

Chapter 1

Introduction

Air pollution is the leading environmental health risk in many areas around the world. The effects of air pollution to the general population range from chronic to less severe health impacts and reduced growth rates of vegetation resulting in economic losses of billions of euros (EEA, 2015). Moreover, the International Agency for Research on Cancer labelled air pollution as carcinogenic (IARC, 2013). Due to these impacts, many governed areas introduced legislation designed to reduce concentrations of many air pollutants.

Tropospheric ozone (O_3) is one of the most problematic air pollutants over Europe with up to 98 % of Europe's urban population exposed to concentrations of ozone above the WHO guidelines (EEA, 2015). Furthermore, in 2011 the EU ozone target value for human health (the EU has no limit value for ozone) was exceeded in 65 % of the EU member states and Europe's ozone target value for vegetation was exceeded in 27 % of the EU-28 agricultural areas (EEA, 2013).

Reducing atmospheric concentrations of tropospheric ozone is a complex problem as ozone is not directly emitted into the troposphere. Tropospheric ozone is produced from the reactions of volatile organic compounds (VOCs) in the presence of nitrogen oxides ($NO_x \equiv NO + NO_2$) and sunlight (Atkinson, 2000). Meteorology and transport also influence tropospheric ozone levels (Jacob and Winner, 2009).

Air quality (AQ) models are an important tool for understanding ozone pollution and predicting future air quality. Many AQ models are available with different scales and dimensions depending on the scope of the modelling experiment. Accurately representing the complexity of ozone production in a computationally efficient model is an ongoing challenge for the modelling community (Russell and Dennis, 2000).

Model intercomparison projects (MIPs) compare the outputs from different models showing differences in tropospheric ozone due to differing representations of key processes. For example, ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) showed different magnitudes of future ozone burden in the same region (Young et al., 2013). A current MIP, CCMI (Chemistry Climate Model Initiative), aims to investigate differences in the representation of chemistry, emissions and transport processes between models to understand the differences between predictions from global models (Eyring et al., 2013).

Detailed process studies are key to understanding differences between simulated ozone levels from different models. This thesis determines the effects of VOC degradation chemistry, VOC emissions and temperature on modelled ozone predictions. This assessment should be beneficial to the modelling community in understanding potential differences between model outputs and improving AQ models.

1.1 Ozone

Ozone is a atmospheric gas found in the stratosphere and troposphere, however its atmospheric effects are very different in these regions. The stratosphere contains ~ 90 % of the atmospheric ozone with a peak mixing ratio of ~ 12 ppm (Seinfeld and Pandis, 2006). Stratospheric ozone absorbs the sun's ultraviolet radiation which is important due to the adverse effects of excess UV radiation on humans and ecosystems.

In contrast, tropospheric (or surface) ozone is both a pollutant and a greenhouse gas. Increased levels of tropospheric ozone are harmful to humans, plants and other living systems. High ozone exposure may lead to pulmonary problems in humans and can decrease both crop yields and forest growth (World Meteorological Organisation, 2011).

Tropospheric ozone is formed via photochemical production from the reactions between VOCs and NO_x , described in Sect. 1.2, while meteorology and atmospheric transport also influence ozone concentrations. For example, a spring-time peak in tropospheric ozone is common in the Northern Hemisphere (NH) mid-latitudes, originally attributed to transport of ozone from the stratosphere into the troposphere via the Stratosphere-Troposphere Exchange (STE) (Monks, 2000). However, ozone transported via the STE rarely influences surface ozone levels

(Lelieveld and Dentener, 2000) and the spring maximum is due to the photochemical reactions occurring in the NH spring after the buildup of reservoir species over winter (Penkett and Brice, 1986).

Understanding the intricacies of surface ozone pollution requires a combined effort from the modelling, observational and chemical kinetic communities – called the “three-legged stool” approach by Abbatt et al. (2014). Modelling of ozone production helped understand the complexity of atmospheric chemistry, such as the non-linear relationship of ozone production with precursor (VOC and NO_x) emissions. Modelling studies attempt to reproduce observational trends of surface ozone and model predictions may inspire new observational studies. Chemical kinetic studies performed by laboratories give insights to missing or incorrect representations of atmospheric chemistry to be included in updated models.

This thesis focuses on the influence on ozone production from the representation of VOC degradation chemistry, VOC emissions and the ozone-temperature relationship within models. Ozone production chemistry is outlined in Sect. 1.2, while sources of emissions of ozone precursors are described in Sect. 1.3. Finally, the effects of meteorology, in particular temperature, on ozone production are presented in Sect. 1.4. For the rest of this thesis, ozone refers to tropospheric ozone.

