Thesis Title

Dissertation zur Erlangung des akademischen Grades

des Doktors der Naturwissenschaftern

am Fachbereich Geowissenschaften

an der Freien Universität Berlin

Vorgelegt von

Jane Coates

im XXX 201X

Abstract

Dedication

Acknowledgements

Table of Contents

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

Ozone (O_3) is an atmospheric constituent gas found in the stratosphere and troposphere, however its atmospheric effects are very different in these distinct regions. About 90% of the atmospheric ozone is present in the stratosphere, with a peak mixing ratio of about 12 ppm (Seinfeld and Pandis, 2006). Stratospheric ozone absorbs the sun's ultraviolet radiation in the wavelength region 280 - 315 nm, this is extremely important as excess UV radiation can cause skin cancer, cataracts and a suppressed immune system in humans and can also damage plant, single-cell organisms and aquatic ecosystems (World Meteorological Organisation, 2011).

In contrast, tropospheric ozone that is found close to the surface is both a pollutant and a greenhouse gas. Increased levels of tropospheric ozone are harmful to humans, plants and other living systems, as high ozone exposure can lead to pulmonary problems in humans and can decrease both crop yields and forest growth (World Meteorological Organisation, 2011). The key component in Los Angeles photochemical smog was determined to be tropospheric ozone (Haagen-Smit and Fox, 1956).

Globally, tropospheric ozone is formed mainly via chemical production and downward transport from the stratosphere into the troposphere, called the Stratosphere-Troposphere Exchange (STE) may also play a role. The STE is driven by the Brewer-Dobson circulation (Brewer, 1949; Dobson, 1956). This is a relatively slow circulation (over a timescale of weeks to months) and is due to planetary wave

disturbances in the troposphere (Haynes et al., 1991). The circulation causes air to move downward from the stratosphere into the troposphere at the mid at high latitudes and is balanced by upward exchange at the tropics. The STE also has a seasonal variability where the maximum transport occurs during spring (Appenzeller et al., 1996), due to the increase in altitude of the tropopause - the boundary level between the troposphere and the stratosphere - which moves stratospheric air into the troposphere. Hence, there is a maximum O_3 transport into the troposphere during late winter and early spring. The amount of tropospheric ozone accounted for by the STE is dependent on the

A spring-time peak in O_3 concentration is common in many areas, especially in the midlatitude Northern Hemisphere, and it was originally thought that the STE was mainly responsible. However, it is only very rarely that O_3 originating via STE can influence tropospheric O_3 levels (Lelieveld and Dentener, 2000). It was later realised that this spring maximum is due to the photochemical reactions occuring in the Northern Hemisphere spring after the buildup of reservoir species over winter (Penkett and Brice, 1986) that are then oxidised photochemically, the increase in these reactions is due to the increase in temperature, moisture and sunlight. Hence, photochemical reactions are the major source of surface tropospheric ozone (Lelieveld and Dentener, 2000) and since O_3 is produced in this way it is termed a secondary pollutant.

1.0.1 Meteorological Impacts on Tropospheric Ozone

Tropospheric O_3 is not only impacted by emission levels, it is also affected by meteorological variables such as temperature, number of hours of sunshine and wind as these impact transport, wet deposition rates and also chemical reaction rates (Hess and Mahowald, 2009). Meteorology influences both regional and global O_3 (Hess and Mahowald, 2009), climate patterns such as El Niño are also known to impact O_3 levels in certain areas (Sudo and Takashi, 2001). El Niño can cause an increase in O_3 in the 70°E to 170°E region is due to downward motion, suppressed

convection and less water vapour, whereas the O_3 decrease in the 170°E to 70°W region results from the opposite conditions.

The effect of meteorology is an aspect of atmospheric chemical transport modelling that needs to be taken into account. However it is also frequently the major source of uncertainty for the calculated O_3 concentrations. Wind speeds in particular may lead to under- or over-predicated values of O_3 concentrations (Sillman, 1999).

Ozone Concentration Predictions based on Meteorological Variables

Although the emphasis in this work is on photochemical model derived O_3 prediction measures, there are ways of predicting O_3 concentrations based on meteorological variables. There are statistical approaches to forecast the O_3 concentration, the most common approach being multivariate linear regresson (Comrie, 1997). Neural networks can also be used to predict O_3 concentrations, although as described in (Comrie, 1997) they give is no significant improvement from multivariate linear regression techniques.

1.0.2 Air Quality Standards

In general, there is great effort to reduce anthropogenic emissions that impact air quality and human health. For example, the EPA in the US and European Union all have regulations related to air quality with a set exceedance limit for O_3 concentrations. Many cities in the US, especially in the northeast and southern California, have reduced the emissions of O_3 precursors - mainly volatile organic compounds (VOC) emissions - due to repeated exceedances (Fiore et al., 1998). These VOC emission reductions have proven successful as the amount of O_3 in these metropolitan areas has been decreased despite nitrogen oxide levels, which also impact O_3 levels, being almost constant (Fiore et al., 1998; Lin et al., 2001).

Modelling of O_3 has greatly influenced the understanding of complexity of atmospheric chemistry, for example the non-linear relationship of O_3 production
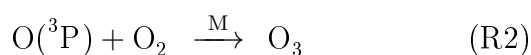
on the VOC and nitrogen oxides concentrations. This in turn has led to a better understanding on how to reduce the O_3 levels for better air quality. The need for more realistic and effective air quality standards in turn also drives the model development and deeper understanding of atmospheric chemistry. Providing detailed information of which VOCs can produce the most O_3 is of greater benefit for regulation purposes rather than lumping all VOCs under one common regulation. Moreover, this can give indication on possibly replacement substances in order to improve air quality.

An example is the modelling study in (Capps et al., 2010), where an investigation into the effect of substituting less-reactive for more-reactive compounds. One consideration of the study was to establish whether there are also increased ozone concentrations due to atmospheric transport. It is shown that the more-reactive compounds do produce more ozone - in terms of mass - when compared to less-reactive compounds. Performing the same study using incremental reactivity scales (discussed in more detail in Section 1.2.1) gives similar conclusions. Thus an investigation into the different ozone production pathways of VOCs can aid in substitution policies.

1.1   Tropospheric Chemistry

1.1.1   Ozone Chemistry

Troposperic ozone is principally formed by the photolysis of nitrogen dioxide (NO_2), which produces nitrogen oxide (NO) and a ground state oxygen atom ($O(^3P)$), this then reacts with molecular oxygen (O_2) to form O_3. Ozone reacts rapidly with NO to return NO_2 and O_2, this is represented by the following reaction cycle.

$$NO_2 + h\upsilon \quad \longrightarrow \quad NO + O(^3P) \quad (R1)$$
$$O(^3P) + O_2 \quad \xrightarrow{M} \quad O_3 \quad\quad\quad\quad (R2)$$
$$NO + O_3 \quad \longrightarrow \quad NO_2 + O_2 \quad\quad (R3)$$

These reactions do not produce net O_3, due to a photoequilibrium between NO, NO_2 and O_3 (Atkinson, 2000). Adding VOCs of both biogenic and anthropogenic origin, such as methane (CH_4), and other gas-phase compounds, such as carbon monoxide (CO) - to the mix, results in net O_3 production. The oxidation mechanism of CO, taking into account reactions that give maximum O_3 yield, is

$$
\begin{array}{lll}
CO + OH & \xrightarrow{O_2} CO_2 + HO_2 & (R4) \\
HO_2 + NO & \longrightarrow NO_2 + OH & (R5) \\
NO_2 + h\upsilon & \longrightarrow NO + O(^3P) & (R1) \\
\hline
\text{Net: } CO + 2\,O_2 + h\upsilon & \longrightarrow CO_2 + O_3 & (R6)
\end{array}
$$
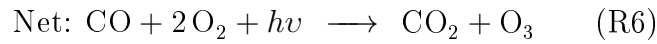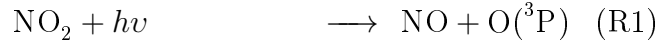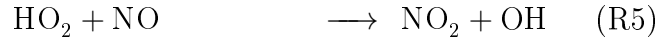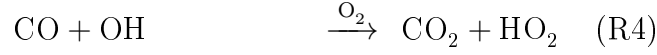
whilst the oxidation mechanism of CH_4 with maximum O_3 yield is

$$
\begin{array}{lll}
CH_4 + OH & \xrightarrow{O_2} CH_3O_2 + H_2O & (R7) \\
CH_3O_2 + NO & \xrightarrow{O_2} HCHO + HO_2 + NO_2 & (R8) \\
HCHO + h\upsilon & \xrightarrow{2\,O_2} 2\,HO_2 + CO & (R9) \\
3(HO_2 + NO & \longrightarrow NO_2 + OH) & (R5) \\
4(NO_2 + h\upsilon & \xrightarrow{O_2} NO + O(^3P)) & (R1) \\
\hline
\text{Net: } CH_4 + 8\,O_2 & \longrightarrow CO + H_2O + 2\,OH + 4\,O_3 & (R10)
\end{array}
$$
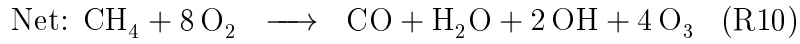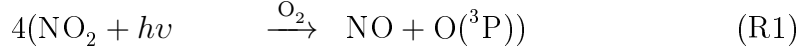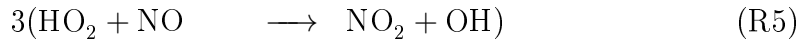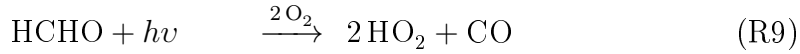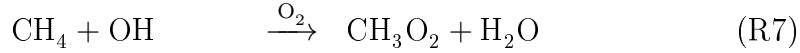
taking into account the net result for the CO oxidation mechanism (R6), the net yield for CH_4 is

$$
CH_4 + 10\,O_2 \longrightarrow CO_2 + H_2O + 2\,OH + 5\,O_3. \quad (R11)
$$
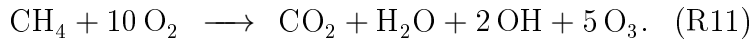
Both mechanisms are taken from (Seinfeld and Pandis, 2006).

