Chapter 4

Overall Discussion and Conclusions

The detailed box modelling studies of Chap. ?? were designed to address the research questions of Sect. ??. These studies compared the effects on ozone production from VOC degradation specified by various chemical mechanisms, varying the input of NMVOC speciation and quantified the effects of temperature with different NO_x conditions. In each study the near-explicit MCM v3.2 was the reference chemical mechanism with the simulations repeated using reduced chemical mechanisms typically used by modelling groups for regional and global studies.

The first study determined the effects of different simplification techniques used by chemical mechanisms on ozone production using a tagging technique that attributed ozone production to emitted VOC. Varying the representation of VOC degradation chemistry in the box model led to differences in the first day peak ozone of 21 ppbv when including the outlier RACM chemical mechanism and 8 ppbv when not including RACM. Moreover, only CRI v2 and RADM2 led to higher ozone mixing ratios than the MCM v3.2 on the first two days of model simulations.

O_x production budgets allocated to emitted NMVOC showed larger differences between chemical mechanisms with VOC represented by lumped mechanism species than explicitly represented NMVOC. In particular, the representation of aromatic VOC consistently produced lower O_x in the reduced chemical mechanisms and was the source of the low ozone mixing ratios in the RACM chemical mechanism. Hence, when modelling urban areas with significant emissions of aromatic VOC, RACM chemistry may underpredict ozone production. Thus the choice of chemical mechanism influenced the amount of ozone produced from the box model simulations.

The lumped intermediate chemical mechanism, CRI v2, produced the most similar amounts of O_x from each VOC to the MCM. The lumped intermediate species used by the CRI v2 were developed to produce similar amounts of ozone as the MCM. Thus the technique of lumping intermediate species rather than lumping VOCs appears very promising for representing ozone production.

Production of O_x from reactive NMVOC, such as alkenes, using both lumped-molecule (MOZART-4, RADM2, RACM, RACM2) and lumped-structure (CBM-IV, CB05) chemical mechanisms was generally similar to that using the MCM v3.2. Peak O_x production from alkane species in lumped-molecule and lumped-structure chemical mechanisms was lower than peak O_x production with the MCM v3.2. As alkanes are less-reactive VOC, they are more likely to be transported downwind of emission sources affecting ozone production in urban background areas. Thus an underestimation in the ozone production from alkanes in reduced chemical mechanisms may impact on simulated background ozone levels.

The representation of NMVOC by lumped-molecule or lumped-structure species in the reduced chemical mechanisms led to generally lower ozone production than the MCM v3.2 with the emitted NMVOC. Moreover, the secondary degradation chemistry specified by the reduced chemical mechanisms for many NMVOC led to a faster breakdown of the emitted species ultimately leading to lower O_x production from the emitted species.

The second study looked at the influence of varying the speciation of NMVOC emissions from the solvent sector on ozone production. The simulations were performed using the MCM v3.2 as the reference chemical mechanism and MOZART-4 and RADM2 were reduced chemical mechanisms. Differences of up to 9 ppbv were obtained between solvent sector EIs using a single chemical mechanism. Difference in peak ozone of up to 15 ppbv were obtained from box model simulations using different solvent sector EIs and the same chemical mechanism. Including NMVOC emissions from all other emissions sectors and varying the NMVOC emissions from the solvent sector, reduced the differences in peak ozone mixing ratios (up to 9 ppbv). Further including emissions from biogenic sources while varying the NMVOC emissions from the solvent sector resulted in lower still differences in ozone mixing ratios while using the same chemical mechanism (up to 8 ppbv). Thus the choice of solvent sector EI and chemical mechanism influenced ozone production.