1.2 Ozone Chemistry

Ozone absorbs UV radiation producing either ground-state atomic oxygen (O(³P)) or excited singlet (O(¹D)) oxygen atoms.



Ground-state oxygen quickly reacts with oxygen to reform ozone.

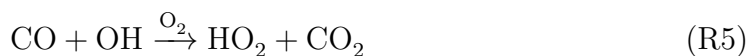


Thus there is no net loss or production of ozone through (R1) and (R3). O(¹D) may collide with N₂ or O₂ (represented as M in chemical reactions) stabilising to the ground-state. This process again leads to a null cycle with ozone destruction balanced by production. However, O(¹D) can react with water vapour producing hydroxyl (OH) radicals. The OH radical is a highly reactive chemical species reacting

with almost all trace chemical species in the troposphere. (Seinfeld and Pandis, 2006; Monks, 2005)



The initial oxidation of VOCs by OH initiates a reaction chain which may lead to net production or loss of ozone depending on the atmospheric conditions. For example, when carbon monoxide (CO) reacts with OH in the presence of oxygen, carbon dioxide and the hydroperoxy (HO_2) radical are formed. In polluted areas with high- NO_x concentrations, HO_2 readily reacts with nitrogen oxide (NO) regenerating OH and producing nitrogen dioxide (NO_2).



Photolysis of NO_2 produces ground-state atomic oxygen leading to ozone production via (R3).



The reaction between OH and NO_2 produces nitric acid (HNO_3) limiting the recycling of OH and NO_2 . Nitric acid may be removed through deposition processes and is a sink for both OH and NO_2 .



In low- NO_x conditions away from polluted areas, OH and HO_2 are interconverted through reactions with ozone.



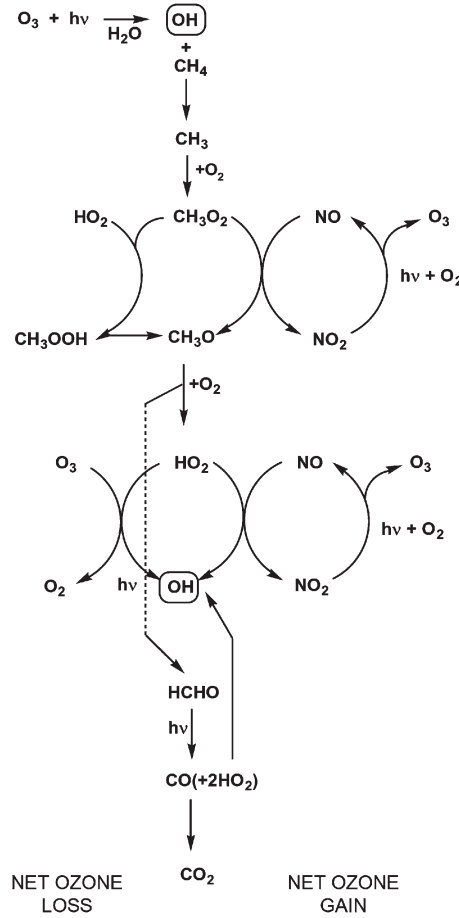
OH and HO_2 may also react in a termination reaction producing water vapour and oxygen.



Other termination reactions involve combination reactions of HO_2 radicals producing hydrogen peroxide (H_2O_2).



Figure 1.1: Methane degradation pathways in low- NO_x and high- NO_x conditions. Taken from Monks (2005).



Hydrogen peroxide may be removed through deposition (Gunz and Hoffmann, 1990) but may also be a temporary sink for the odd-oxygen species OH and HO_2 .



In summary, the secondary degradation of CO produces ozone in high- NO_x conditions while in low- NO_x conditions ozone is destroyed. (Seinfeld and Pandis, 2006; Monks, 2005)

The secondary degradation of more complex VOCs has similar features to that of CO . Methane (CH_4), with a mixing ratio of ~ 1.7 ppmv, is the most abundant VOC in the troposphere. The reaction of methane with OH , in the presence of O_2 , produces the methyl peroxy radical (CH_3O_2) – the simplest organic peroxy radical (RO_2).