To summarise, oxidation of VOCs results in the formation of peroxy radicals which then convert NO to NO_2 and both (R1) and (R2) proceed. These oxidation mechanisms are linked in the sense that the CH_4 mechanism gives a maximum O_3 yield, once the mechanism of CO is also included.

Since these mechanisms produce the maximum O_3 yield, the reactions that cause O_3 destruction or inhibit its production are not included. It should also be noted that some reactions can follow more than one pathway that is indicated above and that products from these pathways can be removed from the atmosphere via deposition

processes. Thus, the maximum O_3 yield outlined in reactions (R6) and (R11) is not reached in the atmosphere.

Another aspect of O_3 production is its dependence on the atmospheric concentrations of both VOCs and nitrogen oxides ($NO_x = NO + NO_2$) and this also influences the reaction pathways. Moreover, the precursors of ozone are linked to anthropogenic activity, hence a so-called weekend effect (i.e. there is a reduction on O_3 concentration over the weekend) is also evident (see for example, (Koo et al., 2012)). Further discussion on the balance of VOC and NO_x concentration to O_3 production shall be given in Section 1.1.6.

1.1.2   Chemical Families

A concept that is extremely useful in atmospheric chemistry is that of a chemical family. This is used to describe two or more compounds that form a rapid cycle of production and destruction. An example is the cycling between NO and NO_2 in (R1) and (R3), hence NO and NO_2 form the nitrogen oxides chemical family NO_x.

A chemical family also has its own chemical lifetime, where the chemical lifetime is the average time that a chemical species takes to be removed - by reaction or deposition processes - from the atmosphere. An equilibrium is reached for the compounds of the chemical family, called a pseudo-steady state, which is then re-balanced when a compound from the family reacts with a species not present in the chemical family.

Examples of important chemical families are given below in Table 1.1 and taken from (Seinfeld and Pandis, 2006).
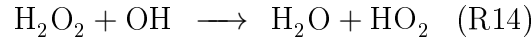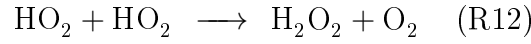
1.1.3   Reservoir Molecules

Compounds that react with radicals or NO_x are called reservoir molecules. These will slow down O_3 production and if they have a sufficiently long enough lifetime, can also transport and then release radicals or NO_x to promote O_3 formation in a separate location. For example, hydrogen peroxide (H_2O_2) is a reservoir molecule

Symbol	Family Name	Components
NO_x	Nitrogen oxides	$NO + NO_2$
O_x	Odd oxygen	$O_3 + O + O(^1D) + NO_2 + NO_3 + N_2O_5$
NO_y	Oxidised nitrogen	$NO + NO_2 + HNO_3 + N_2O_5 + ClONO_2$ $+ NO_3 + HOONO_2 + BrONO_2$
HO_x	Hydrogen radicals	$OH + HO_2$
PAN	Peroxyacyl nitrates	Compounds of general formula $RC(O)OONO_2$

Table 1.1: Chemical Families commonly used in Tropospheric Chemistry (Seinfeld and Pandis, 2006)

for HO_x as shown in the below sequence of reactions (Seinfeld and Pandis, 2006).

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad \text{(R12)}$$

$$H_2O_2 + hv \longrightarrow OH + OH \quad \text{(R13)}$$

$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \quad \text{(R14)}$$

Nitrous acid (HONO) is a reservoir molecule for NO_x and HO_x, formed by a heterogeneous reaction of NO_2 and H_2O. HONO can be formed during night-time and then photodissociates at sunrise to regenerate OH and NO (Seinfeld and Pandis, 2006).

$$HONO + hv \longrightarrow OH + NO \quad \text{(R15)}$$
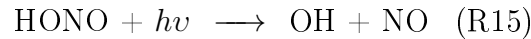
An important class of reservoir molecules are ther peroxyacyl nitrates (PANs) of general formula $RC(O)OONO_2$. The first compound in this class, $CH_3C(O)OONO_2$, is also called PAN and can be formed by reactions of peroxyacetyl radicals with NO_2, PAN then thermally dissociates to return the reactants (Kleinman, 2005).

$$CH_3C(O)O_2 + NO_2 + M \rightleftharpoons CH_3C(O)OONO_2 + M \quad \text{(R16)}$$
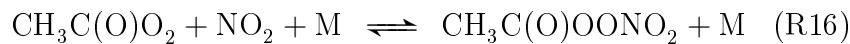
PAN's lifetime is dependent on meteorology due to a strong temperature dependence (Moxim et al., 1996). This can lead to situations where NO_x is transported to different regions and then released by dissociation. PAN is thought to have a regional rather than a global influence on the NO_x budget (Moxim et al., 1996).

1.1.4 Volatile Organic Compounds

Table 1.2 lists Non-Methane Volatile Organic Compounds (NMVOCs) that are emitted from US cities (Baker et al., 2008). The mean is calculated from (Baker et al., 2008) using the total of 31 data points from 28 cities in the United States. Of these NMVOCs there is only one which has a primarily biogenic source and this is isoprene (2-methyl 1,3-butadiene). Although not evident from Table 1.2, biogenic VOCs are globally the most abundant VOCs (Goldstein and Galbally, 2007). Since the data in Table 1.2 are mainly taken from urban cities, the impact of anthropogenic emissions outweigh those of the biogenic sources (Baker et al., 2008) - although isoprene has some anthropogenic sources (see (Borbon et al., 2003)).

Compound	Mean Mixing Ratio (pptv)
Alkanes	
Ethane	2498
Propane	1449
Butane (n-butane)	623
2-methyl propane (i-butane)	386
Pentane (n-pentane)	349
2-methyl butane (i-pentane)	771
Hexane (n-hexane)	137
Heptane (n-heptane)	81
Octane (n-octane)	41
Alkenes and Alkyne	
Ethene	789
Propene	205
1-butene	64
2-methyl propene (i-butene)	200
2-methyl 1,3-butadiene (isoprene)	760
Ethyne	730
Aromatics	
Benzene	175
Methyl benzene (Toluene)	572
1,3-dimethyl benzene (m-xylene)	115
1,4-dimethyl benzene (p-xylene)	61
1,2-dimethyl benzene (o-xylene)	105
Ethyl benzene	91

Table 1.2: NMVOCs emitted from US cities (Baker et al., 2008)

The sources of the alkanes listed below are natural gases, liquified petroleum

gas (LPG), combustion and industry, for the case of octane, vehicle exhaust is also a source. Alkene sources are mainly due to industrial activities and vehicular emissions. Aromatic compounds are mainly due to vehicle emissions, while benzene and toluene are also emitted due to industrial activity and combustion is also a further source for benzene (Arsene et al., 2009).

Alkanes are saturated hydrocarbons, meaning that all bonds between carbon and hydrogen atoms are single bonds, resulting in slow reacting species. The dominant tropospheric process for alkanes is reaction with the hydroxyl (OH) radical, but they also react with the nitrate (NO_3) radical and chlorine atoms. The presence of a double bond in alkenes and a triple bond in alkynes leads to increased reactivity. In the troposphere both alkenes and alkynes react with the OH radical, the NO_3 radical and also with O_3. Aromatic compounds react with the OH and NO_3 radicals. Hence it can be noted that the key reactive species in the troposphere is the OH radical as it reacts with practically all organic compounds, the exceptions being chlorofluorocarbons (CFCs) and halons without hydrogen atoms.

Reaction with the OH radical is predominant during the day, since it is formed mainly by photolysis, during the night there is an increase in the NO_3 radical concentration and so reaction rates with this radical are increased. The reason for this increased night-time concentration of the NO_3 radical is that during the day the reaction that forms NO_3

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (R17)$$

is balanced by the quick photolysis of NO_3

$$NO_3 + h\upsilon \longrightarrow NO + O_2 \qquad (R18)$$
$$NO_3 + h\upsilon \longrightarrow NO_2 + O(^3P). \quad (R19)$$

The main photolysis pathway is via reaction (R19) which occurs about 90% of the time. However, during night-time photolysis does not occur and hence there is a buildup of NO_3 radicals (Atkinson, 1990, 2000).

