes: physical, chemical, and biological. Transport of ozone through the atmosphere depends on surface roughness, wind speed, and atmospheric turbulence; transport across the quasilaminar boundary layer is limited by the diffusivity of the gas in air, while the ocean-surface uptake of ozone depends on the water-side turbulence conditions, ozone solubility, and availability of reaction sites on the ocean surface [14, 15]. Up to now, these processes have been poorly understood and have not generally been considered in deposition schemes commonly applied in atmospheric chemistry models. The difficulty in the definition, and therefore the parameterisation of these processes is exacerbated by the scarcity of in situ measurements of ozone dry deposition velocities. Wesely and Hicks [16] found deposition velocities of ozone to the sea surface to vary between 0.01 and 0.05 cm s$^{-1}$. However, the eddy correlation studies of Gallagher et al. [17] carried out in the North Sea indicate deposition velocities as high as 0.1 cm s$^{-1}$.

The rate of gaseous dry deposition to a surface is parameterised by deposition velocity, $V_d$ (cm s$^{-1}$). $V_d$ is used to calculate the downward flux of ozone to the ocean, $F_{03}$ = $V_d$C where $C$ denotes surface level gas concentration. $V_d$ is computed (in analogy with electrical transport) as the reciprocal of the sum of the resistances encountered by the gas on its journey to the surface sink. Using the standard resistance model to compute deposition velocity, resistances to gaseous deposition are atmospheric resistance, quasilaminar resistance and surface resistance [14].

The gaseous dry deposition scheme of Wesely [18] is widely applied in air quality, atmospheric chemistry, and chemistry climate models to represent gaseous dry depositional sinks. In its evaluation of deposition velocity, this scheme calculates explicitly only aerodynamic resistance and resistance to transfer across the quasilaminar surface layer. Surface resistance is calculated as a series of smaller resistances which are generally provided by look-up tables, with values differing according to land use type, species in question and season. In this system, derivation of surface resistance to deposition at water surfaces is neglected and surface resistance is set to a constant value of 2000 m$^{-1}$ s. The same surface resistance is applied to all water surfaces, irrespective of water body classification, climate, or meteorological conditions, thereby grossly simplifying the complex mechanisms involved in surface transfer. Surface resistance is the most significant parameter in the case of ozone deposition to the ocean [19] and in reality, surface resistance is greatly diminished by turbulence in the ocean surface and by the presence of ocean-depleting chemicals in the ocean surface—namely iodide [20, 21], and organic matter [22], for example, chlorophyll [23] and DMS [5, 20]. Due to the highly reactive nature of ozone, these ocean surface reactions can have a very significant enhancing effect on oceanic ozone deposition and the chemical reactions between ozone and organic matter and chlorophyll have yet to be parameterised and constrained in dry deposition models.

Due to its parameterisation of surface resistance, the dry deposition scheme of Wesely [18] underestimates deposition rate of ozone to the ocean at both high- and low-wind speeds compared to observations [20].

The advanced Fairall et al. [13] scheme described in Section 2.1 is an explicit parameterisation of ozone deposition to the ocean, allowing for enhanced ozone deposition due to ocean surface turbulence and ocean surface layer reactions.

The Fairall et al. scheme has recently been incorporated into a global model, with results indicating the importance of controlling parameters, and validation the parameterisation conducted by Ganzeveld et al. [5]. In this study, the parameterisation is scaled to include reactions of ozone with iodide, dimethyl sulfide (DMS), alkenes, and organic chemistry. The study finds the role of biogeochemistry to dominate in computation of deposition velocities in the tropical and subtropical regions whereas the turbulent forcing of ozone deposition dominated over biogeochemical factors in the mid to high latitudinal regions. Simulation results indicate a small sensitivity of marine boundary layer ozone concentrations to varying biogeochemical and turbulent conditions, despite the wide range of deposition rates simulated using the Fairall et al. [13] scheme which is scaled to include organic reactions. This occurs partly due to interaction of different factors affecting deposition velocity: For example, in tropical regions, the reducing effect of high water temperature values on ozone solubility in water counteracted higher chemical ozone transfer due to elevated iodide concentrations. As a result, applying enhanced iodide concentrations in coastal regions did not explain discrepancies between observed and simulated $V_{dry}$. Furthermore, the lack of sensitivity of simulated boundary layer ozone concentration to dry deposition velocity illustrates the role of compensating effects in climate models due to atmospheric transport and chemistry which maintain ozone concentrations within the marine boundary layer, despite the temporal and spatial variability in oceanic ozone uptake. The global model study also found the use of the advanced Fairall et al. [13] scheme in the model only slightly reduced (~6%) the total dry deposition flux of ozone to the ocean compared to simulations ran using the Wesely [18] scheme with constant surface-resistance. This shows that the Wesely [18] scheme is appropriate for modelling ozone deposition on a global scale for an annual period, but it is thought that due to the North East. Atlantic region being both organically active and prone to turbulent conditions, use of the chemically enhanced Fairall et al. [13] scheme on ozone concentrations in this area may be more significant due to regional-scale, short-term effects than indicated by findings of the global model study of Ganzeveld et al. [5]. Also, as the effect of temperature on molecular diffusivity is accounted for in this study, it is thought that the limiting effect of ozone water solubility on computed deposition velocities will be less pronounced than found in the global model study (see Section 2.2.3). Furthermore, in contrast
with the global model simulations, in this study the effect of salinity on ozone solubility, diffusivity, and ozone-iodide reaction rates are included. Our analysis shows that effect of salinity on ozone-iodide reactions can enhance reaction rates by as much as 23% (Section 2.3.1). Including the effect of salinity on key parameters accounts for further variations between results the global model study and results of regional model simulations presented here.

For this study, the Fairall et al. [13] parameterisation has been adapted to account for enhanced deposition due to iodide-ozone reactions in the ocean-surface layer. Furthermore, a mechanistic scaling to account for marine organic chemistry using oceanic chlorophyll concentrations as a proxy for organic activity has been included in the scheme. The parameterisation is then incorporated into the regional climate model with tracer extensions (REMOTE) [24, 25] and the sensitivity of simulated ozone flux and ambient ozone concentrations to varying oceanic iodide concentrations and inclusion of organic chemistry is investigated.

2. Methods

2.1. Details of the Fairall et al. [13] Parameterisation of Oceanic Ozone Deposition. The ozone deposition parameterisation of Fairall et al. [13] calculates oceanic ozone dry deposition velocity by integration of the turbulent-molecular transport equation in the ocean, while accounting for increased deposition of ozone to the ocean due to sea surface turbulence and due to surface-level chemical reactions. The sea-surface turbulence is a function of wind speed, water density, and the buoyancy flux of water [26].

Chemical reactions are integrated into the scheme by way of reactivity time-scale term, $A_{reac}$ ($s^{-1}$) which characterises the time scale of a chemical reaction for ozone in the sea water. It is calculated as the product of the sea-surface concentration of the ozone reactant ($C_i$) and a second order rate constant ($k_r$) for the reaction in question

$$A_{reac} = \sum C_i k_r$$

Instead of using the three-resistance approach of Wesely [18], this parameterisation combines atmospheric and quasiliamnarin resistance into one resistance term which is calculated using the tropical ocean global atmosphere coupled ocean-atmosphere response experiment (TOGA-COARE) gas transfer model [27, 28]. The bulk of the parameterisation serves the computation of the turbulence-dependent surface resistance with an added chemical enhancement term. The scheme has been modified to allow for variation of iodide reaction rates with temperature [29], variation of ozone diffusivity in water due to temperature [30] and salinity [31], and variation of ozone solubility with temperature [32].

2.2. Sensitivity Analysis

2.2.1. Turbulent/Nonturbulent Scheme. The Fairall et al. [13] scheme computes surface resistance by first solving the conservation equation for the case of negligible turbulence. From this solution, the turbulent solution is calculated by considering a turbulent eddy diffusivity term obtained using surface-layer similarity scaling [27]. From the scheme, deposition velocities are effectively calculated for two cases: negligible turbulence and nonnegligible turbulence. Figure 1 depicts deposition velocities obtained from the turbulent and nonturbulent schemes as a function of reactivity for various wind speeds, displaying how the turbulent and nonturbulent schemes converge for very high water-side reactivity values. This convergence occurs due to destruction of ozone in the surface layer occurring so rapidly that ocean turbulence has no enhancing effect on deposition velocity. The magnitude of the effect of ocean surface turbulence on deposition velocity depends on the reactivity term. For high-wind speeds (conditions of significant ocean surface turbulence), the deposition velocity is less dependent on reactivity than in the nonturbulent case (lower wind speeds). This illustrates the dominance of turbulent forcing over the reactive sink at high-wind speeds.

2.2.2. Sensitivity of Deposition Velocity to Reactivity Term. The deposition velocities predicted by the Fairall et al. [13] scheme following a simulation in REMOTE were replotted against their corresponding wind speeds for various reactivity values, in order to look at the sensitivity of deposition velocity to the reactivity time scale factor ($A_{reac}$), as shown in Figure 2. Deposition velocities computed by the Wesely [18] scheme were also plotted in Figure 2, for comparative purposes. A significant increase in deposition velocity from the Fairall et al. [13] scheme is observed in Figure 2 for wind speeds over 4 m s$^{-1}$ for reactivities exceeding 1000 s$^{-1}$. At lower reactivities, the Wesely [18] scheme predicts higher deposition velocities, especially at low-wind speeds.

The reactivity value needed in the Fairall et al. [13] parameterisation to match deposition velocities computed by the Wesely [18] scheme depends on the wind speed value. For low-wind speeds (under 4 m s$^{-1}$), reactivity of 1000 s$^{-1}$ yields similar deposition velocities to those predicted by Wesely [18]. For high-wind speeds (over 10 m s$^{-1}$), water-side reactivity of 100 s$^{-1}$ would yield deposition velocities in the same range as those predicted by Wesely [18]. Therefore, for deposition velocities exceeding those predicted by the nonchemical, nonturbulent Wesely [18] scheme, reactivity in the ocean should exceed 1000 s$^{-1}$. At low reactivities, the Fairall et al. [13] parameterisation predicts a linear relationship between deposition velocity and wind speed, due to the dominance of the turbulent driven deposition over the chemical sink, as discussed in the previous section.