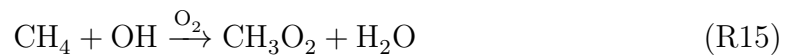
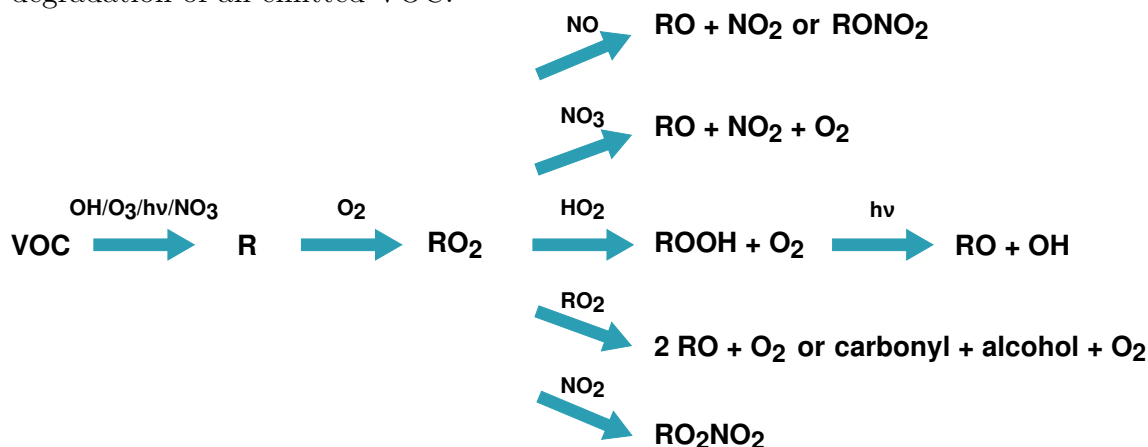


Figure 1.2: Schematic diagram outlining general pathways of the secondary degradation of an emitted VOC.



Similar to CO oxidation, NO_x conditions play a crucial role in the fate of CH_3O_2 and whether ozone is produced or destroyed, depicted in Fig. 1.1.

The general types of secondary degradation products formed during CH_4 degradation can be extended to more complex non-methane VOCs (NMVOCs). Initial oxidation pathways of NMVOCs are reaction with OH, while unsaturated VOCs, such as alkenes, may react with ozone and photolysis is important for carbonyl species. During the night-time, reaction with the nitrate (NO_3) radical is typically more important than OH-oxidation due to the relatively higher concentrations of NO_3 during night-time.

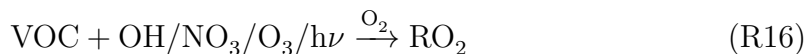
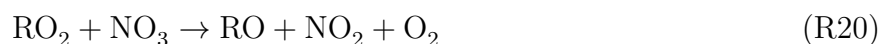
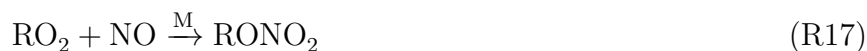


Figure 1.2 represents a general and simplified reaction scheme for VOCs in the troposphere. The initial oxidation of NMVOC produces RO_2 radicals and the fate of the RO_2 determines whether net loss or production of ozone occurs.



All degradation pathways of RO_2 that produce NO_2 result in O_3 formation due to

(R7) and (R3). Reaction with the HO_2 radical forms a hydroperoxide (ROOH) which may either be removed from the system or photolysed producing an alkoxy (RO) radical and OH . The carbonyl and alcohol products resulting from reactions between RO_2 radicals follows a similar sequence of reactions and can produce further O_3 . Thus the subsequent reactions of secondary degradation products of a VOC may lead to further production of ozone.

Reaction of RO_2 with NO_2 (R19) forms peroxy nitrates (RO_2NO_2) which are a temporary reservoir for RO_2 and NO_x . The thermal decomposition rate of RO_2NO_2 is highly temperature dependent. At lower temperatures, RO_2NO_2 builds up and may be transported away from the region of formation. Thus releasing RO_2 and NO_2 in areas away from large sources of NO_x and fuelling ozone production.

The reaction between NO and ozone is another important reaction in polluted regions.



Reactions (R24), (R7) and (R3) form a null cycle of ozone production and destruction which limits ozone levels. On the local urban scale close to NO sources, (R24) decreases ozone levels called ozone titration. Ozone titration is also important during the night where the lack of photochemistry does not regenerate ozone. Urban measurement studies have confirmed the importance of ozone titration near source of NO (Syri et al., 2001).