1.1.5 VOC Chemistry

Figure 1.1 represents a general and simplified reaction scheme for VOCs in the troposphere. Although there are many different VOC classes involved in tropospheric chemistry, there are many similarities between their reaction schemes. This shall be summarised below however for more a more detailed description of tropospheric chemistry, (Atkinson, 2000) should be consulted.
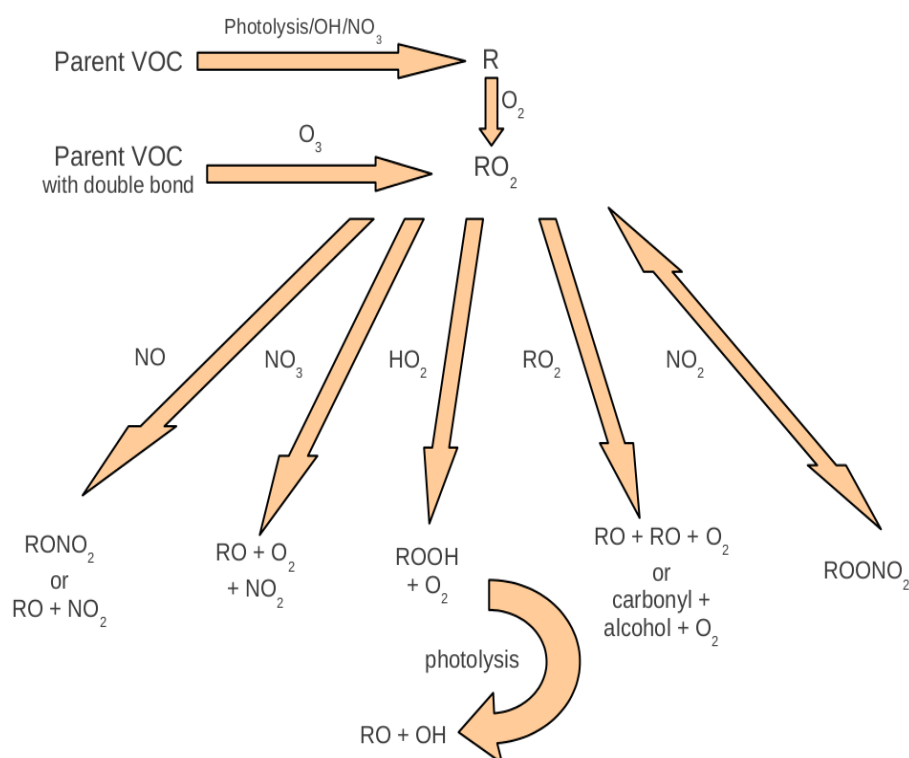
Figure 1.1: VOC reaction pathway

As noted earlier, the most common initiation reaction of a VOC is with the OH radical, and this forms an alkyl or substituted alkyl radical (R) depending on the parent VOC. The addition reaction with O_2 then leads to the formation of alkyl peroxy radicals (RO_2). During the night-time, reaction with the NO_3 radical is of importance and for VOCs containing a double bond, reaction with O_3 also occurs. Photolysis is an important degradation initiator for carbonyl species, this is particularly important throughout the whole degradation mechanism of the VOC as carbonyl species, such as formaldehyde, are common reaction products. These initial reaction pathways all lead to the formation of RO_2 radicals, as shown below.

$$\text{VOC} + \text{OH}/\text{NO}_3/\text{O}_3/h\upsilon \longrightarrow \text{R} \qquad (\text{R20})$$

$$\text{R} + \text{O}_2 \qquad\qquad\qquad \longrightarrow \text{RO}_2 \quad (\text{R21})$$
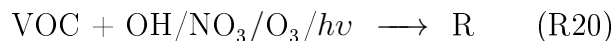
RO_2 radicals can subsequently react with NO, NO_2, hydroperoxy (HO_2) radicals, NO_3 radicals - mainly during night-time - and also with other alkyl peroxy radicals. The competition between these reactions determines the amount of net ozone production or loss from the parent VOC.

$$\text{RO}_2 + \text{NO} + \text{M} \qquad\qquad \longrightarrow \text{RONO}_2 + \text{M} \qquad\qquad\qquad (\text{R22})$$

$$\text{RO}_2 + \text{NO} \qquad\qquad\qquad \longrightarrow \text{RO} + \text{NO}_2 \qquad\qquad\qquad (\text{R23})$$

$$\text{RO}_2 + \text{NO}_2 + \text{M} \qquad\qquad \rightleftharpoons \text{ROONO}_2 + \text{M} \qquad\qquad\qquad (\text{R24})$$

$$\text{RO}_2 + \text{HO}_2 \qquad\qquad\qquad \longrightarrow \text{ROOH} + \text{O}_2 \qquad\qquad\qquad (\text{R25})$$

$$\text{RO}_2 + \text{NO}_3 \qquad\qquad\qquad \longrightarrow \text{RO} + \text{NO}_2 + \text{O}_2 \qquad\qquad (\text{R26})$$

$$\text{RCH(OO)R}' + \text{RCH(OO)R}' \longrightarrow \text{RCH(O)R}' + \text{RCH(O)R}' + \text{O}_2 \quad (\text{R27})$$

$$\text{RCH(OO)R}' + \text{RCH(OO)R}' \longrightarrow \text{RCH(OH)R}' + \text{RC(O)R}' + \text{O}_2 \quad (\text{R28})$$

All pathways in Figure 1.1 that lead to NO_2 formation can result in O_3 formation due to (R1) and (R2). Reaction with the HO_2 radical results in the formation of hydroperoxides (ROOH), which then photolyse to an alkoxy (RO) radical and the OH radical, this OH radical is then available to react with other VOCs. The carbonyl and alcohol products resulting from reaction with other RO_2 radicals will follow a similar sequence of reactions and hence can also produce further O_3. Reaction with NO_2 leads to the formation of alkyl peroxynitrates ($ROONO_2$), however this reaction product can be thermally unstable and may decompose quickly to the reactants, as mentioned in Section 1.1.3.

The RO radical that results from many of the RO_2 pathways undergoes further reactions, either by decomposition, isomerisation or reaction with O_2. The products that result from the reaction pathways depend on the parent VOC and this also determines the number of NO-to-NO_2 conversions, eventually leading to O_3 formation.

All VOCs and their degradation products will ultimately result in carbon dioxide (CO_2) and water vapour. The path that each VOC takes to reach its final products

is dependent on the type of VOC, the radical concentration, the NO_x concentration and other factors such as time of day and year. The detailed atmospheric chemistry of some simple VOCs is well-understood (for example, methane) however for more complex molecules, especially aromatic VOCs, there are a great number of uncertainties. These uncertainties can be related to kinetic data, photolysis rates, reaction branching ratios and in most cases the reaction products. Any uncertainties in reaction pathways and products of VOCs also leads to uncertainties in the ozone forming potential of the respective VOC (Atkinson, 2000).

1.1.6   VOC and NO_x Chemistry

As mentioned above, O_3 chemistry is influenced by both VOC and NO_x concentrations.   Figure 1.2 depicts the non-linear relationship between O_3 concentration when considered as a function of VOC concentration (in ppmC, i.e. parts per million mass of a carbon unit of the VOC, $CH_{2.5}$) and NO_x concentration (in ppm, i.e. parts per million mass).
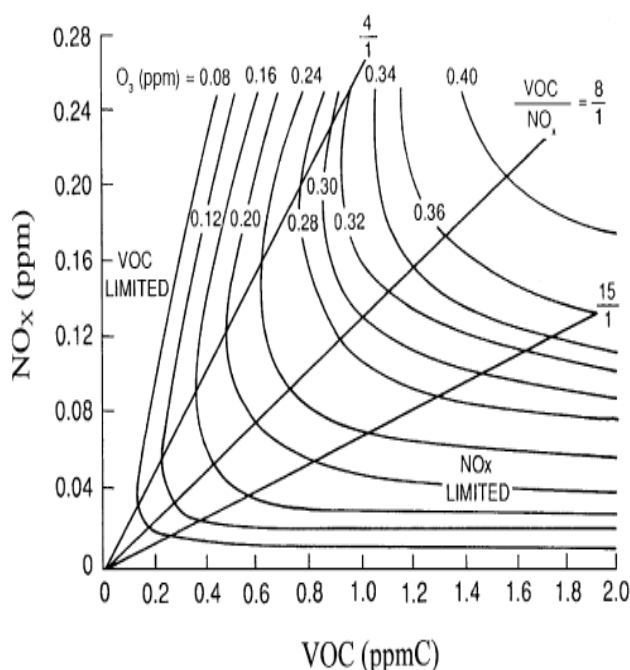

Figure 1.2: Ozone isopleth plots for various initial concentrations of NO_x and a specified VOC mixture. Taken from (Jenkin and Clemitshaw, 2000).
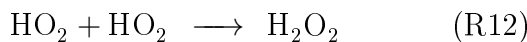
This   relationship   can   be   divided   into   distinct   regimes: *NO_x-sensitive,*

VOC-sensitive and *VOC-and-NO$_x$-sensitive*. The NO$_x$-sensitive regime is the right-most part, the VOC-and-NO$_x$-senstive regime is the middle section and the VOC-sensitive regime is the left-most part of Figure 1.2 and these correspond to high, middle and low VOC:NO$_x$ ratios, respectively. These different regimes arise from how the atmosphere removes NO$_x$ and radicals resulting from VOCs.

In the NO$_x$-sensitive regime, the concentration of NO$_x$ is low compared to that of radicals. Hence, peroxy radicals are removed by reaction with the OH radical such as

$$HO_2 + OH \longrightarrow H_2O + O_2 \quad (R29)$$

or by peroxy radical addition reactions.

$$HO_2 + HO_2 \longrightarrow H_2O_2 \qquad (R12)$$
$$RO_2 + HO_2 \longrightarrow ROOH + O_2 \quad (R25)$$

This results in the NO concentration controlling the number of NO-to-NO$_2$ conversions, rather than the concentration of peroxy radicals produced during VOC oxidation. An increase in NO conversion would thus promote O$_3$ production due to an increase in (R1) and (R2) reactions. Increasing VOC concentrations would not increase O$_3$ production as this only speeds up the formation of peroxy radicals and has no direct effect on the NO$_x$ concentration.

The VOC-sensitive regime corresponds to high NO$_x$ concentrations, hence radicals will tend to react with either NO or NO$_2$. Increasing NO$_x$ concentrations will not increase not increase O$_3$ production as the NO$_x$ will react with the peroxy radicals resulting from VOC degradation. However, this increase in NO$_x$ increases the formation of nitric acid (HNO$_3$) by reaction with the OH radical (Kleinman, 1991, 1994; Kirchner et al., 2001).

$$OH + NO_2 \longrightarrow HNO_3 \quad (R30)$$
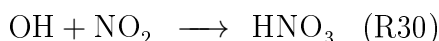
The competition of VOCs and NO$_x$ for reaction with the OH radical is at the heart of O$_3$ production or destruction in the VOC-sensitive regime. Reaction of VOCs with the OH radical will produce more peroxy radicals, increasing O$_3$ production whilst

reaction of NO_x increases HNO_3 by (R30) which reduces O_3 production (Kleinman, 1991, 1994; Kirchner et al., 2001).