In their sensitivity analysis of the parameterisation, Fairall et al. [13] found that using the chemically enhanced turbulent deposition scheme, typical observed ozone deposition velocities of 0.03 cm s$^{-1}$ would require a reactivity rate of 1000 s$^{-1}$. This can be observed from Figure 2. Gallagher et al. [17] observed ozone deposition velocities to the ocean as high as 0.1 cm s$^{-1}$ in the North Sea. Deposition velocities of this magnitude would require a reactivity rate of the order of 10$^4$ s$^{-1}$ using the Fairall et al. [13] scheme at low to moderate wind speeds.
2.2.3. Sensitivity of Deposition Velocity to Sea-Surface Temperature (SST). As mentioned in Section 2.1, the Fairall et al. scheme parameterisation has been constrained to allow for variation of ozone diffusivity in water due to temperature and salinity and variation of ozone solubility with temperature. Using box model simulations, the effect of SST on the deposition velocity was investigated for typical North Eastern Atlantic conditions (wind speed of 8 m s$^{-1}$ and oceanic reactivity of 500 s$^{-1}$). See Figure 3.

Results from box-model simulations confirm that inclusion of temperature dependence of molecular diffusivity renders the simulated deposition velocities less sensitive to SST variations. From Figure 3, the slope of the relationship between ozone deposition velocity and SST is 50% steeper when the effect of SST on molecular diffusivity of ozone is not considered; in this case, the computed deposition velocities are likely to be oversensitive to SST. As discussed in the introduction to this paper, the effect of including variability of ozone diffusivity with SST is thought to compensate for the limiting effect of low-ozone solubility on simulated ozone deposition velocities, compared to the results of the global model study of Ganzeveld et al. [5].

2.3. Chemical Scaling of the Reactivity Term. Accounting for chemical reactions in the Fairall et al. parameterisation requires scaling of the chemical reactivity term $A_{oz,a}$ as defined in (1). In their exploration of impact of chemical reactions on ozone deposition, Chang et al. [20] identified iodide as the most likely chemical compound residing in the sea surface to drive ozone deposition compared to other substances (DMS, alkenes). DMS was recognised as having potential to enhance ozone deposition, but only at extreme oceanic concentrations. At mean oceanic concentrations of DMS, deposition velocity due to molecular gas transfer and chemical reactions of ozone with DMS was an order of magnitude lower than the deposition velocity due to molecular diffusion and chemical reactions of ozone and iodide and deposition velocity due to molecular gas transfer. Reactions of ozone and alkenes were a further two orders of magnitude lower again. For this reason, reactions of ozone with DMS and alkenes were not considered in this study, their chemically enhancing effects on ozone deposition being overshadowed by iodide reactions. Chang et al. [20] did not investigate the effect of chlorophyll on ozone deposition which Clifford et al. [23] found to have a significant enhancement effect of the same order of magnitude as for iodide reactions. In this study, analysis of chemical enhancement to ozone deposition is limited to iodide and chlorophyll reactions.

2.3.1. Iodide Reactions. To scale $A_{oz,a}$, the kinetics between ozone and its various reactants needed to be determined. The enhancing effect of iodide reactions on ozone deposition has been long documented [20, 21]. From the kinetics...
between ozone deposition velocity and SST are given in the legend.

Deviations of ozone di

Johnson and Davis [30] and Jahne et al. [31]. Linear correlations between ozone solubility and molecular diffusivity and SST when temperature dependence of both ozone solubility in seawater is considered based on the theory of Kosak-Channing and Helz [34]. The solid line depicts a relationship between deposition velocity and SST when only temperature dependence of ozone solubility in seawater is considered, as is done in this study.

$k_{\text{obs}}$ and saline water temperature $T$ was deduced for water of ionic strength of seawater (0.7 M) resulting in the linear relationship of (2), where $k_{\text{obs}}$ refers to the reaction rate of ozone in salt water of ionic strength 0.7 M and $T$ refers to water temperature in degrees Kelvin

$$k_{\text{obs}} (10^9 \text{ s}^{-1}) = -40.85 + 0.15 T (K).$$

From the work of Magi et al. [29], the effect of salinity enhances ozone-iodide reaction rates by as much as 23% compared to those for pure water, and so it was considered important to account for the salinity of seawater in parameterising ozone-iodide reactions.

Oceanic iodide concentrations in the North Atlantic vary between 0 and 150 nM [35]. For this study, constant iodide concentrations were varied between 50 nM and 200 nM to evaluate the sensitivity of simulated ozone levels and resulting ozone fluxes to the effect of changing iodide concentrations, in contrast to the global modelling study of Ganzeveld et al. [5] who infer oceanic concentrations using an anticorrelation between nitrate and iodide developed by Campos et al. [36]. Furthermore, the global model study did not include the effect of salinity of seawater on ozone-iodide reaction kinetics, as is done in this study.

2.3.2. Organic Enhancement of Ozone Deposition. It has been long postulated that organic reactions in the sea surface layer can have a significant enhancing effect on ozone deposition [22]. Clifford et al. [23] suggest that the reaction between ozone and chlorophyll can increase ozone deposition velocity by up to a factor of 3 for wind speeds up to 20 m s$^{-1}$ compared to deposition velocities computed solely on ozone-iodide reactions. Considering the ubiquity of chlorophyll in the ocean, the organic enhancement of ozone deposition could have a significant effect on ozone concentrations in the marine boundary layer. This organic enhancement of ozone deposition was mechanistically incorporated into the Fairall et al. [13] deposition scheme using satellite chlorophyll data from MODIS (moderate resolution imaging spectroradiometer) [37]. The upper and lower limits of oceanic chlorophyll concentrations were set to 3 mg m$^{-3}$ and 0 mg m$^{-3}$, respectively, and oceanic iodide concentration was set to a typical value of 100 nM. Figure 4 shows monthly averaged chlorophyll-a concentration (mg m$^{-3}$) as detected by MODIS for June, 2003. Taken from the NASA OceanColor website (http://oceancolor.gsfc.nasa.gov/).

Figure 3: Box-model-derived relationship between deposition velocity and sea-surface temperature, using a typical Atlantic wind speed of 8 m s$^{-1}$ and reactivity of 500 s$^{-1}$. The solid line depicts a relationship between deposition velocity and SST when only temperature dependence of ozone solubility in seawater is considered based on the theory of Kosak-Channing and Helz [34]. The filled circles represent a relationship between deposition velocity and SST when temperature dependence of both ozone solubility and molecular diffusivity in seawater is considered. Variation of ozone diffusivity in seawater is based on the theory of Johnson and Davis [30] and Jahne et al. [31]. Linear correlations between ozone deposition velocity and SST are given in the legend.

**Figure 4**: Monthly averaged chlorophyll-a concentration (mg m$^{-3}$), as detected by MODIS for June, 2003. Taken from the NASA OceanColor website (http://oceancolor.gsfc.nasa.gov/).
The technique employed in this study differs from that of Ganzeveld et al. [5] who applied linear dependence of reactivity term $A_{oc}$ on chlorophyll concentrations whereas in this study, the deposition velocity increases linearly with chlorophyll and the organic reactions are not represented in $A_{oc}$. This organically enhanced version of the Fairall et al. [13] deposition scheme is herein referred to as the mechanistic ozone deposition scheme.

This scaling is a crude approach to the quantification of organic reactions in the computation of ozone deposition velocity and should be interpreted as a first-order representation of organic chemistry within the Fairall et al. [13] scheme, oceanic chlorophyll concentration being used as a proxy for biological activity. Further work is needed to parameterise the role of organic reactions in ozone deposition.

2.4. Ozone-Deposition Driven Upward Iodine Flux. The major source of iodine to the atmosphere is most likely due to emission of organoiodine compounds from the ocean [38]. Martino et al. [8] have recently shown that a proportion of organic iodide found in the marine atmosphere can be formed from volatile organoiodine compounds (VOIs) which are produced via ozone-iodide reactions in the sea surface, thereby uncovering a potentially significant iodine source to the marine atmosphere which is kick started by the deposition of ozone to the sea surface. The VOI species identified by Martino et al. [8] resulting from ozone deposition are CH$_2$I$_2$, CH$_2$ICl, and CHI$_3$. Based on the findings of Martino et al. [8] and the work of Garland et al. [21], the extreme upper limit of iodine vapours released to the atmosphere can be estimated from the ozone flux of ozone to the ocean, assuming all of the new VOIs are emitted from the ocean surface, without any being transported to the ocean mixed layer or being destroyed by photolysis at the sea-air interface. This newly defined halogen source in the marine boundary layer could have significant biogeochemical consequences, in terms of both marine boundary layer (MBL) ozone depletion and new particle formation.

3. Simulation Results and Discussion

Monthly REMOTE simulations were carried out for the month of June, 2003. The model domain spans Northern Europe and is depicted in Figure 11. Resolution of the model is set to 0.5 deg, giving an average grid cell size of 50 km × 50 km. Meteorological and chemical initial and boundary conditions are taken from ECMWF (European Centre for Medium-Range Weather Forecasts) and used to initialise all grid points at the start of each simulation. Lateral boundaries are enforced at six hourly intervals and emission scenarios were supplied from the EMEP site. In 2003, monthly average chlorophyll concentrations in the North East Atlantic were at an annual peak in the month of June [37].

3.1. Ozone Concentration Fields. Figure 5 shows surface level mean monthly ozone concentrations simulated using different deposition schemes within REMOTE. There is little or no difference between simulated surface level ozone concentrations using the nonchemical Wesely [18] scheme and the Fairall et al. [13] scheme for 30 nM or 200 nM iodide concentrations, consistent with findings of the global model study of Ganzeveld et al. [5]. One can conclude from this that ozone concentrations predicted using the Fairall et al. [13] scheme within REMOTE are insensitive to iodide reactions at realistic Atlantic iodide concentrations—even at an upper limit of oceanic iodide concentration of 200 nM. Therefore, although variation in iodide concentration and reaction rate causes variation in ozone deposition velocity, these deposition velocities are not sufficiently significant to overcome other compensating effects in the climate model and substantially decrease simulated ozone concentrations. However, a notable decrease in ozone concentrations is observed around the North East Atlantic when the mechanistic ozone deposition scheme of Fairall et al. [13] is employed. Simulated ozone depletion in this region is due to the relatively high chlorophyll concentrations. In regions of low oceanic chlorophyll concentration (e.g., the Mediterranean), the mechanistic ozone deposition scheme models similar ozone concentrations as computed using the Wesely [18] scheme.