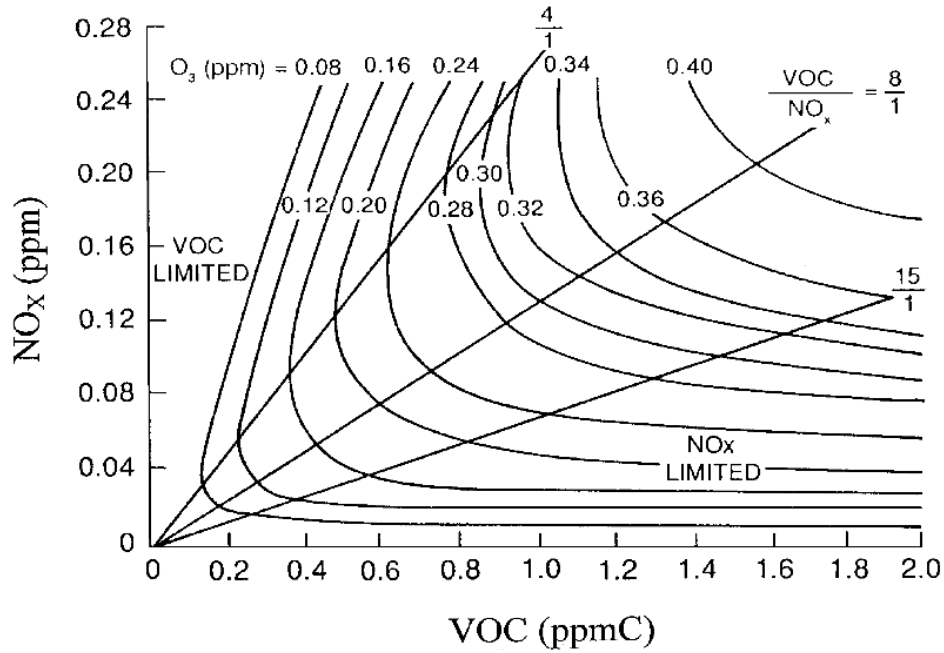
1.2.1 VOC and NO_x Chemistry

The fate of peroxy radicals produced during VOC degradation depends on the ratio of the concentrations of radicals and NO_x (Kleinman, 1991, 1994). In regions with low- NO_x concentrations, RO_2 are more likely to react with other radicals rather than convert NO to NO_2 leading to ozone production. This is *NO_x -limited* chemistry.

On the other hand, reactions between radicals and NO_x in regions with high levels of NO_x are more likely to occur. The production of HNO_3 increases through (R8) removing OH and NO_x . This is *VOC-limited* or *NO_x -saturated* chemistry.

The chemistry in low- NO_x and high- NO_x conditions indicates that ozone production is a non-linear process. Figure 1.3, from Jenkin and Clemitshaw (2000), depicts the non-linear relationship between ozone as a function of VOC and NO_x . This

Figure 1.3: Ozone isopleth plots for various initial mixing ratios of NO_x and VOCs. Taken from Jenkin and Clemitshaw (2000).



relationship can be divided into distinct regimes of ozone production: NO_x -sensitive (or NO_x -limited), NO_x -saturated (or VOC-limited) and VOC-and- NO_x -sensitive regimes.

In the NO_x -sensitive regime, increasing NO_x increases the number of NO to NO_2 conversions by peroxy radicals leading to ozone production. However, increasing VOC levels has little effect on O_3 production due to increased radical-radical reactions.

The NO_x -saturated regime corresponds to high NO_x concentrations where radicals tend to react with NO_x . Increasing levels of VOC increase the likelihood of RO_2 converting NO to NO_2 leading to ozone production. Increasing NO_x levels will not increase O_3 production.

The VOC-and- NO_x -sensitive regime (contour ridges in Fig. 1.3) is characterised by O_3 production being sensitive to both VOC and NO_x levels. Moreover, it is in this atmospheric regime that the maximum amount of ozone is produced. Kleinman (1994) showed that this non-linear relationship can be thought of as a titration process between radicals and NO_x with the VOC-and- NO_x -sensitive regime being the turning point.

The non-linear nature of ozone production is one of the challenges in controlling ozone levels. The difficulty is exacerbated by the fact that the troposphere

can alternate between these regimes depending on the meteorological conditions. Moreover, fresh emissions tend to occur in NO_x -saturated areas before being transported to VOC-and- NO_x -sensitive and NO_x -sensitive regions.