First day production of O_x was controlled by the contribution of reactive NMVOC such as alkenes, however the emission of large quantities of alkenes from the solvent sector is debatable. The cumulative O_x production at the end of the seven days was influenced by the O_x production from less-reactive NMVOC such as alkanes and oxygenated NMVOC. The contribution of alkanes specified by the EIs had a positive correlation with cumulative ozone production while the specified contributions of oxygenated NMVOC had a negative correlation with ozone production. Furthermore, EIs specifying larger emissions from alkanes produced the highest ozone while EIs specifying larger emissions of oxygenated NMVOC produced the lowest amounts of O_x. The EIs of the same country at different time points (Greece 1995 and 2005, United Kingdom 1998 and 2008) indicated that the more recent EI specified more emissions of oxygenated VOC than alkanes. Thus when preparing updated or new EIs the amount of alkane and oxygenated species are particularly important with respect to ozone production.

Changing the speciation of an EI within the box model setup influenced the ozone production with these differences reproduced when using different chemical mechanisms. When considering instantaneous ozone production, alkenes contributed most to ozone production while cumulative ozone production after seven days was influenced by alkanes and oxygenated NMVOC. As a first scoping study as to whether EIs need to be updated do reduce modelling uncertainity, the box modelling study indicates that the differences in solvent sector speciation do influence ozone production. However, these differences may differ when using more complex 3D models and further work is warranted to determine whether different EI speciations influence ozone production under different conditions.

The final study looked at the relationship between ozone, temperature and NO_x broadly using central European conditions. In order to verify whether temperature-dependent increases in reaction rates or isoprene emissions from nature are more important for the increase in ozone with temperature, separate simulations using a temperature-independent and temperature-dependent source of isoprene emissions were performed. Simulations were performed using the MCM v3.2, CRI v2, RADM2, MOZART-4 and CB05 chemical mechanisms to determine whether this relationship differed between representations of atmospheric chemistry.

Each chemical mechanism produced the non-linear relationship between ozone, temperature and NO_x similar to the relationship obtained from previous observational studies. The absolute increase in ozone with temperature due to faster reaction rates was more greater than the increase in ozone with temperature due to increased isoprene emissions with temperature regardless of NO_x conditions. The largest increases in ozone with temperature were obtained using moderate NO_x emissions and the lowest increase using low-NO_x conditions.

The increase in ozone with temperature in all NO_x conditions was due to the faster loss rates of the emitted VOC with temperature. The faster reaction rates was mainly due to the increase in OH with temperature which is coupled to the increase in ozone with temperature. Peroxy nitrate (RO_2NO_2) chemistry also played a role in the increase of O_x production with temperature with increased decomposition to RO_2 and NO_2 leading to ozone production. Thus the loss of VOC and RO_2NO_2 chemistry are critical to modelling the relationship between ozone, temperature and NO_x.

Comparing the box model simulations to observational and 3-D model output showed that the rate of increase in ozone with temperature with the box model was about half the rate of increase of ozone with temperature using both observational and 3-D model data. The spread in the ozone-temperature curves in all NO_x conditions from simulations using the different chemical mechanisms was insignificant compared to the spread in observational and 3-D model output. The box model was setup to consider instantaneous ozone production and included vertical mixing with the free troposphere whereas observations and 3-D models also include data representing stagnant conditions.

Stagnant atmospheric conditions characterised by low-wind speeds lead to the accumulation of reactants and elevated ozone levels as VOC degradation can be fully realised before being transported away from the region. Box model simulations were performed without vertical mixing to approximate stagnant conditions and in each case the rate of increase of ozone with temperature approached the rate of increase of ozone with temperature from the observed and 3-D model data. Thus with the box model, the relationship between ozone, temperature and NO_x is more sensitive to mixing than the choice of chemical mechanism.

Overall, the representation of detailed atmospheric chemistry does influence ozone production as in each of the studies significant differences between ozone levels are produced just from using different chemical mechanisms. The representation of the emitted NMVOC by the chemical mechanisms is critical and lead to differences in ozone production in each study. In particular, the relationship of ozone with temperature was controlled by the representation of the primary degradation of NMVOC. The secondary degradation processes of RO_2NO_2 chemistry and the rate of break down of emitted NMVOC using reduced chemical mechanisms are also important processes. Chapter **??** discusses the implications of these findings in more detail.