Figure 6 depicts ozone concentrations in the North East Atlantic as predicted by REMOTE using three permutations of the Fairall et al. [13] scheme and using the nonchemical Wesely [18] scheme. The Fairall et al. [13] scheme including 100 nM iodide chemistry predicts ozone concentrations similar to those simulated using the Wesely [18] scheme. The impact of chlorophyll on simulated ozone levels in this region can be seen by comparing the mean monthly ozone levels simulated using the Fairall et al. [13] scheme scaled to include iodide chemistry alone (100 nM1 scheme), and the mechanistic version scaled to include both iodide chemistry and organic reactions. Ozone levels simulated by the mechanistic dry deposition scheme are as much as 15 ppb lower than ozone levels simulated by both the Wesely [18] scheme and the 100 nM1 scheme. The Fairall et al. [13] 100 nM1 scheme and the mechanistic scheme differ only by organic enhancement of deposition velocity and so the lower ozone concentrations simulated by the mechanistic schemes are due to inclusion of organic chemistry alone.

Figure 7 compares ozone concentrations measured at the Mace Head atmospheric research station measurement site off the west coast of Ireland to modelled ground-level ozone concentrations in this region. Ozone levels were measured at Mace Head using a continuous ozone analyser by UV photometry. See Tripathi et al. [39] for full description of this data and measurements. All simulated ozone concentrations agree quite well with observations, but the Mace Head ozone concentrations simulated by the mechanistic scheme correlate better with the observed ozone concentrations than other schemes. The root mean square (RMS) deviation between in situ ozone measurements at Mace Head and modelled ozone concentration for this region was 7.7 ppb when using the mechanistic scheme whereas the next closest correlations were obtained using the Fairall et al. [13]
Figure 5: Monthly average O₃ concentrations in ppb as predicted by REMOTE for June 2003 for various dry deposition schemes. 50 nM I plot and 200 nM I plot show simulated ozone concentrations (ppb) using the iodide-only chemical Fairall et al. [13] parameterisation with oceanic iodide concentrations set to 50 nM and 200 nM, respectively. The Wesely [18] plot shows the ozone concentrations simulated by the nonchemical scheme and the Mechanistic Scheme plot depicts the O₃ concentrations simulated using the Fairall et al. [13] scheme with inclusion of a first-approach chlorophyll-based organic chemistry.

scheme with reactivity set to 1000 s⁻¹, and the Wesely [18] scheme which gave RMS deviations of 9.1 ppb and 11.6 ppb, respectively. This shows that on average, deviations between simulated ozone concentrations and in situ measurements are less for results obtained using the mechanistic ozone dry deposition scheme than those generated using other dry deposition schemes. However, firm conclusions on accuracy of dry deposition parameterisation cannot be drawn here, as simulated ozone-mixing ratio is dependent on other model processes including atmospheric chemistry, transport, and boundary conditions. In addition, the in situ measurements represent a point measurement of ozone-mixing ratio, whereas the model output represents average ozone mixing ratio over a grid cell which spans 50 km × 50 km. In this analysis, attempts have been made to account for this by comparing modelled ozone concentrations with in situ ozone measurements averaged over 1.75 hours, the time taken for an air mass to traverse the length of one grid cell (50 km), assuming an average easterly wind speed of 8 m s⁻¹. However, localised effects influencing ozone concentrations at Mace Head will not be represented in model simulations due to the effect of averaging over the grid cell area and so simulated ozone concentrations will not have the same variation as ozone measurements at Mace Head. This would explain large variations between simulated and measured ozone concentrations for example, measurements between Julian Day 166 and 171 are much lower than all model results.

From Figure 7, it can be seen that the 100 nM I Fairall et al. [13] scheme and the Wesely [18] scheme predict higher ozone concentrations than observations or other model set ups during periods of low-wind speeds (e.g., between days 165 and 171). The reactivity of the 100 nM I scheme
is not large enough to account for ozone water surface transfer at low-wind speed and the Wesely [18] scheme does not account for chemical ozone transfer at all. Therefore, using either of these schemes, REMOTE over predicts ozone concentrations at periods of low-wind speed.

Simulations using the Fairall et al. [13] scheme with constant reactivity set to \(1000 \text{s}^{-1}\) predict very similar ozone concentrations around Mace Head to the simulations using the mechanistic scheme (reactivity due to 100 nM Iodide and organic enhancement). Therefore, around the western Irish coast, it can be deduced that effect of organic chemistry causes oceanic reactivity of the order of \(1000 \text{s}^{-1}\). Figure 8 shows monthly average values of deposition velocities computed for the various deposition schemes. In the mechanistic scheme, organic reactions are parameterised by increasing deposition velocity according to oceanic chlorophyll concentration, and so organic reactions are not represented in the reactivity term, \(A_{\text{org}}\) of the Fairall et al. [13] parameterisation. However, by comparing average deposition velocities depicted in Figure 8 with relationship between reactivity and deposition velocity shown in Figures 1 and 2, it can be deduced that the deposition velocities obtained around the Irish coast using the mechanistic scheme (0.6–0.1 cm s\(^{-1}\)) would require reactivity values exceeding \(1000 \text{s}^{-1}\), assuming moderate wind speeds. Variation of \(V_d\) in the Wesely [18] scheme and the \(\text{Reactivity } 1000 \text{s}^{-1}\) scheme occurs due to turbulent effects alone.

### 3.2. Ozone-Loss Rate.

The loss rate of ozone from the mixing volume to the ocean due to dry deposition was calculated in...
order to assess the impact of varying ozone deposition on the rate of atmospheric ozone loss to the ocean as a result of dry deposition and the consequential effect on ambient ozone concentration. The loss rate is given by

\[
\text{Loss Rate} = \frac{F_{OD}}{L},
\]  

(3)

where \(F_{OD}\) is the dry deposition flux of ozone to the ocean (the product of deposition velocity and ambient ozone concentration) and \(L\) is the boundary layer height. Deposition velocities and ozone concentrations were extracted from REMOTE and boundary layer height taken as a constant 800 m. Figure 9 shows ozone-loss rates computed for the various dry deposition schemes.

A higher deposition velocity does not necessarily denote a higher ozone-loss rate, as the loss rate is proportional to both ozone concentration and deposition velocity. The loss rate of ozone to the ocean varies with oceanic iodide concentration as seen from the first two plots of Figure 9, using the iodide-only constrained scheme of Fairall et al. [13]. This occurs due to the different deposition velocities generated from the dry deposition schemes based on reactivity. However, it can be seen that the variation of the iodide concentration has no significant effect on ground level ozone concentration and so the variation in ozone-loss rate due to differences in iodide concentration is too subtle to have a bearing on ambient ozone concentrations, indicating the dominance of other processes over the dry deposition sink in regulation of ambient boundary layer ozone concentrations within REMOTE for lower dry depositional loss rates.

The Wesely [18] scheme predicts a greater ozone-loss rate than the mechanistic ozone deposition scheme. This occurs due to the depletion of ambient ozone concentrations because of enhanced dry deposition in the presence of marine biological activity.

3.3. Upward Iodine Flux. 20% of ozone deposited to the sea surface reacts with iodide [21]. 1% of iodide oxidised by ozone reacts with organic matter to form the VOIs (CHI2, CH2ICl, or CHI3) that are released from the sea surface [8]. The upper limit of potential iodine flux to the marine atmosphere as a result of ozone deposition is predicted using these relationships. Resulting VOI fluxes are shown in Figure 10. The upward VOI flux is derived directly from the downward ozone flux, and so the same factors influence both the downward ozone flux and the upward iodine flux. The upward VOI flux also varies with oceanic iodide concentration. It is stressed that this potential VOI flux to the atmosphere represents an extreme upper limit, and is to be interpreted as such.

The upward VOI flux predicted using the Wesely [18] scheme exceeds that predicted by the Fairall et al. [13] scheme constrained by iodide reactions. The mechanistic ozone dry deposition scheme predicts VOI flux exceeding that predicted using Wesely [18] in some regions (north east of Britain) while the flux is less than that predicted using Wesely [18] in other areas (off the southern Irish coast).

This ozone deposition-driven flux of iodine from the ocean is likely to have significant biogeochemical consequences. Marine aerosols and cloud condensation nuclei (CCN) can be formed from iodine vapours in coastal environments [11, 40]. The addition of new aerosols to the coastal atmosphere could have a significant impact on the global solar radiation budget due to their role in scattering of incoming solar radiation, and therefore accurate prediction of the VOI flux is imperative in predicting future climatic scenarios. To fully assess the atmospheric implications of this extra iodine source in the MBL, the upward organoiodine flux and resulting chemical reactions and particle formation would have to be included in the chemical scheme of REMOTE.

3.4. Area-Averaged Study of Simulation Results. A quantitative comparison of simulation results using the various dry deposition schemes was performed by taking an area average of various parameters over a boxed region in the North Atlantic, off the Irish coast—a region of relatively high biological activity. The region is displayed in Figure 11. In this area, average, maximum, and minimum deposition velocities from the various schemes were compared, as were the average simulated ozone concentrations, average ozone-loss rates, average upward VOI flux and derived average increase in the daily rate of the VOI-mixing ratio. Results are tabulated in Table 1.

![Figure 7: Ozone concentrations (ppb) simulated by REMOTE and measured ozone concentrations (ppb) at Mace Head for June 2003.](image-url)
3.4.1. Deposition Velocity. Deposition velocities simulated using the Fairall et al. [13] parameterisation vary with oceanic iodide concentration, but as we have seen earlier, these variations are too subtle to have a significant effect on ambient ozone concentrations. The mechanistic scheme computes deposition velocities in this region exceeding those computed using the [18] scheme by 18%. Neither the Wesely [18] scheme nor the Fairall et al. [13] scheme constrained to iodide chemistry can account for deposition velocities as high as the observations of Gallagher et al. [17]. Surface resistance is set to a constant 2000 m$^{-1}$ s in the Wesely [18] scheme, and so maximum deposition velocity computed by this scheme deviates very little from the average deposition velocity; using this nonchemical scheme, deposition velocities cannot match the upper limit of observations under any conditions.

Additional chemical reactions must be included in the dry deposition scheme in order to realise deposition velocities as high as observations. Only the mechanistic ozone deposition scheme predicts deposition velocities higher than observations of Gallagher et al. [17]. Therefore, only by integration of organic chemistry into the dry deposition scheme can deposition velocities as high as observations be realised.
3.4.2. Ozone Concentration. Simulated average ozone concentrations in this area are relatively insensitive to oceanic iodide concentration. Inclusion of first-order organic chemistry parameterisation based on Clifford et al. [23] into the dry deposition parameterisation causes a decrease in simulated ozone concentration in the area of 20.5% or 9.5 ppb compared to concentrations simulated using the Wesely [18] scheme. This increase in ozone deposition occurs due to the enhancement of ozone deposition velocity due to inclusion of organic reactions in the mechanistic ozone deposition scheme, as discussed above. The Wesely [18] scheme predicts an average ozone concentration in this area 1.6% lower than that predicted using the Fairall et al. [13] parameterisation constrained by an oceanic iodide concentration of 100 nM.