1.2.2 Representing Atmospheric Chemistry in Models

Representing the degradation chemistry for each VOC in a chemical transport model (CTM) is unrealistic. Even if all the secondary degradation pathways and products were known for every VOC, a CTM is unable to efficiently numerically solve the differential equations.

The representation of atmospheric chemistry in a CTM is called a chemical mechanism. Chemical mechanisms are developed by simplifying and aggregating VOCs, degradation products and reactions. Less aggressive simplification approaches may result in a chemical mechanism having thousands of species while more aggressive simplification may result in only a hundred species. Chemical mechanisms are verified by comparing the concentrations of field studies or controlled chamber study experiments to model simulations (Stockwell et al., 2012). Section ?? includes further details of the simplification techniques used to develop chemical mechanisms.

Chemical mechanism comparison studies, such as Kuhn et al. (1998) and Emmerson and Evans (2009), compare the outputs of different chemical mechanisms using the same model setup and initial conditions. These studies showed that the differences in representing atmospheric chemistry can lead to large differences in simulated ozone concentrations. These comparisons of the concentrations of key atmospheric species (such as ozone, OH and NO_x) indicate that the chemical mechanisms leads to differences but does not help in pointing out the root cause.

Determining the source of differences between chemical mechanisms is a difficult task due to the interlinked chemistry of many key species. As part of this study, the ozone production from different chemical mechanisms is compared and differences in the treatment of VOC degradation chemistry is determined. The research questions driving this comparison are presented in Sect. 1.5 and the results are described in Sect. ??.

1.3 Source and Sinks of Ozone Precursors

Ozone precursors are emitted from many anthropogenic and biogenic sources with varying emissions throughout the year, month or time of day. In many regions, reduced road transport during the weekend leads to a noticeable reduction in NO_x emissions influencing ozone levels. This is called the “weekend-effect”. For example, ozone production is NO_x -saturated during weekdays in San Joaquin Valley, California but during the weekend higher ozone levels are recorded as the reduction in NO_x levels leads to VOC-and- NO_x -sensitive chemistry (Pusede et al., 2014). Many sources of NMVOC, such as industry and solvent use, also reduce activities during the weekend. Residential combustion is highest during the winter months and lowest during the summer (Denier van der Gon et al., 2011).

1.3.1 NO_x

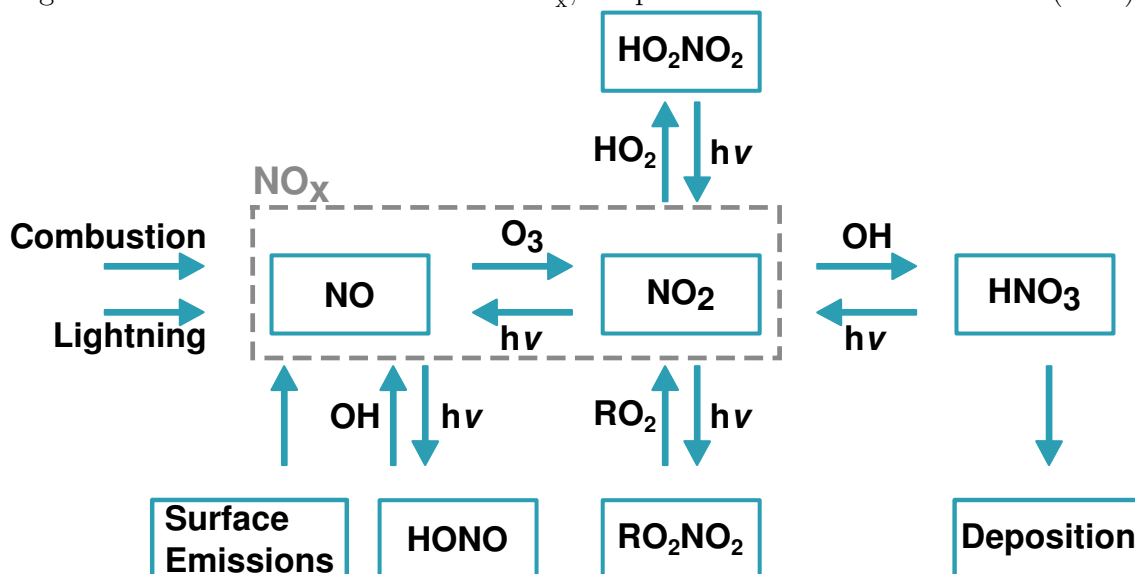
Anthropogenic activities are the main source of NO_x emissions into the atmosphere. In the year 2000, almost 52 Tg N were emitted with 65 % through fossil fuel combustion (Seinfeld and Pandis, 2006). Examples of fossil fuel combustion emitting NO_x are transportation using diesel or petrol vehicles, industrial activities and domestic heating (von Schneidmesser et al., 2015).