The VOC-and-NO_x-sensitive regime is characterised by O_3 production being sensitive to both VOC and NO_x concentrations. The turning point from a VOC-sensitive to a VOC-and-NO_x-sensitive regime is when the maximum O_3 production for a particular VOC concentration has been reached. The shift into a NO_x-sensitive occurs when increases in VOC concentrations result in very little O_3 production (Kirchner et al., 2001). The non-linear relationship can be thought of as a titration process between the amount of radicals and the NO_x present in the atmosphere.

This non-linear nature of the atmosphere must be taken into account when policymakers consider control strategies for O_3 concentrations. The difficulty is exacerbated by the fact that regions can alternate between these regimes depending on the season, time of day etc.

Moreover, an air parcel emitted in an urban area may also evolve as outlined in Figure 1.3, as it moves downwind. Once the air parcel has been emitted, it would
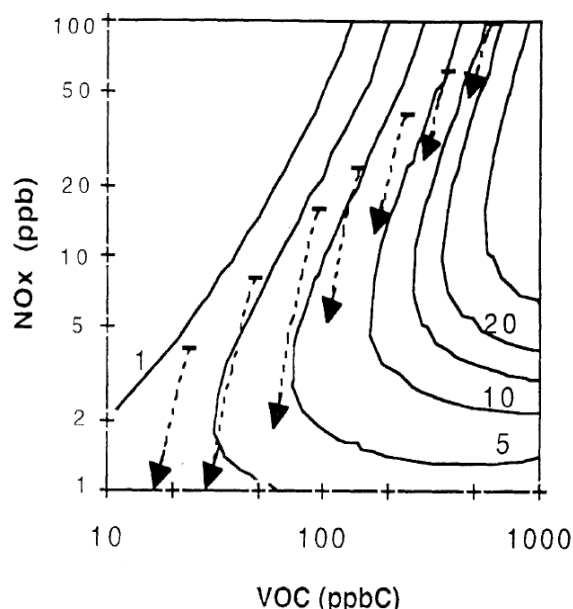

Figure 1.3: Air parcel evolution overlayed with ozone isopleth plots for various initial concentrations of NO_x and VOCs. Taken from (Sillman, 1999).

typically fall into the VOC-sensitive regime but as the parcel ages it would move into

the NO_x-sensitive regime. Reducing VOC and NO_x would reduce tropospheric O_3, whilst reducing VOC levels would only be effective during VOC-sensitive regimes and reducing NO_x levels is only effective in NO_x-sensitive regimes and can even increase O_3 concentrations (Sillman, 1999). This is due to the radical or NO_x removal pathways that may or may not promote O_3 production as discussed above.

Given the importance of determining the particular atmospheric regime at a specific time, a number of indicators that can be calculated from observational data have been determined. For example, in (Kirchner et al., 2001), the parameter $\Theta = \tau_{OH}^{VOC}/\tau_{OH}^{NO_x}$, where τ_{OH}^{VOC} is the lifetime of the OH radical against the loss by reaction with VOC and $\tau_{OH}^{NO_x}$ is the lifetime of the OH radical against the loss by reaction with NO_x. Θ can be used as such an indicator as it represents the relationship between the competing reactions of $VOC + OH$ and $NO_x + OH$.

Another measure of whether the atmosphere is in a VOC- or NO_x-sensitive state is to calculate the chemical rate of O_3 production, $P(O_3)$. (Kleinman, 2005) derived an analytical formula for $P(O_3)$ and showed that the rate of O_3 production as a function of time is determined by L_N/Q, where L_N is the rate of radical removal via reaction with NO_x and Q is the rate of radical production. L_N/Q thus represents the fraction of free radicals that are removed with NO_x and the remaining radicals being removed by addition reactions between free radicals.

1.2   Ozone Production Potential

The difficulty in applying uniform and successful emission control strategies due to the different regimes of the atmosphere has given rise to a more thorough investigation into the ozone production capabilities of different VOCs, also called the Ozone Production Potential (OPP) of the VOC in question. This potential can be calculated via modelling studies and has given rise to reactivity scales classifying the OPP of VOCs or classes of VOCs. The OPP of a VOC is dependent on the meteorological conditions, the reactivity of the VOC and the location of its emission. A wide range of such scales have been developed and are discussed below.

1.2.1 MIR and MOIR Incremental Reactivity Scales

(Carter, 1994) outlines three incremental reactivity scales, the Maximum Incremental Reactivity (MIR), Maximum Ozone Incremental Reactivty (MOIR) and Equal Benefit Incremental Reactivity (EBIR) scales. The incremental reactivity of a VOC is defined as the change in O_3 concentration caused when adding a small amount of the VOC in question to the emissions. Incremental reactivities are typically investigated through modelling studies although they can also be determined by means of airshed studies.

The VOC reactivity, mechanism pathways and the atmospheric regime into which it is emitted all influence the incremental reactivity value of the VOC. Hence, the total NO_x available is extremely important, as this determines the atmospheric regime present. For example, in VOC-sensitive regimes, the VOCs will have larger incremental reactivities than in a NO_x-sensitive regime.

The MIR scale is calculated by adjusting the NO_x levels so that the largest incremental reactivity was achieved for the individual VOC. The MOIR scale differs from the MIR as it is calculated using NO_x levels that give the maximum ozone concentration for the whole VOC mix. Whilst calculating the EBIR scale involves adjusting the NO_x inputs so that the effect on O_3 for a specific percentage change in VOC has the same effect of an equal percentange change in NO_x (Carter, 1994). The MOIR and EBIR scales are also shown in (Carter, 1994) to be practically equivalent when factoring in uncertainties during their calculation.

The MIR and MOIR scales are applicable to different regions due to their differences in NO_x concentrations. The MIR scale is applicable to places that have high transport emissions such as Los Angeles, as this implies an increased amount of NO_x in the atmosphere when compared with the amount of VOCs. In contrast, the MOIR scale is more relevant to areas that have higher VOC (biogenic or anthropogenic) emissions. However, both scales do not include transport or multi-day scenarios during their calculation and this may effect their applicabilty (Capps et al., 2010).

1.2.2 Photochemical Ozone Creation Potential

The Photochemical Ozone Creation Potential (POCP) was introduced in (Derwent et al., 1996) and was used to calculate ozone production under the conditions applicable to northwestern Europe. This is in contrast to the MIR and MOIR which are both applicable to the US, due to the NO_x levels used for their calculations and that in Europe the transport of reactive species and multi-day photochemistry are more important. Hence, the POCP values are calculated over a five day period.

The POCP is calculated by increasing the amount of a VOC in a photochemical trajectory model and calculating the increase in O_3 concentration. This is then expressed as a percentage using the ozone increase due to the same amount in mass of ethene as reference. The increased time period in the model runs to calculate the POCP values showed that almost all VOC increase their ozone formation potential over time. The exceptions to this are the highly reactive VOC as they are completely oxidised during the initial emission phase (Derwent et al., 1996).

The calculation of the POCP was further refined in (Derwent et al., 1998) by using a more detailed chemical mechanism in the atmospheric model than that used in (Derwent et al., 1996) and by also studying the influence of different NO_x concentrations. The Master Chemical Mechanism (MCM) is used as this provides a lot of chemical detail in the reaction mechanisms of the VOCs.

The general trend of the POCP values did not change when using the MCM, however the individual values themselves were affected. The NO_x inputs were also adjusted in order to mirror planned changes in NO_x emission standards and to investigate the robustness of these planned policies if based on POCPs. Once again, the same general trend of the POCP values was noted, although there are some VOCs (e.g. 1,3-butadiene) whose reactivity changed drastically depending on the NO_x conditions (Derwent et al., 1998). This again demonstrates the importance of taking into consideration the different possible regimes in the atmosphere as described in Section 1.1.6.

The use of incremental reactivity scales has been used in regulatory control in

some US cities (Luecken and Mebust, 2008), where the MIR has mainly been used for such purposes. Due to the assumptions made during the generation of the scale itself, such as the NO_x levels, it is not straightforward to extend the use of an incremental reactivity scale to a larger geographical area. Moreover, the incremental reactivity scales are typically calculated using a box-model which does not include such factors as meteorology and may not include effects of transported air masses that, as previously discussed, can all influence the amount of O_3 produced.

A VOC's direct or indirect impact on ozone production cannot be distinguished when using incremental reactivity scales. The direct impact is the incremental effect of both the extra VOC and the resulting oxidation intermediates. Whilst the indirect impact is the effect that these VOC increments have on the availability of radical species which in turn influences the ozone production from other compounds in the base VOC mixture (Butler et al., 2011), as discussed in Section 1.1.6. Another disadvantage is that the reactivity scales do not include detailed chemical information on the oxidation reactions of the VOC and how this is related to the OPP, moreover some scales do not account for the temporal effects of ozone production.

1.2.3   Tagged Ozone Production Potential

This led to a new approach outlined in (Butler et al., 2011) that links the degradation products of VOCs by using a tagging approach, called the Tagged Ozone Production Potential (TOPP). The calculation of the TOPP is taken over multiple days and calculates the direct impact of a particular VOC on its total impact on the O_x family, defined previously in Section 1.1.3. The TOPP was calculated for NMVOCs listed in Table 1.2 and the atmospheric conditions related to Los Angeles and Beijing and gave similar results despite these two cities having different NMVOC profiles.