3.4.3. Ozone-Loss Rate. Average ozone-loss rate computed by Wesely [18] exceeds that computed by the mechanistic ozone deposition scheme by nearly 6% in this region. The lower loss rate is due to the lower ambient ozone concentrations in the boundary layer due to organic enhancement of ozone deposition computed by the mechanistic ozone deposition scheme. The less reactive scheme constrained only by iodide reactions also computes ozone-loss rate less than that of the Wesely [18] scheme due to the higher deposition velocity.
computed by the Wesely [18] scheme. The relatively small changes in loss rates are shown not to have a large effect on ambient ozone concentrations in REMOTE, but accurate estimation of ozone dry deposition flux is necessary to evaluate ozone-deposition driven upward VOI flux.

3.4.4. Potential Upward VOI Flux. This flux is estimated linearly from the downward ozone flux. The simulated potential VOI flux emitted from the ocean in this area is of the order of $10^7$ molecules cm$^{-2}$ s$^{-1}$. Martino et al. [8] compute a typical downward depositional iodine flux of $3 \times 10^7$ atoms cm$^{-2}$ s$^{-1}$. The potential upward VOI flux exceeds the depositional iodine flux, thus constituting a significant additional source of atmospheric iodine in marine environments, especially in regions of high biological activity when organic enhancement of ozone deposition is factored into the dry deposition parameterisation.

3.4.5. Increase of VOI-Mixing Ratio. Recent measurements of iodocarbon fluxes taken in the North East Atlantic [41] have found open ocean sea-air fluxes of the ozone-deposition derived VOIs (CH$_3$I, CH$_2$I$_2$, and CH$_2$ICl) as high as $9.6 \times 10^7$ molecules cm$^{-2}$ day$^{-1}$, which would lead to a mixing ratio increase of 4.24 ppt per day. The average flux value observed in this region would lead to a VOI increase of 1.2 ppt per day. In the more biologically active shelf and coastal regions, measured VOI sea-air fluxes have been measured that would result in mixing ratio increases as high as 9.3 ppt per day and 18.1 ppt per day, respectively. The measurements were taken in the biologically active regions off the west coast of Ireland where organic enhancement of ozone deposition is likely to occur.

The average simulated increase of potential VOI-mixing ratio in this area is of the order of 4 ppt per day and the range of ozone-driven iodocarbon flux in this region...
Table 1: Results from area average analysis carried out over a boxed region in the North Atlantic.

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Average deposition velocity (cm/s)</th>
<th>Maximum deposition velocity (cm/s)</th>
<th>Minimum deposition velocity (cm/s)</th>
<th>Average [O3] in ppb</th>
<th>Average O3 loss rate (ppb per day)</th>
<th>Average upward VOI flux (molecules cm$^{-2}$ s$^{-1}$)</th>
<th>Average mixing ratio VOI increase (ppt per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity of 50 nM Iodide</td>
<td>0.0305</td>
<td>0.0509</td>
<td>0.00123</td>
<td>47.8647</td>
<td>1.57031</td>
<td>7.11E + 07</td>
<td>3.14E + 00</td>
</tr>
<tr>
<td>Reactivity of 100 nM Iodide</td>
<td>0.0355</td>
<td>0.0575</td>
<td>0.00127</td>
<td>47.5876</td>
<td>1.82221</td>
<td>8.26E + 07</td>
<td>3.64E + 00</td>
</tr>
<tr>
<td>Reactivity of 150 nM Iodide</td>
<td>0.0392</td>
<td>0.0623</td>
<td>0.00129</td>
<td>47.3911</td>
<td>2.00809</td>
<td>9.07E + 07</td>
<td>4.00E + 00</td>
</tr>
<tr>
<td>Reactivity of 200 nM Iodide</td>
<td>0.0421</td>
<td>0.0661</td>
<td>0.0013</td>
<td>47.2334</td>
<td>2.1445</td>
<td>9.72E + 07</td>
<td>4.29E + 00</td>
</tr>
<tr>
<td>Reactivity 1000 s$^{-1}$</td>
<td>0.0573</td>
<td>0.0848</td>
<td>0.00334</td>
<td>36.6113</td>
<td>2.26644</td>
<td>1.03E + 08</td>
<td>4.53E + 00</td>
</tr>
<tr>
<td>Wesely [18] scheme</td>
<td>0.0463</td>
<td>0.0488</td>
<td>0.0019</td>
<td>46.8433</td>
<td>2.34064</td>
<td>1.06E + 08</td>
<td>4.68E + 00</td>
</tr>
<tr>
<td>Mechanistic scheme (Reactivity of 100 nM Iodide and Organic reactions)</td>
<td>0.0547</td>
<td>0.161</td>
<td>0.00173</td>
<td>37.2185</td>
<td>2.20302</td>
<td>9.98E + 07</td>
<td>4.40E + 00</td>
</tr>
<tr>
<td>Percentage difference between Wesely [18] and Mechanistic Scheme</td>
<td>–18.171</td>
<td>–230.38</td>
<td>8.86149</td>
<td>20.5468</td>
<td>5.87979</td>
<td>5.87979</td>
<td>5.87979</td>
</tr>
<tr>
<td>Percentage difference between Wesely [18] and 100 nM F scheme</td>
<td>23.1573</td>
<td>–17.915</td>
<td>33.0857</td>
<td>–1.5888</td>
<td>22.1493</td>
<td>22.1493</td>
<td>22.1493</td>
</tr>
</tbody>
</table>

Figure 11: Location of boxed region in the North Atlantic off the west coast of Ireland in which the area-averaged analysis was performed.

is 2.5–500 M molec cm$^{-2}$ s$^{-1}$ which would correspond to a mixing-layer enhancement of VOI concentrations of 0.1–22.0 ppt per day. This enhancement to the mixing ratio was calculated using ideal gas theory and assuming a boundary layer height of 800 m and should be interpreted as the extreme upper limit of potential VOI flux occurring as a result of ozone deposition—in reality, a proportion of this flux would be mixed downwards and a further proportion will be photolysed at the sea surface [8]. Taking this into consideration, simulated VOI-mixing ratio enhancement is well within range of the recently observed iodocarbon fluxes [41], especially considering large iodocarbon fluxes observed in shelf and coastal regions. Considering the molar mixing ratio of total organic iodine ranges between 3–4 ppt in the boundary layer [42–44], even a small mixing ratio enhancement of these proportions would enhance atmospheric iodine concentrations considerably.

The extra iodine compounds released to the atmosphere could further add to ozone depletion in the marine boundary layer, thus forming a catalytic cycle of ozone destruction. Read et al. [45] investigated halogen-mediated ozone destruction over the tropical Atlantic Ocean and found that based on typical organic iodine molar mixing ratios of 3–4 ppt in the MBL [44], resulting IO concentrations of 1 ppt would cause ozone loss of 1.24 ppb per day due to atmospheric reactions with IO.Crudely assuming a linear relationship between organic iodine concentrations and resulting ozone loss, additional influx of 22 ppt organic iodine per day into the mixing layer due to the ozone-deposition driven VOI flux would result in a further ozone loss of 7.8 ppb per day. Even though this case represents the upper limit VOI flux to MBL, it is evident that the halogen-mediated ozone destruction cycle is likely to have significant consequences for ozone concentrations in the marine boundary layer, depleting ozone mixing ratios to the order of a ppb per day. To further investigate this feedback mechanism, REMOTE would need to be adapted to include halogen chemistry and the upward VOI flux. This is scheduled for further work.

4. Conclusions

Consistent with results of global model study conducted by Ganzeveld et al. [5], our results show that ozone...
concentrations predicted by the Fairall et al. [13] parameterisation within REMOTE are insensitive to realistic variations of oceanic iodide concentrations. Furthermore, the ozone concentrations predicted by this turbulent and chemically enhanced deposition scheme do not exceed those predicted by the highly parameterised Wesely [18] scheme when the parameterisation is constrained by iodide chemistry alone for typical oceanic iodide concentrations. In order for the new scheme to simulate deposition rates as high as field observations, oceanic reactivity must be in the order of 1000 s⁻¹. The source of this extra reactivity is most likely due to ozone reacting with organic matter and chlorophyll in the sea surface [22, 23].

Deposition velocities as high as the observations of Gallagher et al. [17] were realised in regions of high biological activity using the mechanistic ozone deposition scheme, in which a crude first-order scaling of organic ozone reactions was applied to the Fairall et al. [13] parameterisation. Use of this mechanistic ozone deposition scheme including organic reactions yielded boundary layer ozone concentrations much lower than those predicted using the highly parameterised, constant surface-resistance deposition scheme of Wesely [18]. This result is in contrast with findings of Ganzeveld et al. [5] who found the use of mechanistic approach to evaluation of surface resistance in fact reduced total dry deposition flux of ozone to the ocean compared to simulations run using the Wesely [18] scheme with constant surface-resistance, even though the global model study incorporated additional chemical reactions of ozone with DMS, C₂H₄, and C₃H₆, which were deemed negligible in this study. However, variations between the global model results and results from this are most likely due to variation between the temporal and spatial resolution of the two model studies: the focus of this study is limited to a biologically active region for a time of year in which biological activity is at a maximum and so it would be expected that biochemical effects would be significant in resulting simulations. In contrast, the Ganzeveld et al. [5] study was performed on a global scale for a yearly period and simulated annual mean mixing ratios were analysed which would not reflect short-term seasonal effects. As stated in the introduction, the Wesely [18] scheme serves well in simulating ozone deposition for large-scale simulations, but the mechanistic Fairall et al. [13] parameterisation serves best for simulating ozone deposition velocity to the ocean for particular regional or seasonal effects, as in the case of high biological activity due to a phytoplankton bloom. In addition, Ganzeveld et al. [5] used variable inferred oceanic iodide concentration fields as opposed to constant oceanic iodide fields utilised in this study. Also, the global model study did not allow for the enhancing effect of high sea surface temperature (SST) on diffusivity of ozone in water and so ozone transfer in regions of high SST was limited by solubility and the enhancing effect of seawater salinity on ozone-iodide reaction kinetics was not considered in the global model study.