Up to 95 % of NO_x emissions from combustion are emitted as NO , which is oxidised to form NO_2 through (R24) and (R6). However, due to the increase in diesel vehicles and the implementation of diesel filters the fraction of emitted NO_2 from vehicles has increased. Grice et al. (2009) showed that over Europe, emissions of NO_2 from diesel vehicles have increased from 8.6 % in 2000 to 12.4 % in 2004.

Despite the majority of NO_x emissions coming from human activities, there are also natural sources of NO_x . Lightning is an important source of NO_x in the free troposphere while emissions of NO_x from soils are important in remote regions with little anthropogenic influence. Lightning and soils each contributed ~ 10 % to global NO_x emissions in 2000 (Seinfeld and Pandis, 2006).

The main sink of NO_x is through deposition of nitric acid, formed via (R8). Temporary reservoirs, such as peroxy nitrates and HONO , may be transported away from sources into areas devoid of large sources of NO_x . These sources and sinks of NO_x are illustrated in Fig. 1.4.

Figure 1.4: The sources and sinks of NO_x , adapted from Seinfeld and Pandis (2006).



1.3.2 VOCs

The main sink of VOCs is the oxidation chemistry described in Sect. 1.2. The degradation of a VOC yields the maximum possible amount of ozone when every peroxy radical converts NO to NO_2 called the *ozone production potential* (OPP) of a VOC. In reality, the OPP of a VOC is never achieved as other reactions with peroxy radicals occur however the OPP is useful for assessing the amount of ozone produced from emitted VOCs.

Carbon Monoxide

Carbon monoxide is emitted directly into the troposphere through combustion and industrial processes. An equally-important source of CO is its formation during the degradation of VOCs. Hauglustaine et al. (1998) estimated that 881 Tg yr^{-1} of CO was produced globally from chemical oxidation of VOC while 1219 Tg yr^{-1} of CO was directly emitted.

The reaction between CO and OH (R5) is the main sink of CO . The OPP of CO is one as the degradation of CO produces one peroxy radical (HO_2), thus a maximum of one molecule of ozone may be produced during CO degradation.

Methane

Emissions of methane range between 500 and 600 Tg CH₄ yr⁻¹ with ~ 60 % of the emissions from anthropogenic sources. The main anthropogenic sources of CH₄ are agriculture, fossil fuels and biomass burning with agriculture contributing 60 % of the anthropogenically emitted CH₄. Emissions from wetlands are the main natural source of methane emissions (Kirschke et al., 2013).

Methane has a lifetime of about 9 years, significantly longer than other VOCs. Thus, methane influences ozone production on the global rather than the regional scale.

Reaction with OH (R15) is the main sink of methane and the secondary degradation of CH₄ (Fig. 1.1) produces CO and four peroxy radicals (1× CH₃O₂, 3× HO₂). Thus the OPP of methane is five as methane degradation can produce a maximum five molecules of O₃ per molecule of CH₄ oxidised.

NMVOCs

A wide variety of NMVOCs are emitted from anthropogenic activities directly into the troposphere. Solvent use, industry, fossil fuel burning and transportation are all major activities emitting NMVOCs of varying functional groups, carbon numbers and reactivity. Emissions of NMVOC from vegetation depends on meteorological variables (such as, temperature and radiation) and biological variables (such as, leaf age and leaf area index) (Guenther et al., 2012).

Lamarque et al. (2010) estimated that in 2000, 130 Tg NMVOC were globally emitted from anthropogenic sources. This amount is dwarfed by emissions from biogenic sources – 1000 Tg NMVOC yr⁻¹ (Guenther et al., 2012). Isoprene (C₅H₈) emitted from vegetation dominates at the global scale however emissions of monoterpenes and sesquiterpenes from vegetation may also be significant.

Although isoprene is considered as a biogenic VOC (BVOC), it has been measured in the urban areas of London and Paris away from biogenic emission sources. Transport of isoprene is unlikely as isoprene is a highly reactive NMVOC indicating anthropogenic sources of isoprene (von Schneidmesser et al., 2011). Other NMVOC emitted from anthropogenic sources, such as methanol and acetaldehyde, are also emitted from vegetation (Guenther et al., 2012).

