

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 followed by the model set-up used in the separate studies (Sect. 2.1). The chemical mechanisms used in this work are introduced in Sect. 2.2 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 every 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 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 models may

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

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, a Rosenbrock solver (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 included 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 (20°C) and the boundary layer height was fixed at 1000 m. In the final study, MECCA was updated to include a variable 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 based on the approach of the MCM (Jenkin et al., 1997). This parameterisation

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)

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 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 a 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 commonly 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 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 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) tagged the MOZART-4 chemistry to attribute ozone production to emission sources of NO_x .

In Butler et al. (2011), tagged VOC chemistry allows allocation of ozone production to emitted VOC. 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 (CO_2 and H_2O) are produced, thus every VOC has a separate set of reactions fully describing its degradation. This tagging approach uses O_x production as a proxy for O_3 production and is only valid for NO_x -limited and VOC-and- NO_x sensitive chemistry not NO_x -saturated conditions. The O_x family includes O_3 , NO_2 , $\text{O}(^1\text{D})$, $\text{O}(^3\text{P})$, NO_3 , N_2O_5 and other species involved in fast production and loss cycles with NO_2 .

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_x-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_x 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_x conditions were performed with non-tagged versions of the chemical mechanisms.

2.3 Initial and Boundary Conditions

In all simulations of this work, methane (CH₄) was fixed to 1.75 ppmv while carbon monoxide (CO) and O₃ 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 (Chaps. ??-??). The first study used the initial conditions of the Los Angeles simulation in Butler et al. (2011) to determine the emissions needed for constant mixing ratios of the initial NMVOCs. These emissions were mapped to the appropriate chemical species of each chemical mechanism in Table 2.2 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 km² 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 other sectors (remaining 570 tons/day) while varying the solvent sector NMVOC emissions. Additional simulations included BVOC emissions of isoprene and monoterpenes while varying the speciation of NMVOC emissions from the solvent sector.

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 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 affected the differences in ozone concentrations between the solvent sector emission inventories.

The final study looked at the ozone-temperature relationship over central Europe and used the emissions of NMVOC from Benelux (Belgium, Netherlands and Luxembourg). 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_x Initial Conditions

NO_x conditions generating VOC-and-NO_x 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_x conditions. For these simulations, a constant source of NO emissions was systematically varied between 5.0×10^9 and 1.5×10^{12} molecules (NO) cm⁻² s⁻¹ 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 experiments considered a contained box. In the final study, MECCA included a diurnal profile of the PBL with vertical mixing into the free troposphere using the PBL 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, 2014.

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