Based on the findings of this study, it is postulated that high ozone fluxes can be theoretically explained only by consideration of reactions of ozone with ocean dwelling organic matter.

Simulated ozone concentrations agree closely with in situ measurements at Mace Head. On average the mechanistic ozone deposition scheme displayed least deviation from measurements. This indicates a closer correlation between actual ozone concentrations and simulated ozone concentrations using the mechanistic scheme (RMS deviation of 7.7 ppb) than using the iodide-only scheme or the nonchemical Wesely [18] scheme (RMS deviation of 11.6 ppb).

Ozone dry deposition flux depends on both ozone concentration and deposition. Variations in ozone flux do not necessarily have a significant effect on ambient ozone concentration due to dominance of other model processes over the dry deposition processes at low deposition velocities.

To the best of authors’ knowledge, this is the first study to use the advanced mechanistic ozone deposition scheme of Fairall et al. [13] to quantitatively evaluate the newly discovered ozone deposition-driven upward flux of iodine from the ocean outlined by Martino et al. [8], which is likely to have significant biogeochemical consequences. Ambient ozone concentrations are insensitive to oceanic iodide concentrations, but ozone dry deposition flux (and resulting upward iodine flux) varies with oceanic iodide concentration and so iodide reactions must be explicit within dry deposition models to adequately simulate biogeochemical consequences of dry depositional ozone flux.

Acknowledgments

The authors gratefully acknowledge the Environmental Protection Agency (EPA) for its support (EPA Project 2006-AQ-MS-50: Ozone levels, changes and trends over Ireland—an Integrated Analysis). Chris Fairall of NOAA is also gratefully acknowledged for making available the parameterisation used in this study. The authors would also like to thank anonymous reviewers for their comments and reviews that served to significantly improve the quality of the paper.

References


Paper II
Research Article

Photochemical Impact on Ozone Fluxes in Coastal Waters

L. Coleman,1 P. McVeigh,1 H. Berresheim,1 M. Martino,2 and C. D. O’Dowd1

1 School of Physics and Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland
2 Laboratory for Global Marine and Atmospheric Chemistry, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Correspondence should be addressed to M. Martino, m.martino@uea.ac.uk

Received 27 February 2012; Accepted 12 April 2012

Academic Editor: Raymond Desjardins

Copyright © 2012 L. Coleman et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ozone fluxes, derived from gradient measurements in Northeast Atlantic coastal waters, were observed to depend on both tide height and solar radiation. Peak ozone fluxes of $-0.26 \pm 0.04 \mu \text{gm}^{-2} \text{s}^{-1}$ occurred during low-tide conditions when exposed microalgae fields contributed to the flux footprint. Additionally, at mid-to-high tide, when water surfaces contribute predominantly to the flux footprint, fluxes of the order of $-0.12 \pm 0.03 \mu \text{gm}^{-2} \text{s}^{-1}$ were observed. Considering only fluxes over water covered surfaces, and using an advanced ozone deposition model that accounts for surface-water chemistry enhancing the deposition sink, it is demonstrated that a photochemical enhancement reaction with dissolved organic carbon (DOC) is required to explain the enhanced ozone deposition during daylight hours. This sink amounts to an ozone loss rate of up to 0.6 ppb per hour under peak solar irradiance and points to a missing sink in the marine boundary layer ozone budget.

1. Introduction

Tropospheric ozone has negative impacts on human health and vegetation [1] and also acts as an important greenhouse gas. Recent trend analysis in background North Atlantic air at the Mace Head research station in western Ireland shows background ozone levels to be on the increase by 0.16 ppb per annum (1988 to 2007) [2]. Mace Head is a clean marine site, representing air transported over the North Atlantic towards Europe in the marine boundary layer. Consequently, rising ozone levels at Mace Head cannot be explained by changes in anthropogenic emission patterns, and model studies have not been able to recreate observed trends [3, 4]; hence, there is a need to investigate processes influencing background ozone concentrations. Jenkin [5] identified gradual hemispheric ozone increase due to global-scale effects, influencing the ozone advected into Western Europe over the Atlantic as one of the three major influences on locally measured ozone data in the UK. The rise in background ozone concentration constitutes a significant contribution to regional ozone pollution, and so is of significant concern for pollution control policy makers. Hence, in order to assess the future trends in background ozone levels, the intercontinental transport of ozone should be well represented in assessment models as well as any relevant removal processes, one of which is the dry deposition of ozone to the ocean.

The deposition of ozone to surface waters via physical uptake (solubility, turbulent mixing) and chemical reactions in the surface layer [6] is an ozone removal process likely to influence surface ozone concentrations during intercontinental transport. From field measurements [7, 8], deposition velocity of ozone to the ocean is known to span the range of 0.53 to 1.0 mm s$^{-1}$. Coleman et al. [9] describe the inclusion of the advanced ozone dry deposition parameterisation of Fairall et al. [10] in the regional climate model REMOTE. The Fairall ozone dry deposition parameterisation scheme accounts for turbulent and chemical enhancement of ozone deposition to water surfaces. Within their study, Coleman et al. [9] expanded the Fairall scheme to include ozone depletion via reactions with iodide and dissolved organic matter (DOM). The parameterisation was also adapted to account for variability of ozone diffusivity, solubility, and reactivity with sea surface temperature and to estimate emissions of volatile organoiodine (VOI) vapours following
reactions of ozone with iodide and DOC (e.g., [11]). In the present study, the Fairall parameterisation was further developed to parameterise ozone-DOC reactions with a second-order reaction rate empirically derived from the laboratory work of [12]. Box model results of the updated Fairall parameterisation are compared to in situ ozone gradient fluxes measured at Mace Head.

2. Measurement Methods

Ozone gradient flux measurements were conducted on a 22 m tower at Mace Head atmospheric research facility [13] on the west coast of Ireland (53°20’N, 9°54’W). The shoreline to the westward side of the 22 m tower is inhomogeneous, rocky, and slanted with a tidal region extending 50 m to 150 m from the base of the tower. Two Thermo Scientific (model 49i) photometric O3 analysers with response time of 20 seconds sampled at 22 m and 10 m heights to obtain O3 concentration profiles at 1-minute intervals. Colocated with the O3 analysers, a Gill R3 3-dimensional ultrasonic anemometer sampling at 10Hz was used to quantify micrometeorological parameters. The Monin-Obukhov length (L) was used in conjunction with measurement height (z) to calculate a dimensionless scaling parameter, z/L, which defined the thermal stability state of the boundary layer. This parameter was used to ensure only that data pertaining to neutral or slightly unstable conditions were considered. Simultaneous filtering for data corresponding to the Mace Head clean marine sector (190° < wind direction < 350°) ensured the considered data corresponded to an oceanic footprint. The peak of the footprint is located approximately 1 km offshore, as in the study of Geever et al. [14]. The relative contributions to the flux footprints at midday on each measurement day are depicted in Figure 1.

In order to ensure data quality, intercomparisons between the O3 analysers were performed at a single height on a regular basis. The mean difference from these intercomparison periods (0.491 ppb) was then subtracted from the difference between them to give a final gradient. Only final gradients that were larger than the mean added to standard deviation of the difference between both instruments during an intercomparison were deemed acceptable for further analysis. Such filtering of data ensured readings were not biased by instrumental drift and eliminated noise, ensuring only strong-signal gradient data were considered.

Gradient fluxes, based on K-theory [15] and previously deployed at Mace Head, described by Ceburnis et al. [16], were computed using the vertical profiles of ozone concentration between 10 m and 22 m and the turbulent-transfer coefficient K derived from the micrometeorological measurements. This calculation assumes that the eddy diffusivity coefficients for momentum and O3 are similar, which is not always the case. Analogous to Fick’s law of molecular diffusion, the O3 flux \( F_{O3} \) can be calculated by multiplying the vertical concentration gradient with the eddy diffusivity coefficient, \( K_{O3} \), as follows:

\[
F_{O3} = -K_{O3} \frac{\partial O3}{\partial z}.
\]

From the calculated fluxes, ozone deposition velocity \( (v_d) \) to ocean surface was calculated \( v_d = F_{O3}/O_3 \). Ideally, measured fluxes should be validated by assessing energy budget closure, but unfortunately the necessary data were not available for assessment of energy balance.

3. Model Development

The Fairall parameterisation, including chemical reactivity was further developed based on the laboratory studies [12, 17] in which the chemical enhancement of the ozone deposition velocity was quantified for iodide and DOC reactants. The reaction rate for ozone and DOC, \( k_{DOC-O3} \), was calculated by comparing the results from ozone-iodide reactions with the Fairall dry deposition theory and known ozone-iodide reaction kinetics [18] and determining systematic constants for the experimental setup. Results from the ozone-iodide experiments could then be extrapolated back to the ozone-DOC experiments, assuming consistent experimental setup. Fairall calculated the O3 dry deposition in terms of the sum of the surface resistance \( (R_s) \) and aerodynamic resistance \( (R_a) \) to be zero, and so resistance to dry deposition is due to \( R_s \) only. Using data of Jones, \( R_s \) was estimated as the inverse to deposition velocity and found to be 3130 s m-1. This was used as typical for \( R_s \) for laboratory conditions such as those in which these experiments were executed. Combining \( R_s \) and the rate constant used in Magi et al. [18] for sea-surface O3-1 reactions, we can define the experimental setup in terms of Fairall’s dry deposition velocity equation. A surface turbulence term \( (\tau) \) is required to be combined with \( R_s \) to replicate the Martino et al. [12] experiments. Consequently, the dry deposition velocity to seawater can be written as follows:

\[
v_d = \frac{1}{[1/\alpha K_{O3-C} C] \tau + R_s} = \frac{1}{\alpha \tau + 3130}, \tag{2}
\]

where \( \alpha \) is the solubility of ozone, \( K_{O3-C} \) is the 2nd order rate constant of ozone and reactant C, \( [C] \) is the molar constant of reactant in the water surface, and \( D \) is the diffusivity of ozone in seawater. First, by fitting the right hand side version of the equation to the Martino data (Figure 2), we calculate \( \tau = 1.47 \), then we calculate the 2nd order rate constant for ozone and DOC reactions \( k_{DOC-O3} = 3.44 \mu M^{-1} s^{-1} \). Oceanic DOC concentrations were estimated using the relationship between chlorophyll and DOC as described by Kepkay and Wells [19] based on their study in the North Atlantic: [DOC] \( \mu M = 110 + 2.27[chlorophyll] \) mg/m². Typical iodide concentrations for summer-period coastal waters off the west coast of Ireland were taken as 50 nM [20] and a typical chlorophyll-a concentration of 1 mg/m³ derived from MODIS (http://oceancolor.gsfc.nasa.gov). Other variables in the model, including ozone solubility and diffusivity were set up as outlined in Coleman et al. [9].
4. Results and Discussion

The measured and modelled fluxes and corresponding deposition velocities are illustrated in Figure 3 for the duration of the short campaign study (days 222–225 or August 10–13, 2010). The measured fluxes were averaged over 30 minute intervals. Uncertainty in measurements is represented by error bars in Figure 3. The primary source of uncertainty is in the O₃ analysers which are precise only to the nearest ppb. Periods of low tide influence the measurements, as was similarly observed by Whitehead et al. [21] and are depicted in the shaded areas. U₂₂ values during this period were mostly below 10 m s⁻¹, with predominant NW wind directions. Gradient fluxes were mostly negative, indicating a surface sink. It can be noted here that low tide occurred around midday on all four days, coinciding with the daily solar radiation maximum, as shown in Figure 3.