The maximum number of molecules of O₃ produced per degradation of an

Table 1.1: Emission source sectors for anthropogenic emissions listed in the TNO_MACCIII inventory (Kuenen et al., 2014).

Description	Description
Public Power	Road Transport: Others
Residential Combustion	Road Transport: Evaporation
Industry	Road Transport: Wear
Fossil Fuel	Non-road Transport
Solvent Use	Waste
Road Transport: Gasoline	Agriculture
Road Transport: Diesel	

emitted NMVOC depends on the type and the number of carbons of the NMVOC leading to a wide range of OPPs for different NMVOC. Unsaturated NMVOC, such as alkenes, tend to have larger OPPs than alkanes (saturated NMVOC). Even within a functional group of NMVOC different OPPs are calculated. For example, benzene and xylene are both aromatic compounds but as benzene is a more chemically stable molecule it has a lower OPP than xylene (Carter, 1994).

OPPs for complex NMVOCs are calculated using models by incrementally varying the concentration of an NMVOC and calculating the change in ozone. Different scales calculating the OPP of NMVOC have been developed using different NO_x conditions. The Maximum Incremental Reactivity (MIR) and Maximum Ozone Incremental Reactivity scales of Carter (1994) and the Tagged Ozone Production Potential (TOPP) are examples of OPP scales for NMVOCs.

1.3.3 Representing NMVOC Emissions in Models

Emissions of NMVOC species are a critical input in models and emission inventories are used to specify the type and quantity of emissions from source categories. Table 1.1 lists the source sectors of emissions used by the TNO_MACCIII emission inventory (Kuenen et al., 2014). Emission inventories are available for the global or regional emissions. For example, EDGAR (JGJ et al., 1996) specifies global emissions while TNO_MACCIII (Kuenen et al., 2014) specifies european emissions.

Many uncertainties are associated with emission inventories. For example, Coll et al. (2010) showed that large discrepancies arise between ambient measurements and emission inventories. Also, the temporal variation of emissions are not captured by emission inventories (Boynard et al., 2014).

BVOC emissions depend on meteorological and biological variables and

Table 1.2: Influence of meteorological variables on ozone production, taken from Jacob and Winner (2009).

Meteorological Variable	Influence on Ozone
Temperature	Consistently positive
Stagnation	Consistently positive
Wind Speed	Generally negative
Mixing Height	Weak or variable
Humidity	Weak or variable
Cloud Cover	Generally negative
Precipitation	Weak or variable

algorithms estimating BVOC emissions may be calculated as part of the model simulation instead of an emission inventory. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006, 2012) calculates BVOC emissions at each model time-step using the temperature and radiation values determined from the model. The choice of on-line algorithm or emission inventory to specify BVOC emissions influences modelled ozone concentrations. For example, Curci et al. (2009) noted large differences in summertime ozone concentrations over Europe when using a gridded emission inventory or an on-line algorithm.

Emissions of the NMVOCs specified by an emission inventory are mapped to the chemical mechanism species used in the model. This mapping is not standardised throughout the modelling community with the same NMVOC emissions possibly being allocated to different chemical species even if using the same chemical mechanism (Carter, 2015).

The influence of the speciation of NMVOC emissions on modelled ozone production is determined as part of this work. Moreover, the effect of using the same speciations of NMVOC emissions with different chemical mechanisms is also explored. Section 1.5 outlines the research questions and the results are presented in Sect. ??.

1.4 Effects of Meteorology on Ozone Production

Meteorological conditions influence the production of ozone with clear and calm summer days typically having high ozone levels (Dueñas et al., 2002). Comrie (1997) noted a complex relationship between meteorology and ozone due to competing positive and negative effects on ozone production. Table 1.2, taken from Jacob and Winner (2009), details the effects of specific meteorological variables on ozone production.

Climate change is predicted to influence many meteorological variables and increase the number of heatwaves. Thus understanding the influence of meteorology on ozone production is particularly important for future predictions of air quality and tackling ozone pollution in a changing climate.

Humidity

Humidity influences ozone production both positively and negatively. When $O(^1D)$, originating from ozone photolysis (R2) reacts with water vapour (R4), the production of OH radicals leads to ozone loss. However, the initiation of VOC degradation through reaction with OH can lead to ozone production (Sect. 1.2). These competing effects of water vapour on ozone production lead to a weak correlation of ozone production with water vapour (Jacob and Winner, 2009).

