

# Chapter 2

## Methodology

This chapter details the methodology used to address the research questions of this work (Sect. ??). A brief description of AQ modelling is given, followed by the model set-up used in the separate studies (Sect. 2.1.1). The chemical mechanisms used in this work are introduced in Sect. ?? and the required initial and boundary conditions are described in Sect. 2.3

### 2.1 Air Quality Modelling

AQ models are mathematical representations of the atmosphere designed to produce continuous output fields that aid in explaining sources of air pollution. All models numerically solve the system of differential equations describing the conservation of chemical species used by the model (Russell and Dennis, 2000).

Solving the system of differential equations requires initial and boundary conditions for each chemical species. Initial conditions fix the starting concentrations of each species in each grid-box. Boundary conditions require knowledge of the concentration and transport of each species at the boundary edges of the model grid.

Eulerian models are the most common type of AQ model (Russell and Dennis, 2000). These models describe the atmosphere by fixed grid-boxes where species are transported in and out of the boxes (Seinfeld and Pandis, 2006). Box models are the simplest type of model (zero-dimensional) having uniform atmospheric concentrations that are only a function of time. Whereas 3-D models describe atmospheric concentrations as a function of time, latitude, longitude and height requiring more computing power than a box model (Seinfeld and Pandis, 2006). Box

Table 2.1: MECCA box model settings.

Model Parameter	Setting
Pressure	1013 hPa
Relative Humidity	81 %
Starting Date and Time	27th March 06:00
Model Time Step	20 mins

models may lack realism but are useful for studying detailed processes influencing air quality.

### 2.1.1 Model Description and Setup

The MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) box model was used throughout this work. MECCA was developed by Sander et al. (2005) and adapted to include MCM v3.1 chemistry by Butler et al. (2011). MECCA was used in the published studies of Kubistin et al. (2010) and Lourens et al. (2016).

MECCA is written in Fortran code and runs on UNIX/Linux platforms. The Kinetic Pre-Processor (KPP, Damian et al. (2002)) processed the chemical mechanism and generated Fortran code further compiled within MECCA. KPP has many choices of numerical solver for solving the differential equations, Rosenbrock solver (the `ros3` option) was used throughout this work.

Emissions of species into the box and deposition of species out of the box were handled by KPP. The chemical mechanism file includes pseudo-unimolecular reactions specifying the emissions and dry deposition of chemical species with the relevant rate. The emitted chemical species and emission rates were read into the model using a namelist file. Namelist files also specified the initial and boundary conditions of chemical species.

The physical parameters used in MECCA throughout this work are detailed in Table 2.1. In the first two studies, temperature was held constant at 293 K and the boundary layer height was fixed at 1000 m. In the final study, MECCA was updated to include a diurnal boundary layer height and temperature was systematically varied between 288 and 313 K (15–40 °C). These changes to the model setup for the final study are outlined in Paper III (Chap. ??).

Photolysis rates were parameterised as a function of the solar zenith angle

Table 2.2: Chemical mechanisms used in this work.

Chemical Mechanism	Lumping Type	Reference
MCM v3.1 and v3.2	No lumping	Jenkin et al. (1997), Jenkin et al. (2003) Saunders et al. (2003), Bloss et al. (2005) Rickard et al. (2015)
CRIv2	Lumped intermediate	Jenkin et al. (2008)
MOZART-4	Lumped molecule	Emmons et al. (2010)
RADM2	Lumped molecule	Stockwell et al. (1990)
RACM	Lumped molecule	Stockwell et al. (1997)
RACM2	Lumped molecule	Goliff et al. (2013)
CBM-IV	Lumped structure	Gery et al. (1989)
CB05	Lumped structure	Yarwood et al. (2005)

based on the approach of the MCM (Jenkin et al., 1997). This parameterisation utilises the degree of latitude and in the first two studies 34 °N, roughly the city of Los Angeles, was used. In the final study, the latitude was set to 51 °N simulating central European conditions.

## 2.2 Chemical Mechanisms

The chemical mechanisms used in this study are listed in Table 2.2. A brief description is found below with more details found in Paper I (Sect. ??). These chemical mechanisms were chosen as they are commonly used by the AQ modelling community as outlined by the review of European modelling groups by Baklanov et al. (2014).