The TOPP values also indicate two groups of NMVOCs, those that reach a maximum in the first day of the simulation followed by a decrease and those reaching a maximum TOPP after the first day. The first group includes many reactive

NMVOCs such as alkenes and xylenes whilst the second group includes the slower reacting species such as alkanes and benzene. These groups can be determined as the time taken for a VOC to reach its maximum O_3 production potential is dependent on the rate at which VOCs yield smaller peroxy radical oxidation fragments.

(Butler et al., 2011) also compares the TOPP to the MIR, MOIR and POCP showing that the TOPP compares well with all three, although to differing degrees for different classes of NMVOCs in the cases of the MIR and MOIR. An added advantage of the tagging approach used for the TOPP calculations is that the reaction pathways of the VOC in question that contribute to O_3 production can be determined. As in (Butler et al., 2011), these reactions can be compared for different VOCs to determine the reactions that directly effect ozone production.

1.3   Atmospheric Chemical Transport Models

Predictions of future O_3 pollution levels are typically performed using mathematical atmospheric chemical transport models, these can be of different types depending on the study being performed. What is common between models is that they all must include an emission inventory, transport of the species, atmospheric physical and chemical transformation and numerical solutions to the applicable differential equations.

Models are usually defined as either Eulerian or Lagrangian. The former describes the atmosphere in terms of fixed computational cells where species enter in and out of the cell walls and the concentrations of the species are then calculated as a function of time. Whilst the latter simulate changes of selected air parcels during advection through the atmosphere, hence there is no mass exchange between the surroundings and the air parcel (besides the emissions) and the model calculates concentrations at different locations at different times (Seinfeld and Pandis, 2006). Despite the differences that Eulerian and Langrangian models offer when undertaking a modelling study, Eulerian photochemical models constitute the majority of photochemical models (i.e. models dealing with atmospheric chemistry

driven by photolysis as opposed to heterogeneous reactions) (Russell and Dennis, 2000).

Atmospheric models can also have different dimensions, ranging from zero-dimensional (also called a box model) to three-dimensional models. Box models have uniform atmospheric concentrations and are only a function of time, they are mainly used for focusing on the atmospheric chemistry or other detailed processes. Column models (or one-dimensional models) use concentrations that are a function of time and height, thus the grid is made up of many horizontally homogeneous layers. Two-dimensional models assume that concentration is constant in one direction and dependent on the other two directions and time. These models are used to describe global atmospheric chemistry with the assumption that concentration is a function of latitude and altitude but not longitude. Three-dimensional models calculate concentration as a function of all three directions and time. Accuracy, simplicity and use of computing power all increase with the dimension of the model (Seinfeld and Pandis, 2006).

The model inputs may include meteorology, atmospheric concentrations (also used for initial and boundary conditions), emissions, topography and the grid structure (Russell and Dennis, 2000). Some models include online calculations of these inputs at each time step. Boundary conditions are typically the most difficult initial condition to set accurately as this requires knowledge of the investigated species concentrations at the boundary edges (if applicable) of the model grid. The model's dimension and type determine the set of differential equations that will be solved at each time step of the model run. Numerical methods are then used to solve the differential equations with the specified initial and boundary conditions. These methods vary between models and may be Runge-Kutta (Sandu et al., 1997b), Finite Element (Russell and Dennis, 2000) or Rosenbrock methods (Sandu et al., 1997a), to name three.

Setting the initial conditions involves fixing the starting concentrations of the species being studied, these conditions are dependent on the area being studied and

whether it is an urban or rural area, amongst other considerations. The importance of setting the initial conditions depends on the model type, these conditions in Langrangian models are much more important than in Eulerian models, as this is the starting point at which the air parcel and its concentrations will be studied throughout the model run. Boundary conditions are concentration flows of species and are important for both Eulerian and Lagrangian models. Emission inventories of the studied area are typically used, this is also believed to be one of the more uncertain inputs in a modelling study (Russell and Dennis, 2000).

1.4   Chemical Mechanisms

Models use chemical mechanisms to implement the atmospheric chemistry at each time step during a model run. The mechanism includes rate coefficients, reaction pathways with the corresponding branching ratios, photolysis rates and reaction products, amongst other parameters. This part of a model consumes a great deal of the computing resources, hence, when using a three-dimensional model the mechanism will include less chemical detail compared to a study incorporating a box-model. To achieve this, mechanisms used primarily in three-dimensional models will aggregate compounds, include more assumptions about how reactions proceed and how the degradation products are treated when compared to mechanisms used in box-modelling studies.

The Master Chemical Mechanism (MCM) in (Saunders et al., 2003; Jenkin et al., 2003) is a near-explicit mechanism that is used for box modelling studies. Regional and global mechanisms include the Regional Atmospheric Chemistry Mechanism (RACM), the Carbon Bond Mechanism (CB-05 in (Yarwood et al., 2005)), the National Center for Atmospheric Research (NCAR) master mechanism ((Madronich and Calvert, 1989)) and the Statewide Air Pollution Research Center (SAPRC), although many mechanisms include reduced mechanisms that are applicable to different model dimensions. A brief discussion of these mechanisms are included in (Russell and Dennis, 2000) whilst the MCM, RACM and SAPRC mechanisms

are discussed in more detail below.

1.4.1   Self-Generating Mechanisms

The self-generating mechanism is the type of chemical mechanism that reflects the details of the atmospheric chemistry summarised in Section 1.1 the most and is also called an explicit mechanism. This requires thousands of reactions as the degradation of minor products is often more complex than that of the parent VOC. It also represents a compact method of obtaining a detailed mechanism that describes tropospheric chemistry.

(Aumont et al., 2005) outlines a way of including all reaction pathways that does not imply manually writing all the reactions with their respective parameters, as is the case for other mechanisms. This would also include the possibilty of heterogeneous chemistry and aerosol formation being accouted for in the mechanism, these are aspects of atmospheric chemistry that are not treated in great detail in chemical mechanisms used for gas-phase calculations.

The approach in (Aumont et al., 2005) is to write a so-called 'generator' program that analyses the chemical structure of the VOC being studied to determine the reactive sites which then give the reaction pathways. The generator then accesses another file which includes the available reaction parameters and the reaction products. Structure activity relationships (SARs) are used when no reaction parameters are available. A file is then created that contains the final reaction, it includes the reactants, products and rate coefficients amongst other information. This process is then repeated for the products until all the oxidation reactions have been completed.

There are a number of advantages of this type of mechanism over mechanisms that are manually written up reaction by reaction. Firstly, a self-generating mechanism is faster to write since there are less reactions that need to be written due to the use of a generator program. This also implies increased accuracy (less manually written reactions means less typographical errors) and also maintenance is

much easier as far less code needs to be updated. Currently, this type of mechanism has not been used in relation to ozone production potential calculations.

1.4.2   Master Chemical Mechanism

The Master Chemical Mechanism (MCM) v3.2 is a near-explicit mechanism describing the chemical degradation of 107 non-aromatic VOCs in (Saunders et al., 2003) and 18 aromatic VOCs in (Jenkin et al., 2003). In total the MCM v3.2 has 12,691 reactions including 4351 organic compounds and 46 associated inorganic compounds. The MCM includes alkanes, alkenes, dienes, monoterpenes, aromatics, aldehydes and ketones amongst others, the complete list is found online (`http://mcm.leeds.ac.uk/MCM/`). The VOCs were chosen in accordance with the UK National Atmospheric Emissions Inventory and include those that make up about 70% of the mass emissions of unique species achieved.

Each primary VOC and each degradation product, is individually degraded until it is broken down to CO_2, CO or an organic product (or radical) already found in the MCM (Jenkin et al., 1997). The main assumptions made to reduce the number of reactions and compounds in the MCM are given below and are taken from (Jenkin et al., 1997).

1. The number of product channels resulting from reaction with the OH radical is limited by disregarding those pathways of low probability.

2. Many permutation (i.e. self and cross) reactions of organic peroxy radicals are represented by a single parameterised reaction. This is particularly required as inclusion of all peroxy radical reactions would involve about 400,000 reactions.

3. The degradation chemistry is simplified, especially for those "side" products deemed to be minor.

Figure 1.4 shows the reaction pathways represented in the MCM of a primary VOC, these shall be summarised below. First the schemes used for the degradation reactions of non-aromatic VOCs in (Saunders et al., 2003) shall be discussed. As

mentioned above, the main reaction pathway for VOC degradation is by OH radical reaction and hence this is included for the vast majority of VOCs considered. Reaction with O_3 is deemed to only be important for alkenes, dienes, monoterpenes and some unsaturated oxygenated products. Reaction with the NO_3 radical is mainly important during the night-time and for alkenes, dienes, aldehydes and ethers.