Wind Speed

High wind speeds transport ozone precursors away from their sources leading to a generally negative effect on ozone pollution over a region. Model projections of Doherty et al. (2013) showed that while climate change is expected to change large-scale atmospheric transport there is little influence on the spatial patterns of mean concentrations of ozone.

Stagnation

During periods of low wind speeds, emissions of ozone precursors remain close to their sources. These stagnant conditions over polluted urban areas are highly correlated with increased ozone production over urban areas (Jacob and Winner, 2009). Heatwaves result from stagnant conditions along with high temperatures enhancing the ozone pollution over a region.

Mixing Height

The effects of the mixing height of the planetary boundary layer (PBL) with the free troposphere depend on the region. For example, Dawson et al. (2007) found that over the Eastern U.S., regions with low ozone are positively correlated with mixing height whereas regions with high ozone levels are negatively affected.

This spatial effect of mixing height on ozone production depends on the difference between ozone levels within the PBL and the free troposphere (Jacob and Winner, 2009).

Mixing between the PBL and free troposphere into regions with levels of surface ozone lower than the free troposphere is an additional source of ozone. Conversely, mixing of the elevated levels of ozone from polluted areas into the free troposphere reduces the surface ozone burden.

Temperature

Temperature is positively correlated with ozone in many areas. Otero et al. (2016) showed that temperature was the main driver of summertime ozone values over many areas of central Europe while Camalier et al. (2007) correlated ozone with temperature over the Eastern US. Sillman and Samson (1995) illustrated that only ozone pollution produced from the chemistry described in Sect. 1.2 is correlated with temperature rather than background ozone, the ozone levels without the influence of anthropogenic emissions.

Temperature directly influences ozone levels in two ways: increasing the emissions of VOCs from vegetation and speeding up the rates of chemical reactions. The review of Pusede et al. (2015) showed that the temperature dependence of radical production, organic reactivity, the shorter lifetime of RO_2NO_2 and the formation of alkyl nitrates (R18) affects ozone production.

There is a lack of detailed process studies separating the direct effects of temperature on ozone over differing NO_x conditions despite observational and regional modelling studies correlating temperature with ozone production. The final part of this work addresses whether the increase in BVOC emissions or faster reaction rates with temperature is more important for ozone production. The research questions for this study are detailed in Sect. 1.5 and results are presented in Sect. ??.

1.5 Research Questions

The detailed chemistry producing ozone cannot be fully represented in models for reasons of computational efficiency. Thus models select a particular representation of atmospheric chemistry raising the overarching research questions for this thesis:

- How do representations of detailed atmospheric chemistry influence simulated ozone production?
- What are the most important chemical processes when simulating ozone production?

This question is addressed through detailed modelling studies highlighting the chemical processes having the largest impact on simulated ozone production under three different conditions.

Firstly, different simplified versions of the ozone production chemistry are available to the modelling community with comparison studies showing that ozone concentrations vary between chemical mechanisms. These chemical mechanism comparison studies do not determine the root causes of the differences between chemical mechanism, leading to the research questions:

- How do the simplification techniques used by different chemical mechanisms affect ozone production?
- Which processes are responsible for differences in ozone production with different chemical mechanisms?

Secondly, NMVOC emissions are a known source of uncertainty in modelling experiments. The choice of emission inventory influences the speciation of individual NMVOC emissions possibly influencing ozone production. By comparing the ozone produced using different emission inventories, the following research questions are addressed:

- What is the influence on modelled ozone production when using different speciations of emitted NMVOCs?
- Does this influence change when using different chemical mechanisms?

Finally, meteorology influences ozone production with temperature having the strongest positive correlation with ozone. Temperature directly influences ozone production through increasing biogenic emissions and speeding up the reaction rates of chemical reactions.

- Are temperature-dependent emissions or chemical processes more important for ozone production with increasing temperature?
- How is the ozone-temperature relationship treated by different chemical mechanisms?

Detailed processed studies are performed using a box model to address these research questions, details of the experiments are presented in Chap. ???. The results of the experiments are found in Chap. ??, the general discussion and conclusions of the thesis are in Chap. ??.

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description of sources and related data (activity levels, emission factors, maps used to allocate emissions on grid) ; resulting emission inventories (by region and on grid) including a first validation ; uncertainties and limitations ; policy applications ; and conclusions summarising the achievements of this project.

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