The Master Chemical Mechanism (MCM, Jenkin et al. (1997, 2003); Saunders et al. (2003); Bloss et al. (2005); Rickard et al. (2015)) is a near-explicit chemical mechanism with a high level of detail making it ideal as the reference chemical mechanism in each study of this work. The Common Representative Intermediates (CRI) chemical mechanism (Jenkin et al., 2008) is an lumped intermediate mechanism where the degradation productions are aggregated (lumped) rather than emitted VOC.

Lumped molecule chemical mechanisms aggregate primary VOC into mechanism species and is the most common used simplification technique. The lumped-molecule chemical mechanisms used in this work were Model for Ozone and Related chemical Tracers (MOZART, Emmons et al. (2010)), Regional Acid Deposition Model (RADM2, Stockwell et al. (1990)), Regional Atmospheric Chemistry Mechanism (RACM, Stockwell et al. (1997)) and RACM2 Goliff et al. (2013). Lumped structure chemical mechanism represent emissions of NMVOC through emissions

of mechanism species representing the bonds present in the emitted NMVOC. The Carbon Bond mechanisms CBM-IV (Gery et al., 1989) and CB05 (Yarwood et al., 2005) were the lumped-structure chemical mechanisms used in this work.

### 2.2.1 Implementing Chemical Mechanisms in MECCA

Each chemical mechanism listed in Table 2.2 was adapted to the KPP format used in the MECCA box model. The WRF-Chem model (Grell et al., 2005) includes KPP versions of RADM2, RACM and CBM-IV and this was the source for these chemical mechanisms. The full version of the CRI v2 was obtained from <http://mcm.leeds.ac.uk/CRI> while the original reference was the source for all other chemical mechanisms in Table 2.2.

In order to focus on the differences in the representation of VOC degradation between the chemical mechanisms, a number of harmonisations between the chemical mechanisms were implemented. For these harmonisations, the approaches used by the reference chemical mechanism (MCM v3.2) were implemented in the reduced chemical mechanisms. These changes are detailed in the supplementary material of Paper I (Chap. ??).

### 2.2.2 Tagging of Chemical Mechanisms

AQ models can be used to allocate the effects of different precursors or emission sources on ozone production. For example, source removal studies perform separate model simulations with and without emissions from a sector to quantify the effect of the sector on ozone production, such as the quantification of megacity emissions on ozone production in Butler and Lawrence (2009). Tagging is another approach where the chemical mechanism includes additional chemical species labelled (tagged) with source information. For example, Emmons et al. (2012) updated the MOZART-4 chemistry to attribute ozone production to emission sources of  $\text{NO}_x$ .

In Butler et al. (2011), tagged NMVOC chemistry allows allocation of ozone production to emitted NMVOC. Tagging involves labelling every organic degradation product produced during the degradation of a VOC with the name of the VOC. This labelling is repeated for every degradation product until the final degradation products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) are produced, thus every VOC has a separate set of reactions fully describing its degradation. This tagging approach uses  $\text{O}_x$  production as a proxy for  $\text{O}_3$  production, this assumption is only valid for

NO<sub>x</sub>-limited and VOC-and-NO<sub>x</sub> sensitive chemistry not in high NO<sub>x</sub> conditions. The O<sub>x</sub> family includes O<sub>3</sub>, NO<sub>2</sub>, O(<sup>1</sup>D), O(<sup>3</sup>P), NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and other species involved in fast production and loss cycles with NO<sub>2</sub>.

All chemical mechanisms in Table 2.2 were tagged using the approach of Butler et al. (2011). In the first study, the tagging approach was the basis for comparing the representations of VOC degradation chemistry and their effects on ozone production. The second study used VOC-and-NO<sub>x</sub>-sensitive conditions and simulations using the tagged chemical mechanisms determined sources of differences in ozone production from the solvent sector emission inventories of Table 2.3. Variable NO<sub>x</sub> conditions were used in the third study hence using the tagging approach was not possible. Thus all model simulations assessing the ozone-temperature relationship with different NO<sub>x</sub> conditions were performed with non-tagged versions of the chemical mechanisms.