Both the modelled and measured fluxes are in accordance with those observed by Gallagher et al. [7] using the eddy covariance technique. Although the modelled fluxes are the same order of magnitude as the measured fluxes, variations in measured fluxes are not reproduced in initial box model results. The surface transfer represents the main bottleneck in ozone deposition to water surfaces [10]. Reactivity (A₀₃),
a first order loss rate representing chemical depletion of ozone in the sea surface layer, represents the biggest uncertainty in surface transfer, and comparison with the observations suggests that some important reactivity processes are either missing or unknown.

Referring to Figure 3, it is apparent that, excluding fluxes associated with low-tide conditions, episodes of large negative fluxes coincide with high solar irradiation. This suggests that there may be photoenhancement of ozone reactions. Gas-phase reactions above the water surface but below the lowest measurement level may partially contribute to the discrepancy between the model results and measurements; however, given that halogen concentrations are more than an order of magnitude lower than O$_3$ [22], the contribution of such reactions to the gradient is thought to be negligible; consequently, the increased flux was attributed to water-phase ozone reactions. Although Küpper et al. [23] found reactions of ozone and iodide to be light-independent, a recent study by Reeser et al. [6] demonstrated photoenhancement of reactions between ozone and organic substances. A possible reason for the photoenhancement of ozone-organic reactions can be deduced from the study of Zepp et al. [24] which describes how UV radiation alters the availability of aquatic dissolved organic matter (DOM) to microorganisms and accelerates photodegradation of DOM which may increase ocean reactivity to ozone by exposing more reactive species. In an attempt to replicate the nontidal ozone flux trends associated with irradiance, we introduce a photochemical enhancement factor for the modelled ozone-DOC reactions, whereby ozone reactions are enhanced by a factor of 20 in the presence of maximum solar radiation, and a linear scaling was applied to the reactivity term. This

Figure 2: Experimental data from Martino et al., (2012), where deposition velocity of ozone was measured as a function of varying (a) iodide and (b) DOC concentrations.

Figure 3: Ozone fluxes at Mace Head between August 10 and 13, 2010, measured using the gradient technique and modelled using deposition scheme of Fairall et al. [10].
scaling is a crude first order approximation, and the scaling limits were chosen to match the box-model results to the in situ data, results are depicted in Figure 3. While we are lacking quantitative information relating to the enhancing effect of light on ozone-DOC reactivity, it is clear that introducing this photochemical enhancement significantly improves the replication of the experimental data by the model. The inclusion of this new photochemical term results in an increase of the ozone deposition loss rate of up to 0.6 ppb per hour without the photochemistry.

Episodes of high downward ozone observed on days 223.5 and 224.5 are not reproduced by the model, but are most likely due to a combination of high wind speeds and levels of photoenhancement of sea-surface ozone reactions. The macroalgae exposure during low tide enhances ozone deposition on both physical and chemical levels: physically, ozone deposition to the rougher macroalgae surface would be more significant than to a water surface, while chemically, exposure of macroalgae to ozone stimulates oxidative stress, inducing release of molecular iodine [25] which rapidly reacts with ambient ozone, causing further depletion and perhaps an apparent increase in the downward ozone flux. Referring to Figure 1, a significant portion of the flux footprint lies within the tidal zone, indicating an augmented tidal influence during these periods. Increased depositional fluxes observed at nocturnal high tide on days 223 and 224 are not reproduced by the model. These high fluxes occur at periods of low wind speeds, and so it is likely that the flux enhancement occurs due to variations in water phase chemical reactivity. The model parameterises oceanic chemical reactivity using typical oceanic iodide and DOC concentrations and so variations in ocean tide reactivity are not accounted for in these results.

5. Conclusion

Photoenhancement of ozone-DOC reactions must be considered in the ozone dry deposition parameterisation to yield results corresponding to in situ gradient flux measurements. Presuming turbulence is adequately accounted for in surface transfer in the Fairall scheme, the ozone reactivity must be solar dependent. Inclusion of the solar radiation enhancement of sea-surface ozone reactions in the ozone deposition parameterisation causes an increase in modelled ozone flux of 38.5%, a significant enhancement to an ozone marine loss mechanism. Laboratory studies are required to quantify the effect of solar radiation on ozone with DOC, but this work indicates that failure to consider photoenhancement of ozone reactions with DOC would result in underestimation of ozone lost to sea surface via dry deposition, a loss mechanism especially pertinent for modelling intercontinental transport of ozone. Coupled with the knowledge that global concentrations of ocean-dwelling phytoplankton are in decline [26, 27], the decrease in organic matter in the Atlantic, and associated deposition flux reduction, may be a contributing factor in the previously unexplained rise in background ozone concentration as found in Mace Head [2].

Acknowledgments

The EPA, under Contracts CCRP5.3 (EASI-AQCIS), 2006-AQ-MS-50 (Ozone Trends in Ireland), and CCRP-09-FS-4-2, and Air Quality-Climate Interactions are acknowledged for support of this work.

References


Assessment of changing meteorology and emissions on air quality using a regional climate model: Impact on ozone

L. Coleman, D. Martin*, S. Varghese, S.G. Jennings, C.D. O’Dowd

School of Physics & Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland

HIGHLIGHTS

► Future simulations indicate that ozone levels will decrease under the RCP6 emission storyline.
► This reduction is most significant after 2050 when the most significant changes in emissions occur.
► An analysis of the ozone variance illustrates a significant decrease in extreme ozone events.

ARTICLE INFO

Article history:
Received 12 February 2012
Received in revised form
15 November 2012
Accepted 20 November 2012

Keywords:
Ozone
Changing meteorology
RCP emission scenarios

ABSTRACT

A regional climate model is used to assess changes in atmospheric ozone for the years 2030, 2050 and 2100 relative to 2006 brought about by changes in meteorology and emissions. The simulations are evaluated against ozone measurements for 2006, exhibiting good agreement between the model-predicted measurements and the measured annual cycles. 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 between 2006 and 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 summer time over mainland Europe by 2100. Model output was studied for three relevant sub-domains, namely the North East Atlantic, Ireland and Europe. The relative contribution of changes in both emissions and meteorology is 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 meteorology.

1. Introduction

Future air quality levels are influenced by a large number of factors. One of the most important contributing factors is the impact of a changing climate: this can affect air quality in a number of ways. Warmer climate could negatively influence air quality by increasing the number of stagnation events, which lead to significant build-up of pollutants and an increase in 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 inducing more frequent summer rains, causing more wash-out and thereby decreasing atmospheric pollution concentrations. 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 projecting potential impacts on future air quality occurring as a result of changing emissions and meteorology, with a particular focus on ozone. 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 emissions from continental-scale source regions, with uncertainties quantified according to spread of results from the different models.

On a global scale, trends in ozone have been previously investigated — Johnson et al. (2001) simulated global ozone up to 2100 using a regional 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 storyline (Van Vuuren et al., 2007). The CLE scenario reflects 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 to achieve the security, environmental and economic goals of the EU (Roadmap2050, 2011).

In this study, the regional influence of changing meteorology and emissions on simulated surface ozone over Europe and the North East Atlantic is assessed using the regional climate REMOTE (Regional climate MÖdel 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 meteorological data from the ECHAM5-HAM global circulation model (GCAM) (Stier et al., 2006) coupled with the MPI-OM—HAMOCC (Wetzel et al., 2006) ocean model run using the A1B emission scenario from the IPCC SRES. The Regional climate model deployed in this work was driven by global model data from long-term climate simulations with a number of time-slice years chosen to illustrate changing meteorology and the inherent changing levels of ozone that informs. 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 at the time of global simulations. However, reports show that the radiative forcing occurring in 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—MPI-OM—HAMOCC model results predicting a 5 % global temperature increase by 2100, the effect of changing meteorology 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 meteorology 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 meteorology is considered by using data from global climate change simulations. In addition, simulations are performed for 2100, allowing for more long-term predictions of air-quality trends over Europe, albeit determined using the slice-method, thus not accounting for inter-annual variability. The time-slice years chosen are used to indicate absolute changes in ozone within the model domain over the selected range (2006–2100).

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 changing meteorology 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.

2. Methodology

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). Previous IPCC emission scenarios reported in the IPCC Special Report on Emission Scenarios (IPCC SRES) (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 therefore limited in predicting future air quality with respect to particulate matter. RCP emission scenarios were developed for years 2005–2100 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 W m⁻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).

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).

2.3. Chemical mechanism

Photochemical production and loss in REMOTE is determined by the RADM II chemical scheme (Steele et al., 1994) 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 H₂O₂, O₃, methylhydrogenperoxide, peroxy-acetic acid and is catalysed by Fe³⁺ and Mn²⁺. Calculation of cloud water pH is by iteratively solving a continuously-maintained ion balance (Walcek and Taylor, 1986).
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 (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 andionic molarities (Maggi et al., 1997).

2.5. Model set up

Numerical simulations are carried out with the REMOTE model for the domain (Fig. 1) comprising Europe and North East Atlantic with horizontal resolution of 0.5° (~50 km), 81 x 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 runs with a time step of 300 s. 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—MPI-OM—HAMOCC model (Kloster et al., 2007), which are updated at the lateral boundaries every 6 h 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 Fig. 6(b) 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—MPI-OM—HAMOCC model and the same data set is used at the lateral boundaries for the monthly simulation. The impact of long-range transport on European ozone levels has been discussed in the HTAP 2010 synthesis report (Detente et al., 2010). This report finds that although current global models can simulate the path of pollutants during inter-continental transport, they have failed to reproduce historical trends, and so confidence in their ability to predict future trends in hemispherically transported ozone is open to conjecture.