For all reactions in the MCM, rate coefficients are taken from literature, where available, if not then they are estimated using methods also described in literature (for example, via SAR and group reactivity (GR) methods). The branching ratios of all reactions are also taken or estimated from literature. The reactions with O_3 and the NO_3 radical are also included if the parent VOC has a rate of removal that is more than 1% of its removal rate with the OH radical and its lifetime with respect to reaction with O_3 (or NO_3, accordingly) is less than 10^7 seconds.
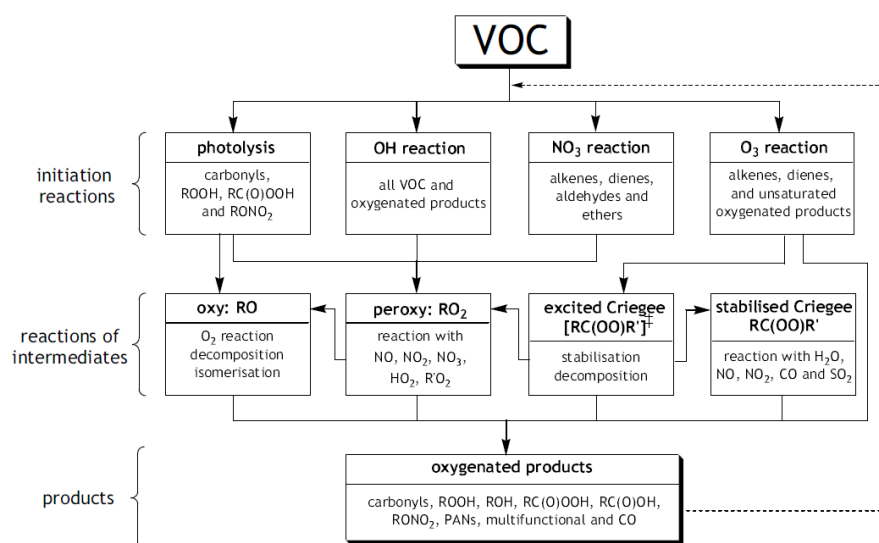
Figure 1.4: Flowchart of the major reactions, reactions of intermediates and products considered in the MCM. Taken from (Saunders et al., 2003)

Photolysis is included for those compounds that absorb at wavelengths less than 290 nm. The photolysis parameters are given for those compounds for which absorption cross-sections and quantum yield data is known and they are also determined as a function of the solar zenith angle.

The degradation products are also treated in detail, these first generation

products are also degraded further as part of the MCM. Those products that have significant tropospheric concentrations are already treated in the MCM. To simplify this part of the mechanism, the products are limited to their reaction pathways with the OH radical. Those products which are deemed as minor are also greatly simplified whilst retaining product lifetimes and maintaining the carbon and nitrogen balance. However, many of these reactions are unbalanced in their O_2 or H_2O output (Jenkin et al., 1997). The kinetic data, where available, is taken from literature however mainly SAR estimations are used due to the lack of data.

In (Jenkin et al., 2003) the treatment of the aromatic VOCs included in the MCM v3.2 is described, this is summarised below. Where possible the treatment follows that of non-aromatic VOCs as outlined above and in (Saunders et al., 2003). However this is not possible for many reactions due to the intricacies of aromatic VOC chemistry and the fact that there is a lack of knowledge of the detailed degradation schemes. Also, similar simplifications are again present to reduce the complexity of the mechanism, this is particularly true for the C_6-C_{11} aromatic compounds.

Reaction with the OH radical is the main reaction pathway of aromatic compounds, the relevant rate coefficients are taken from literature, where available, or estimated depending on the functional group (Jenkin et al., 2003). The reaction pathways are known to proceed by H-atom abstraction or by addition to the aromatic ring. The branching ratios are taken from literature or applied from the analogous molecule for which there is information. H-atom abstraction is typically deemed to be a minor pathway, at this point the simplification applied is that only one pathway during the initial OH radical attack is chosen. Literature provides the data at which point in the aromatic ring the addition reaction occurs and also the following reaction with O_2. Some specific cases are treated separately according to the relevant literature (Jenkin et al., 2003).

The previous conditions outlined above for reaction with O_3 and with the NO_3 radical are also applied to aromatics VOCs. Again, all rate coefficients and branching

ratios are either taken or estimated from the available data and the reaction pathways also proceed as described in literature. Photolysis is only considered for some aromatic VOCs based on the conditions described above. For those cases in which data are not available, the photolysis rates are taken by extension of the data available (Jenkin et al., 2003). Hence, all reactions proceed as described in literature with estimations used for those cases lacking data.

The degradation products are also further degraded in the MCM, these are split into two general groups - those still containing an aromatic ring and those formed after ring-opening. The latter are then treated as non-aromatic compounds as described above in (Saunders et al., 2003). The former group is then further divided into four categories depending on the resulting product and these are then degraded according to (Jenkin et al., 2003).

1.4.3 Statewide Air Pollution Research Center Mechanism

The Statewide Air Pollution Research Center (SAPRC) mechanism, whose current version (SAPRC-07) is described in (Carter, 2010). This mechanism is used by the California Air Resources Board (CARB) for air quality measurements, calculation of the MIR and other regulatory applications. The SAPRC-07 is an update of the previous version (SAPRC-99) which is described in (Carter, 2000).

The SAPRC-07 is modular in structure so that different parts of the mechanism can be used for different applications. The base mechanism includes inorganic compounds, organic products along with their intermediate radicals and the main additional module is the base chlorine mechanism that deals with the reactions of chlorine-containing organic compounds.

Altogether 745 VOCs are represented with 320 VOCs represented as aggregated VOCs, for example, ARO1 and AR02 represent aromatic compounds that have an OH radical rate coefficient less than 2×10^4 ppm^{-1} min^{-1} and greater than 2×10^4 ppm^{-1} min^{-1} respectively. This aggregation is applied only when there is a lack of mechanistic information, species similarity or relatively lower emission importance.

The vast majority of the compounds are unchanged from the SAPRC-99 but some species that were previously explicitly described are now included in model species. The rate coefficients and photolysis rates present in literature are included for the reactions.

Chemical operators are used to minimise the amount of peroxy radical reactions, these operators typically represent the organic products formed when peroxy radicals (except for methyl peroxy) react with other peroxy radicals. For example, the acetyl peroxy radicals are represented by MECO3 and methyl peroxy radicals are included as MEO2. In order to ensure a robust parameterisation of the peroxy radical reactions, different model species are used to represent the peroxy radicals and the oxidation products. Moreover, alternate model species are used for different types of peroxy radicals, for example formation of alkoxy radicals (xPROD) are represented differently than hydroperoxide products (yPROD) (Carter, 2010).

The majority of the VOC degradation included in the SAPRC-07 are generated by using an automated mechanism estimation software that is described in (Carter, 2000). This software outputs the rate coefficients and branching ratios of the VOC degration processes, the output is taken from literature and when not available it is obtained by the values that best fit chamber data. This differs in the approach used in the MCM, since the MCM uses solely theoretical methods when there is a lack of data. Some subclasses of aromatic compounds are not included in the mechanism generation software. Due to the mechanisic uncertainties of aromatic compounds in general, their reaction parameters reflect the available literature or best fit experimental data.

Compounds that have many mechanistic uncertainties or when the mechanism of the compound has little difference with that of another compound (or isomers of the compound) then a representative molecule is used for representation in the SAPRC-07. An example of this is RCHO which represents aldehydes with a carbon number greater than three, the degradation follows that of propionaldehyde. Weighted averages of the individual compounds are used to determine the reaction

parameters of the grouped compounds (Carter, 2010).

1.4.4 Regional Atmospheric Chemistry Mechanism

Another chemical mechanism is the Regional Atmospheric Chemistry Mechanism
(RACM), described in (Stockwell et al., 1997) and described below. This is a
complete revision of the Regional Acid Deposition (RADM2) mechanism and is
applicable to regional modelling and capable of simulating the gas phase tropospheric
chemistry over remote and heavily polluted urban regions, including at the Earth's
surface and in the upper troposphere. The RACM includes 17 inorganic, four
inorganic intermediates and 32 organic species, four of which are of biogenic origin
that altogether entail about 237 reactions. The inorganic reactions are practically
fully described with the relevant rate coefficients, quantum yields and photolysis
coefficients taken from literature.

In order to reduce computational resources for the mechanistic part of a regional
model, the organic compounds are grouped into 16 anthropogenic and three biogenic
model species. This grouping is based upon emission rates, functional group
similarity and OH radical reactivity. Obtaining the final model species was done in
two steps, first the hundreds of anthropogenic VOCs were grouped into 32 emission
categories and then these were aggregated into the final 16 model species. Another
aspect of reducing computational requirements was achieved by reducing the number
of reaction pathways by only taking one reaction pathway from those available and
also not treating all the organic intermediates explicitly.

The reaction rate coefficients of the model species are obtained by a weighted
mean of all the rate coefficients of the organic species aggregated into the model
species, this is done to account for the difference in reactivities between the model
and chemical species. The individual rate coefficients are taken from literature or
estimated by means of a SAR. Some organic compounds (for example, methane
and ethene) are explicitly treated, if not then the compounds are represented by
a model species. For example, excluding ethene, anthropogenic alkenes with their

double bond at the end of the molecule are included as the model species as OLT whilst anthropogenic alkenes with their double bond not at the end of the molecule are represented by OLI (Stockwell et al., 1997).

The different functional groups in a model species give rise to different reaction products, hence other model species are introduced with the relevant product yield fractions, as illustrated in the below reactions.

$$\text{OLT} + \text{OH} \longrightarrow \text{OLTP} \quad \text{(R31)}$$
$$\text{OLI} + \text{OH} \longrightarrow \text{OLIP} \quad \text{(R32)}$$
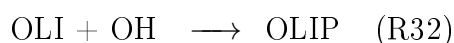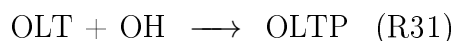
These product species are calculated as a weighted mean of the product yields of all the chemical species represented by the model species, where the individual yields are taken from literature.

The branching ratios of certain reactions are also parameterised, for example the slow-reacting aromatic species, represented by the model species TOL, are assumed to react with the OH radical by addition to the aromatic ring with a 0.1 fraction of the reactions proceeding by H-atom abstraction.

$$\text{TOL} + \text{OH} \longrightarrow 0.90 \text{ ADDT} + 0.10 \text{ XO}_2 + 0.10 \text{ HO}_2 \quad \text{(R33)}$$

Furthermore, the branching ratios of the reactions of the aromatic-OH adduct (ADDT) are determined by simulating the environmental chamber data and this calculation is dependent on the secondary products formed from the reactions of unsaturated dicarbonyls. This is a source of uncertainity in the mechanism and since these three pathways after the O_3 production rate, obtaining the correct branching ratio is of importance (Stockwell et al., 1997).