## 2.3 Initial and Boundary Conditions

In all simulations of this work, methane (CH<sub>4</sub>) was fixed to 1.75 ppmv while carbon monoxide (CO) and O<sub>3</sub> were initialised at 200 ppbv and 40 ppbv and then allowed to evolve freely. The initial conditions for NMVOC emissions were held constant until noon of the first day of simulations to simulate a fresh emissions plume.

### NMVOC Initial Conditions

The initial conditions for NMVOC species differed in each experiment, a brief summary is given below and details are found in the respective publications (Chap. ??, Chap. ?? and Chap. ??). The first study used the initial conditions of the Los Angeles experiments in Butler et al. (2011) to determine the emissions needed for constant mixing ratios of the NMVOCs. These emissions were mapped to the appropriate chemical species of each chemical mechanism in Table 2.2 thus keeping the amount of emitted NMVOC constant between model runs.

The second study used NMVOC emissions specified by the emission inventories for the solvent sector listed in Table 2.3 over a theoretical urban area of 1000 km<sup>2</sup> with total NMVOC emissions of 1000 tons/day. The solvent sector contributes ~ 43 % by mass of total emissions (EEA, 2011), thus total NMVOC emissions of 430 tons/day were used. Further simulations used emissions from all

Table 2.3: The solvent sector emission inventories compared in this work.

Speciation	Comment	Reference
TNO	European average	Builtjes et al. (2002)
IPCC	Model Specific	Ehhalt et al. (2001)
EMEP	Model Specific	Simpson et al. (2012)
DE94	Country Specific	Friedrich et al. (2002)
GR95	Country Specific	Sidiropoulos and Tsilingiridis (2007)
GR05	Country Specific	Sidiropoulos and Tsilingiridis (2007)
UK98	Country Specific	Goodwin (2000)
UK08	Country Specific	Murrells et al. (2010)

the other sectors (remaining 570 tons/day) while varying the solvent sector NMVOC emissions. Another set of simulations further included BVOC emissions sources of isoprene and monoterpenes while varying the speciation of NMVOC emissions from the solvent sector.

The NMVOC emissions of the solvent sector were assigned to MCM v3.2 species based on the speciations of each emission inventory. Model simulations were repeated using MOZART-4 and RADM2 to investigate whether changing the chemical mechanism affects the differences in ozone concentrations between the solvent sector emission inventories.

The final study looked at the ozone-temperature relationship over central Europe and the emissions of NMVOC over Benelux (Belgium, Netherlands and Luxembourg) were used. The TNO\_MACCIII emissions for the year 2011 were used as anthropogenic NMVOC emissions and mapped to MCM v3.2 species. Temperature independent emissions of biogenic species (isoprene and monoterpenes) were taken from the EMEP speciation (Simpson et al., 2012). Simulations using temperature-dependent emissions of isoprene used the MEGAN2.1 (Guenther et al., 2012) algorithm. All simulations were repeated using the CRI v2, MOZART-4, RADM2 and CB05 chemical mechanisms.

### NO<sub>x</sub> Initial Conditions

NO<sub>x</sub> conditions generating VOC-and-NO<sub>x</sub> sensitive chemistry were used in the first two studies. This was achieved by emitting the amount of NO required to balance the source of radicals at each time step. While the final study assessed the relationship between ozone and temperature with different NO<sub>x</sub> conditions. For these simulations, a constant source of NO emissions was systematically varied between  $5.0 \times 10^9$  and  $1.5 \times 10^{12}$  molecules (NO) cm<sup>-2</sup> s<sup>-1</sup> at each temperature used in this study (15–40 °C).

## Boundary Conditions

No chemical boundary conditions were used in the first two studies as the experiment was setup as a contained box. In the final study, MECCA included a diurnal profile of the PBL with vertical mixing into the free troposphere with the heights from the BAERLIN2014 campaign (Bonn et al., 2016). The boundary conditions for the free troposphere mixing ratios for  $O_3$ ,  $CH_4$  and  $CO$  were set to 50 ppbv, 1.8 ppmv and 116 ppbv respectively. These mixing ratios were taken from the 700 hPa height using the MATCH-MPIC chemical weather forecast data (<http://cwf.iass-potsdam.de/>) from March 21st.





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