Given our model domain, use of boundary conditions for future simulations derived from a global model would introduce an unknown uncertainty related to the long-range transport of ozone and so lateral boundary ozone values remain fixed for each time slice year; however it’s recognised that changes in global emissions could affect the ozone levels within the domain. From the HTAP report, it’s estimated that a 20% reduction in North American precursors would lead to a 1% decrease in European levels. Future anthropogenic emissions of SO\(_2\), 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 NO\(_2\) (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 (Anttila 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).

3. Results and discussion

3.1. Model validation

REMOTE output has previously been validated against EMEP measurement site data (Varghese et al., 2011). Comparison of model output ozone at different at resolutions (1°, 0.5°, 0.25°) for Mace Head have shown good agreement with replicating day to day variation. Monthly mean values (June) were also compared 123 EMEP stations and these values are compared to modelled values at both 00:00 GMT at 12:00 GMT. These results suggest reasonable agreement between modelled and observed ozone mixing ratios at the EMEP sites.

Fig. 2. Comparison between seasonal CYCLE in observed and modelled ozone mixing ratios (ppb) at (a) Mace Head, Ireland (b) Tustervatn, Norway (c) Neuglobsow, Germany and (d) Schauinsland, Germany (e) Zingst, Germany and (f) Sonnblick, Austria.
agreement between modelled and measured agreement with the better agreement occurring during daylight hours than night-time.

For this study, model evaluation was performed by comparing annual ozone cycles simulated for 2006 with measurements at four EMEP sites representative of rural ozone levels, suitable for analysing long-term trends. Simulated ozone mixing ratios for the Irish domain for 2006 were compared with in situ ozone measurements taken at four representative rural sites in Europe (Fig. 2).

At Mace Head, Galway, 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; simulated trends using the ozone deposition scheme of Wesely (1989) giving a RMSE of 2.59 ppb and a difference between observed and simulated annual means of 1.07 ppb.

At Tustervatn, Norway (Fig. 2(b)) the annual trend is reproduced very well for the first half of the year, but deviates in the latter part. This may be due to the proximity of the station to local agricultural activity and consequent emission of nitrogen compounds emitted in the summer months. At Neuglobsow in Germany (Fig. 2(c)) the model follows the annual trend well; this measurement site is situated in a remote forested/meadow area and relatively unaffected by anthropogenic emissions.

In the comparison at forested area of Schauinsland, Germany (Fig. 2(d)), the model fails to capture the mid-summer peak in ozone concentration. This peak occurs at the time of maximum photochemical production which is most likely enhanced by the seasonal peak in emissions of biogenic VOCs (isoprene). At times of high irradiance and high temperature, isoprene emissions are at a peak (Guenther et al., 1993). Isoprene oxidation leads to significant ozone production in the presence of NOx. This model underestimation is likely as a result of a previously identified underestimation of isoprene ozone production within the RADM II mechanism (Carter, 1996). Despite this underestimation, the model performs very well in reproducing the annual ozone level at Schauinsland, with a 1.4% overestimation in the model. This confirms that the model is a valid tool for the long-term simulations of ozone, despite the underestimation of the summer time peak in Germany.

At Zingst in Germany (Fig. 2(e)), the model performs well in replicating the seasonal cycle, but with a year-round underestimation in levels (average 3 ppb). The site is on the shore of the Baltic Sea with a predominant westerly air flow and so would have an oceanic fetch. The underestimation in simulated ozone mixing ratios may be due to the comparison of a point measurement with oceanic fetch and a grid cell average, encompassing ozone levels over land and water, with more ozone undergoing dry deposition on terrestrial surfaces.

![Figure 3](image-url)
In the final comparison at Sonnblick, Austria (Fig. 2(f)), the model reproduces the seasonal trend well, but with a slight underestimation of the summer peak as in Schauinsland, but not as pronounced.

All chosen sites for model validation are relatively remote regions. Apart from the anomaly between comparison of a point measurement with a 56 km (approx) grid cell average, further discrepancies between model results and measurements may occur due to seasonal agricultural activity in proximity to the measurement site, the use of RCP6.0 emission data instead of historical emission data. At most sites (except Schauinsland), the model does a fair job in replicating the seasonal trend, RMSEs ranging between 2.8 ppbv (Mace Head) and 9.1 ppbv (Schauinsland). Overall chosen stations, the correlation coefficient ($R^2$) between observed and simulated monthly mean ozone concentrations is 0.76 and RMSE is 5.7 ppbv. This is most likely due to the remote location of sites chosen and the subsequent lack of influence of emissions on local ozone levels. A graph depicting the correlation between observed and simulated ozone concentrations at 6 EMEP sites is given in the supporting information.

### 3.2. Monthly mean values and future ozone mixing

Fig. 3 shows the simulated monthly mean ozone mixing ratios (ppb) for January and August 2006, 2050 and 2100 within the REMOTE model domain; changing patterns in ozone concentrations 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 facilitates ozone destruction by NO$_x$ titration and so the effect of reducing NO$_x$ emissions during winter months is to increase ozone, hence the rise in ozone concentrations in January. These findings are consistent with those of Wild et al. (2011) who simulated a 2 ppb reduction over a European continental scale domain by 2050 under RCP6.0. Their study estimated regionally averaged changes in surface O$_3$ 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 concentrations evaluated with the uncertainty based on the variation between models each model using its own best estimate of 2001 meteorology and emissions. The effect of emissions on future ozone was elucidated and individual effects of changing particular atmospheric precursors by the establishment of continental-scale source–receptor relationships. The source–receptor relationships were assumed to be linearly additive over the range of emission perturbation studied. The European domain chosen for the Wild et al. (2011) study covers less of the North East Atlantic and more of the Eastern European domain, so one might expect the changes in surface level ozone due to changing emissions to be more pronounced.

The work presented here attempts to quantify changes on a more regional level as well as distinguishing between changing meteorology and air quality under a particular emission storyline. Table 1 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 changes in 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.

### Table 1

Regional annual and summer-time (May to August) mean annual and summer-time surface ozone means (ppb) over representative sub-domains and full REMOTE model domain for time slice years.

<table>
<thead>
<tr>
<th>Domain</th>
<th>Annual 2006</th>
<th>Summer 2006</th>
<th>Annual 2030</th>
<th>Summer 2030</th>
<th>Annual 2050</th>
<th>Summer 2050</th>
<th>Annual 2100</th>
<th>Summer 2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>North East Atlantic</td>
<td>41.70</td>
<td>35.85</td>
<td>38.68</td>
<td>34.96</td>
<td>31.77</td>
<td>38.56</td>
<td>38.33</td>
<td>38.79</td>
</tr>
<tr>
<td>Ireland</td>
<td>41.17</td>
<td>35.21</td>
<td>39.14</td>
<td>34.96</td>
<td>33.48</td>
<td>37.79</td>
<td>38.20</td>
<td>38.82</td>
</tr>
<tr>
<td>Europe</td>
<td>40.07</td>
<td>34.40</td>
<td>38.86</td>
<td>33.98</td>
<td>33.72</td>
<td>33.93</td>
<td>37.87</td>
<td>35.40</td>
</tr>
<tr>
<td>Model domain</td>
<td>39.86</td>
<td>31.33</td>
<td>38.67</td>
<td>30.69</td>
<td>32.33</td>
<td>28.51</td>
<td>36.16</td>
<td>30.79</td>
</tr>
</tbody>
</table>

Fig. 4. (a) Ozone deposition velocity (cm s$^{-1}$) in North East Atlantic. (b) Monthly mean DOM (μM Phosphorous) mixing ratios in North East Atlantic.
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, coinciding with periods of maximum ozone photodestruction. 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. Fig. 4 shows the ocean productivity and ozone deposition velocity for the simulation years under investigation. From Fig. 4(a), ocean productivity is set to decrease between now and 2100 due to changing oceanic stratification patterns with a consequential decrease in ozone deposition velocity (Fig. 4(b)). 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 influence the ozone budget over the ocean.

3.4. Effect of both meteorological changes and changing emissions on ozone levels

Fig. 5 depicts the monthly mean surface ozone concentrations simulated for January and August 2006 and 2100, with an additional plot of ozone concentrations simulated using 2006 climatology (including natural emissions) and 2100 RCP6.0 anthropogenic emissions. From the figure, the simulated change in ozone concentrations for the coming century can be attributed to either changing emissions or changing meteorology. 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 Fig. 1 are quantified in Table 2.

Included for comparison purposes in Table 2 are the equivalent values for NO2 and SO2. These values indicate that the effect of changing emissions is by far the most important parameter in determining future concentrations of these gases. The impact of changing meteorology on future SO2 levels is more variable than with NO2 due to the oceanic source of SO2 from the oxidation of dimethylsulphide. Although the primary focus of this paper is on future trends in ozone, information is provided on simulated future SO2 and NO2 levels in supplementary data.

Fig. 5. Impact of changing RCP6.0 emissions (2006, 2100 scenarios) on simulated ozone mixing ratios (ppb) for 2006.
Previous studies found an average ozone increase of 4.8 ppb over the US due to a rise in surface temperatures (Bell et al., 2007) with maximum 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). From Table 2, it can be seen that the changing emissions predominantly determine future surface ozone levels except in the North East Atlantic – a region representative of clean marine air influenced by hemispheric transport. The isolated effect of changing meteorology on future ozone levels is regionally variable, but generally it causes an increase in surface ozone in January and a decrease in surface ozone in August. This is not the case in the North East Atlantic, where changing meteorology causes a decrease in winter-time surface ozone concentrations brought about by an increase in the photo-destruction of ozone, and due to the NOx-poor marine environment, this is not compensated for by increased photochemical ozone production.