The model species XO_2 is used to represent peroxy radicals where the appropriate XO_2 radical is dependent on the rate coefficient of the generating reaction. Also, the product yields are once again obtained via a weighted mean of the product yields of the individual species. To paramaterise the vast amount of reactions, very fast reactions are ignored and reactions with O_3 are estimated due to the lack of experimental data.

(Kirchner and Stockwell, 1996) details the treatment of organic peroxy radicals. The organic-peroxy radical-organic peroxy radical reactions are represented by reactions of the organic-peroxy radical with the two most important peroxy radicals (CH_3O_2 and $CH_3C(O)O_2$) and all other reactions with organic-peroxy radicals are ignored. The reaction rate coefficients of organic-peroxy radical self and cross reactions were estimated using the method described in (Kirchner and Stockwell, 1996). Experimental data is used for the rate coefficients of alkyl peroxy radicals reaction with NO.

1.5   Comparison of Chemical Mechanisms

Given the different chemical mechanisms and their differing approaches towards simplifying the complexities of atmospheric chemistry, there have been many comparative studies to determine the differences between calculation results obtained when performing the same modelling study but altering the mechanism. In (Dunker et al., 1984) four mechanisms that were used in atmospheric modelling studies were compared by means of atmospheric simulations of box, trajectory and grid modelling studies and also against chamber study results. The comparison parameters were plotted O_3, NO_2 and PAN isopleths as well as the time span required for the maximum one hour average O_3, NO_2 and PAN concentrations to be reached. The largest differences between the mechanisms were found during the box model study whereas the other simulations correlated well. It is also highlighted that differences in chemistry can be masked by the effects of the meteorology and other parameters not included in a box model.

A study of the chemical mechanisms used mainly for European regional studies are compared in (Gross and Stockwell, 2003). Here, a box model study with the three different mechanisms is used to generate the concentrations of O_3, NO, NO_2, OH radical, HO_2 radical and organic peroxy radicals RO_2. O_3 isopleth plots are also generated by performing the study over a range of NO_x and VOC concentrations. A common set of photolysis coefficients were used so that the results would mirror

only differences in the chemistry, the study also accounted for both urban and rural conditions in separate model runs.

The results show that the greatest differences between these mechanisms are in the O_3, NO_2 and RO_2 radical concentrations. The differences in the O_3 concentrations are linked to the discrepancies between the NO_2 and RO_2 concentrations as these are reactions that lead to O_3 production or loss. This emphasises the importance of the treatment of organic peroxy radicals, which is typically one of the major areas of difference between chemical mechanisms. The rural study showed little difference in the comparison parameters whilst the urban study showed larger differences. This can be attributed to the complexity of the organic chemistry prevalent in urban areas. (Gross and Stockwell, 2003) recommends that many different urban scenarios be considered and that O_3 isopleth plots giving the O_3 concentration over a range of NO_x and VOC values should be used for such mechanism comparison studies.

(Emmerson and Evans, 2009) compares the gas-phase chemical mechanisms used in global models. Since the MCM contains more chemical details than the reduced schemes used in global models it is used as a reference to which these are compared. The comparison is performed by box model runs simulating a large number of scenarios that are characteristic of global situations - industrial, clean, cold and dry, hot and wet, biogenic and non-biogenic conditions. Moreover, a particular recorded event (where the data are taken from the summer 2003 TORCH campaign) is also simulated with all the models to determine how close the simulation results are to the actual recorded concentrations.

The simulations were ran without heterogenous chemistry and all set to begin at midnight in order to investigate the effect of night-time chemistry, which would be affected most by not including heterogenous chemistry. The length of each simulation is five days as a compromise between very long and very short run times which can affect the chemistry in different ways. Long model runs would imply significant aging of the air masses that would drive the chemistry and very short

model runs would not test the chemistry pertaining to the degradation products at all, hence a compromise needs to be found. Separate model runs were also performed to determine differences in the inorganic chemistry, full chemistry and night-time chemistry.

The resulting concentrations of specific compounds were plotted and compared to verify where mechanistic differences arise. The little difference between inorganic chemistry regimes can be attributed to the differences between kinetic data supplied by IUPAC and JPL, whilst there are more differences between the full chemistry and night-time chemistry. The greatest differences in the organic chemistry is when biogenic compounds, such as isoprene, are considered and are present in larger concentrations. For the specific pollution event that was modelled, the greatest differences arise for the night-time chemistry and O_3 concentrations.

Reactivity scales have also been used as comparison tool for chemical mechanisms, this was proposed as in a single number, they provide a lot chemical kinetic data. In (Derwent et al., 2010), the MCM and SAPRC are compared by calculation of the POCP of 116 organic compounds from the major atmospheric classes within both mechanisms. A series of photochemical trajectory model runs simulating a single day were performed, many parameters other than the mechanisms were adjusted as incremental reactivities are not solely geophysical measures but rely on many other parameters.

The MCM and the SAPRC were chosen for this study as they are near-explicit mechanisms with the main difference being in how they treat the first generation products - the MCM continues in an explicit manner while the SAPRC uses aggregation techniques. In general, the POCP values correlate very well between the two mechanisms, with a small number of exceptions. These can be attributed to the lack of detailed understanding of the degradation reactions of these compounds. The good correlation of reactivities of the aromatic compounds merely indicates that both mechanisms treat aromatic compounds similarly rather than having a detailed knowledge of these degradation schemes.

A detailed look at the chemistry affecting different mechanisms used in air quality modelling is described in (Stockwell et al., 2012), where a box modelling study is undertaken with near-explicit and aggregated chemical mechanisms. The model system used is the same as that used in (Seefeld and Stockwell, 1999) with only gas-phase chemistry and constant meteorological conditions. Different model runs were also undertaken with different temperatures in order to determine the temperature dependency of model results.

The study highlights that the temperature dependence of gas phase reactions is uncertain for both organic and inorganic compounds. Also, night-time chemistry is a major source of uncertainty. Other knowledge gaps include the rate coefficients of the reactions of organic peroxy radicals as well as the products resulting from these reactions, the detailed degradation of both aromatic and biogenic compounds.

1.6   Project Outline

This study shall highlight differences in ozone production potential from specific NMVOCs using a boxmodel with the MCM v3.2, SAPRC-07 and RACM chemical mechanisms. The NMVOCs in Table 1.2 shall be used as a starting point but may deviate from this as deemed necessary. The main comparison parameter shall be the TOPP outlined in Section 1.2.3. Moreover, the TOPP values shall be calculated over a range of NO_x concentrations, thus invoking the different regimes of the atmosphere as discussed in Section 1.1.6.

The method of determining the TOPP (see supplementary material to (Butler et al., 2011)) involves simulations using the photochemical box model MECCA (Sander et al., 2005, 2011) which uses the Kinetic PreProcessor (KPP-2.1) (Sandu and Sander, 2006). The model is then run with the NMVOCs being studied and all degradation products belonging to a parent NMVOC are tagged with the parent NMVOC's name.

The model runs are then allowed to elapse for seven diurnal cycles under equinoctical conditions with the photolysis rates of the applicable latitude. The

NO_x level at each time-step is calculated on-line by setting the NO emission level to be equal to the source of radicals minus the chemical source of NO_x. This ensures that the calculations are not influenced by excessive NO_x levels and also so that O_3 production via NMVOC oxidation is maximised.

The next part of the study shall determine the TOPP values for the NMVOCs used over a range of NO_x concentrations. This shall invoke the different atmospheric regimes outlined in Section 1.1.6 and is especially necessary so that the TOPP can be applied to different regions at different times.

Chapter 2

Methodology

Chapter 3

Results

Chapter 4

Conclusions

Appendix

References

Christof Appenzeller, James R. Holton, and Karen H. Rosenlof. Seasonal variation of mass transport across the tropopause. *Journal of Geophysical Research*, 101(D10): 15,071–15,078, 1996.

C. Arsene, A. Bougiatioti, and N. Mihalopoulos. Sources and variability of non-methane hydrocarbons in the Eastern Mediterranean. *Global NEST Journal*, 11(3):333–340, 2009.

Roger Atkinson. Gas phase tropospheric chemistry of organic compounds: a review. *Atmospheric Environment*, 24A(1):1–41, 1990.

Roger Atkinson. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*, 34(12-14):2063–2101, 2000.

B. Aumont, S. Szopa, and S. Madronich. Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: Development of an explicit model based on a self generating approach. *Atmospheric Chemistry and Physics*, 5(9):2497–2517, 2005.

Angela K. Baker, Andreas J. Beyersdorf, Lambert A. Doezema, Aaron Katzenstein, Simone Meinardi, Isobel J. Simpson, Donald R. Blake, and F. Sherwood Rowland. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmospheric Environment*, 42:170–182, 2008.

Agnès Borbon, Hervè Fontaine, Nadine Locoge, Marc Veillerot, and J. C. Galloo. Developing receptor-oriented methods for non-methane hydrocarbon

characterisation in urban air - Part I: source identification. *Atmospheric Environment*, 37:4051–4064, 2003.

A. W. Brewer. Evidence of a world circulation provided by the measurements of helium and water vapour distribution in the stratosphere. *Quarterly Journal of the Royal Meteorological Society*, 75(326):351–363, 1949.

T. M. Butler, M. G. Lawrence, D. Taraborrelli, and J. Lelieveld. Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach. *Atmospheric Environment*, 45(24):4082–4090, 2011.

Shannon L. Capps, Yongtao Hu, and Armistead G. Russell. Assessing Near-Field and Downwind Impacts of Reactivity-Based Substitutions. *Journal of the Air and Waste Management Association*, 60:316–327, 2010.

William P. L. Carter. Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air and Waste Management Association*, 44:881–899, 1994.

William P. L. Carter. Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment. Technical report, Report to Califonia Air Resources Board, 2000.

William P. L. Carter. Development of the SAPRC-07 chemical mechanism. *Atmospheric Environment*, 44(40):5324–5335, 2010.

Andrew C. Comrie. Comparing Neural Networks and Regression Models for Ozone Forecasting. *Journal of the Air and Waste Management Association*, 47:653–663, 1997.

R. G. Derwent, M. E. Jenkin, and S. M. Saunders. Photochemical Ozone Creation Potentials for a Large Number of Reactive Hydrocarbons under European Conditions. *Atmospheric Environment*, 30(2):181–199, 1996.

Richard G. Derwent, Michael E. Jenkin, Sandra M. Saunders, and Michael J. Pilling. Photochemical Ozone Creation Potentials for Organic Compounds in Northwest Europe Calculated with a Master Chemical Mechanism. *Atmospheric Environment*, 32(14/15):2429–2441, 1998.

Richard G. Derwent, Michael E. Jenkin, Michael J. Pilling, William P. L. Carter, and Ajith Kaduwela. Reactivity Scales as Comparative Tools for Chemical Mechanisms. *Journal of the Air and Waste Management Association*, 60:914–924, 2010.

G. B. M. Dobson. Origin and distribution of polyatomic molecules in the atmosphere. *Proceedings of the Royal Society London A*, 236(1205):187–193, 1956.

Alan M. Dunker, Sudarshan Kumar, and Peteris H. Berzins. A Comparison of Chemical Mechanisms Used In Atmospheric Models. *Atmospheric Environment*, 18 (2):311–321, 1984.

K. M. Emmerson and M. J. Evans. Comparison of tropospheric gas-phase chemistry schemes for use within global models. *Atmospheric Chemistry and Physics*, 9: 1831–1845, 2009.

Arlene M. Fiore, Daniel J. Jacob, Jennifer A. Logan, and Jeffrey H. Yin. Long-term trends in ground level ozone over the contiguous United States, 1980-1995. *Journal of Geophysical Research*, 103(D1):1471–1480, 1998.

A. H. Goldstein and I. E. Galbally. Known and unexplored organic constituents in the Earth's atmosphere. *Environmental Science and Technology*, 41(5):1514–1521, 2007.

Allan Gross and William R. Stockwell. Comparison of the EMEP, RADM2 and RACM Mechanisms. *Journal of Atmospheric Chemistry*, 44:151–170, 2003.

A. J. Haagen-Smit and M. M. Fox. Ozone Formation in Photochemical Oxidation of Organic Substances. *Industrial and Engineering Chemistry*, 48(9):1484–1487, 1956.

P. H. Haynes, C. J. Marks, M. E. McIntyre, T. G. Shephard, and K. P. Shine. On the "Downward Control" of Extratropical Diabatic Circulations by Eddy-Induced Mean Zonal Forces. *Journal of the Atmospheric Sciences*, 48(4):651–687, 1991.

P. Hess and N. Mahowald. Interannual variability in hindcasts of atmospheric chemistry: the role of meteorology. *Atmospheric Chemistry and Physics*, 9: 5261–5280, 2009.

M. E. Jenkin, S. M. Saunders, V. Wagner, and M. J. Pilling. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1):181–193, 2003.

Michael E. Jenkin and Kevin C. Clemitshaw. Ozone and other secondary photochemical pollutants: Chemical processes governing their formation in the planetary boundary layer. *Atmospheric Environment*, 34(16):2499–2527, 2000.

Michael E. Jenkin, Sandra M. Saunders, and Michael J. Pilling. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment*, 31(1):81–104, 1997.

Frank Kirchner and William R. Stockwell. Effect of peroxy radical reactions on the predicted concentrations of ozone, nitrogenous compounds and radicals. *Journal of Geophysical Research*, 101(D15):21,007–21,002, 1996.

Frank Kirchner, Francois Jenneret, Alain Clappier, Bernd Krüger, Hubert van den Bergh, and Bertrand Calpini. Total VOC reactivity in the planetary boundary layer 2. A new indicator for determining the sensitivity of the ozone production to VOC and NO_x. *Journal of Geophysical Research*, 106(D3):3095–3110, 2001.

Lawrence I. Kleinman. Seasonal Dependence of Boundary Layer Peroxide Concentration: The Low and High NO_x Regimes. *Journal of Geophysical Research*, 96(D11):20,721–20,733, 1991.

Lawrence I. Kleinman. Low and high NO_x tropospheric photochemistry. *Journal of Geophysical Research*, 99(D8):16,831–16,838, 1994.

L.I. Kleinman. The dependence of tropospheric ozone production rate on ozone precursors. *Atmospheric Environment*, 39(3):575–586, 2005.

J.-H. Koo, Y. Wang, T. P. Kurosu, K. Chance, A. Rozanov, A. Richter, S. J. Oltmans, A. M. Thompson, J. W. Hair, M. A. Fenn, A. J. Weinheimer, T. B. Ryerson, S. Solberg, L. G. Huey, J. Liao, J. E. Dibb, J. A. Neuman, J. B. Nowak, R. B. Pierce, M. Natarajan, and J. Al-Saadi. Characteristics of tropospheric ozone depletion events in the Arctic spring: analysis of the ARCTAS, ARCPAC, and ARCIONS measurements and satellite BrO observations. *Atmospheric Chemistry and Physics*, 12:9909–9922, 2012.

Jos Lelieveld and Frank J. Dentener. What controls tropospheric ozone? *Journal of Geophysical Research*, 105(D3):3531–3551, 2000.

C.-Y. Cynthia Lin, Daniel J. Jacob, and Arlene M. Fiore. Trends in exceedances of the ozone air quality standard in the continental United States, 1980-1998. *Atmospheric Environment*, 35:3217–3228, 2001.

D. J. Luecken and M. R. Mebust. Technical Challenges Involved in Implementation of VOC Reactivity-Based Control of Ozone. *Environmental Science and Technology*, 42(5):1615–1622, 2008.

Sasha Madronich and Jack G. Calvert. The NCAR Master Mechanism of the Gas Phase Chemistry - Version 2.0. Technical report, National Center of Atmospheric Research, 1989.

W. J. Moxim, W. Levy II, and P. S. Kasibhatla. Simulated global tropospheric PAN: Its transport and impact on NO_x. *Journal of Geophysical Research*, 101(D7): 12,621–12,638, 1996.

S. A. Penkett and K. A. Brice. The spring maximum of photo-oxidants in the Northern Hemisphere troposphere. *Nature*, 319:655–657, 1986.

Armistead Russell and Robin Dennis. NARSTO critical review of photochemical models and modeling. *Atmospheric Environment*, 34:2283–2324, 2000.

R. Sander, A. Kerkweg, P. Jöckel, and J. Lelieveld. Technical Note: The new comprehensive atmospheric chemistry module MECCA. *Atmospheric Chemistry and Physics*, 5:445–450, 2005.

R. Sander, A. Baumgaertner, S. Gromov, H. Harder, P. Jöckel, A. Kerkweg, D. Kubistin, E. Regelin, H. Riede, A. Sandu, D. Taraborrelli, H. Tost, and Z.-Q. Xie. The atmospheric chemistry box model CAABA/MECCA-3.0. *Geoscientific Model Development*, 4:373–380, 2011.

A. Sandu and R. Sander. Technical Note: Simulating chemical systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1. *Atmospheric Chemistry and Physics*, 6:187–195, 2006.

A. Sandu, J. G. Verwer, J. G. Blom, E. J. Spee, G. R. Carmichael, and F. A. Potra. Benchmarking stiff ODE solvers for atmospheric chemistry problems II: Rosenbrock solvers. *Atmospheric Environment*, 31(20):3459–3472, 1997a.

A. Sandu, J. G. Verwer, M Van Loon, G. R. Carmichael, F. A. Potra, D. Dabdub, and J. H. Seinfeld. Benchmarking stiff ODE solvers for atmospheric chemistry problems I: implicit vs explicit. *Atmospheric Environment*, 31(19):3151–3166, 1997b.

S. M. Saunders, M. E. Jenkin, R. G. Derwent, and M. J. Pilling. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1):161–180, 2003.

S. Seefeld and W.R. Stockwell. First-order sensitivity analysis of models with time-dependent parameters: An application to PAN and ozone. *Atmospheric Environment*, 33(18):2941–2953, 1999.

John H. Seinfeld and Spyros N. Pandis. *Atmospheric Chemistry and Physics: From*

Air Pollution to Climate Change. John Wiley & Sons Inc, 2 edition, 2006. ISBN 978-0-471-72018-8.

Sanford Sillman. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment*, 33(12):1821–1845, 1999.

William R. Stockwell, Frank Kirchner, Michael Kuhn, and Stephan Seefeld. A new mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research D: Atmospheres*, 102(22):25,847–25,879, 1997.

William R. Stockwell, Charlene V. Lawson, Emily Saunders, and Wendy S. Goliff. A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling. *Atmosphere*, 3:1–32, 2012.

Kengo Sudo and Masaaki Takashi. Simulation of tropospheric ozone changes during 1997-1998 El Niño: Meteorological impact on tropospheric photochemistry. *Geophysical Research Letters*, 28(21):4091–4094, 2001.

World Meteorological Organisation. Scientific Assessment of Ozone Depletion: 2010. Technical Report 516 pp., World Meteorological Organisation, Geneva, Switzerland, March 2011.

Greg Yarwood, Sunja Rao, Mark Yocke, and Gary Z. Whitten. Updates to the Carbon Bond Chemical Mechanism: CB05. Technical report, U. S Environmental Protection Agency, 2005.