Table 2
Regional simulated percentage changes in surface ozone, NO2 and SO2 between 2006 and 2100 for January and August due to combined a) changing anthropogenic emissions and meteorology, b) changing anthropogenic emissions alone and c) changing meteorology alone.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% Change O3</td>
<td>January</td>
<td>August</td>
<td>January</td>
</tr>
<tr>
<td>a) Meteorology &amp; emissions</td>
<td>−0.54</td>
<td>−15.61</td>
<td>18.59</td>
</tr>
<tr>
<td>b) Emissions only</td>
<td>3.25</td>
<td>−4.31</td>
<td>16.62</td>
</tr>
<tr>
<td>c) Meteorology</td>
<td>−3.79</td>
<td>−11.30</td>
<td>1.97</td>
</tr>
<tr>
<td>% Change NO2</td>
<td>January</td>
<td>August</td>
<td>January</td>
</tr>
<tr>
<td>a) Meteorology &amp; emissions</td>
<td>−38.91</td>
<td>−54.49</td>
<td>−96.14</td>
</tr>
<tr>
<td>b) Emissions only</td>
<td>−68.87</td>
<td>−69.60</td>
<td>−95.67</td>
</tr>
<tr>
<td>c) Meteorology</td>
<td>29.96</td>
<td>14.11</td>
<td>−0.48</td>
</tr>
<tr>
<td>% Change SO2</td>
<td>January</td>
<td>August</td>
<td>January</td>
</tr>
<tr>
<td>a) Meteorology &amp; emissions</td>
<td>−52.61</td>
<td>−19.40</td>
<td>−93.25</td>
</tr>
<tr>
<td>b) Emissions only</td>
<td>−79.14</td>
<td>−18.38</td>
<td>−97.10</td>
</tr>
<tr>
<td>c) Meteorology</td>
<td>26.51</td>
<td>−1.02</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Fig. 6. Difference in monthly mean average temperature (°K) for January and August 2030, 2050 and 2100 compared to the base year of 2006.
Over Eastern Europe and parts of Scandinavia, the simulated rise in temperature caused by changing meteorology causes a reduction in ozone mixing ratios. Monthly mean values (January and August) for temperature difference of future simulated years compared to 2006 are shown in Fig. 6. The simulated decrease in ozone as a result of rising surface temperature can be explained by a number of factors can be explained by a number of factors, one of which is a predicted increase in temperature-driven biogenic VOC emissions. The emission of isoprene decreases surface ozone by depleting NO\textsubscript{x} through formation of isoprene nitrates, thus suppressing O\textsubscript{3} formation and by direct ozonolysis of isoprene (Fiore et al., 2005). Although the RADM II chemical mechanism recycles isoprene nitrates to replenish the NO\textsubscript{x} budget, ozone formation is not stimulated in the unpolluted environment, especially when pollution mitigation takes effect. An increase in atmospheric water vapour mixing ratios would facilitate an increase in photochemical ozone destruction (Stevenson et al., 2006). 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 sub-domains. Monthly mean ozone concentrations with 2006 climatology and future RCP6.0 anthropogenic emission projections are shown in Fig. 7. The decrease in ozone levels in 2100 is apparent in all domains, with a prominent summer time decrease. The influence of the seasonal variation of ozone concentrations over the ocean on ozone levels in Ireland is apparent. In the North East Atlantic, the changing emissions do not change surface ozone trends, the decrease in 2100 levels attributable solely to changing meteorology.

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 2, and by comparison of seasonal trends with the monthly means generated using 2006 meteorology and future RCP emissions, trends can be generally attributed to the effect of anthropogenic emissions. Over the entire model domain, the seasonal trend is driven predominantly by changing emissions, but with changing meteorology having a contributory reducing effect in August, accounting for roughly 25% of the decrease between 2006 and 2100. In 2100 when emission precursors are very low, the prominent summer time seasonal minimum in ozone levels coincides with the seasonal peak of photodestruction and by 2100, means summer-time ozone concentrations over the whole domain are simulated to be as low as 27 ppb.

It is noted that the effect of future changes in emissions outside the model domain is not accounted for in these simulations. Considering the HTAP report estimated the effect of reducing North American ozone precursors by 20% as causing a 1% reduction in European levels, the effect of changing emissions and meteorology exceed this significantly. However, the future decrease in North

![Fig. 7. Regional analysis of monthly mean ozone mixing ratios (ppb) for time-slice years 2006, 2030, 2050 and 2100 for model domain and sub-domains.](image-url)
American precursors would enhance the decrease in future ozone mixing ratios over the domains under the RCP6.0 emission scenario.

3.5. Variances, exceedences and extreme events

The variance is a statistical measure of the range of ozone concentrations. Fig. 8 shows the monthly variance in ozone concentrations for representative months over for 2006, 2050 and 2100. It can be seen that most extreme events occur in the summer time 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 Fig. 9, the effect of emissions and changing meteorology 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 changing meteorology. 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 m⁻³) ozone. Daily 8 h means are not to exceed this value more than 25 times per annum. To relate the simulated ozone concentrations to these air quality guidelines, annual exceedences of 60 ppb are graphed in Fig. 10. The values presented here are 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 Fig. 10, some extreme ozone concentrations 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 concentrations 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.

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 concentrations are presented in Fig. 8 and Fig. 9.
concentrations are shown in Fig. 11. In Ireland, the seasonal trend 2006–2050 has a pronounced peak in summer time months. The aforementioned advection patterns in summer 2030 cause extreme ozone concentrations, but by 2100 when emission controls have taken effect, extreme ozone concentrations fall below the 60 ppb limit all year round. Comparing the seasonal trends to monthly means of emission control simulations, it is noted that the extreme ozone concentrations are not only determined by emissions, but are significantly influenced by meteorology. Monthly exceedences for January and August simulated with the emission control runs are shown in the Supporting Information. From Air Quality Ontario (2010), ozone

Fig. 9. Impact of changing meteorology and emissions on simulated variance of ozone mixing ratios for January and August 2006, 2100 and 2006 meteorology run with RCP6.0 emissions for 2100.

Fig. 10. Simulated annual number of exceedences of the current European CAFE Directive air quality limit of 60 ppb as 8 hourly mean ozone mixing ratios for 2006, 2030, 2050 and 2100 over Europe.
4. Conclusions

Model comparison of the monthly mean annual cycle of ozone mixing ratios with measurements at a number of measurement sites shows good agreement for the 2006 reference year (a $R^2$ of 0.76 and RMSE of 5.7 ppbv). Future simulations for 2030, 2050 and 2100 indicate that ozone mixing ratios over the model domain are set to decrease under changing meteorology and the RCP6.0 emission storyline. Using individual time-slice years with changing meteorological conditions may allow an increase in the spatial scale and generation of more specific evidence in the simulated changes in ozone mixing ratios.

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 the regional spatial 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 the 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 summer time 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.

Acknowledgements

The authors would like to thank Environmental Protection Agency (Ireland) for financial support and Irish High Performance Computing Centre for the computing resources and technical support. In addition, the authors would also like to thank M. Hartnett and A. Oblert.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.11.048.

References

Assessment of changing meteorology and emissions on air quality using a regional climate model: Part 1-Impact on Ozone

L. Coleman, D. Martin, S. Varghese, S.G. Jennings, C.D. O’Dowd

School of Physics & Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland

Abstract
A regional climate model is used to assess changes in ozone for the years 2030, 2050 and 2100 relative to 2006 brought about by varying meteorology and emissions. The simulations are evaluated against ozone measurements for 2006, exhibiting good agreement between the model-predicted and the measured annual cycles. 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 between 2006 and 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 changes in both emissions and meteorology is 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 meteorology.

Keywords:
Ozone, air quality, changing meteorology, RCP emission scenarios

Supporting Information
Table 1: Regional annual and summer-time (May to August) means in annual and summer-time surface \( \text{NO}_2 \) & \( \text{SO}_2 \) means (ppb) over representative sub-domains and full REMOTE model domain for time slice years

<table>
<thead>
<tr>
<th></th>
<th>Annual</th>
<th>Summer</th>
<th>Annual</th>
<th>Summer</th>
<th>Annual</th>
<th>Summer</th>
<th>Annual</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NO(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>0.248</td>
<td>0.221</td>
<td>1.399</td>
<td>0.907</td>
<td>7.337</td>
<td>5.437</td>
<td>1.973</td>
<td>1.583</td>
</tr>
<tr>
<td>2030</td>
<td>0.24</td>
<td>0.199</td>
<td>0.708</td>
<td>0.617</td>
<td>4.130</td>
<td>3.584</td>
<td>1.281</td>
<td>1.097</td>
</tr>
<tr>
<td>2050</td>
<td>0.179</td>
<td>0.183</td>
<td>0.430</td>
<td>0.374</td>
<td>2.034</td>
<td>1.687</td>
<td>0.791</td>
<td>0.710</td>
</tr>
<tr>
<td>2100</td>
<td>0.106</td>
<td>0.093</td>
<td>0.083</td>
<td>0.087</td>
<td>0.658</td>
<td>0.318</td>
<td>0.296</td>
<td>0.282</td>
</tr>
<tr>
<td><strong>SO(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>0.108</td>
<td>0.093</td>
<td>0.281</td>
<td>0.228</td>
<td>1.834</td>
<td>1.843</td>
<td>0.686</td>
<td>0.689</td>
</tr>
<tr>
<td>2030</td>
<td>0.150</td>
<td>0.137</td>
<td>0.218</td>
<td>0.213</td>
<td>0.767</td>
<td>0.921</td>
<td>0.384</td>
<td>0.4244</td>
</tr>
<tr>
<td>2050</td>
<td>0.120</td>
<td>0.141</td>
<td>0.158</td>
<td>0.178</td>
<td>0.1511</td>
<td>0.230</td>
<td>0.256</td>
<td>0.2922</td>
</tr>
<tr>
<td>2100</td>
<td>0.117</td>
<td>0.134</td>
<td>0.066</td>
<td>0.068</td>
<td>0.053</td>
<td>0.067</td>
<td>0.114</td>
<td>0.1393</td>
</tr>
</tbody>
</table>

Figure 1: Simulated monthly mean \( \text{NO}_2 \) (ppb) mixing ratios for 2006, 2030, 2050 and 2100 over model domain and subdomains

(a) North East Atlantic
(b) Ireland
(c) Europe
(d) Model Domain
Figure 2: Simulated monthly max $NO_2$ (ppb) mixing ratios simulated over Ireland and over the whole domain for each simulated year.

Figure 3: Simulated monthly mean $SO_2$ (ppb) mixing ratios for 2006, 2030, 2050 and 2100 over model domain and subdomains.

Figure 4: Simulated monthly max $SO_2$ (ppb) mixing ratios simulated over Ireland and over the whole domain for each simulated year.
Figure 5: Simulated monthly mean $NO_2$ (ppb) mixing ratios for January and August 2006, 2050 and 2100.
Figure 6: Simulated monthly mean $SO_2$ (ppb) mixing ratios for January and August 2006, 2050 and 2100.
Figure 7: Difference in clear sky net surface solar radiation (Wm$^{-2}$) for January and August 2030, 2050 and 2100 compared to the base year of 2006.