

Chapter 3

Papers

This chapter outlines the main findings in each scientific paper published as part of this thesis. These publications addressed the research questions framed in Sect. ?? and are found in Chaps. ??–??.

3.1 Paper I: A comparison of chemical mechanisms using tagged ozone production potential (TOPP) analysis

Published: J. Coates and T. M. Butler. A comparison of chemical mechanisms using tagged ozone production potential (TOPP) analysis. *Atmospheric Chemistry and Physics*, 15(15):8795–8808, 2015.

The first paper presents a box modelling study where the effects on ozone production from VOC degradation chemistry in reduced chemical mechanisms (Table ??) were compared to the effects in the detailed MCM v3.2 chemical mechanism. This chemical mechanism comparison used the tagging approach described in Sect. ?? to give insights into how the simplified representation of VOC degradation by chemical mechanisms influenced maximum ozone production.

The difference in peak ozone between all chemical mechanisms on the first day was 21 ppbv when including the outlier RACM chemical mechanism and 8 ppbv when not including RACM. The ozone mixing ratios using reduced chemical mechanisms, except CRI v2 and RADM2, were lower than the ozone mixing ratios using the MCM v3.2 on the first two days of simulations. The representation of the degradation of aromatic VOC in RACM led to the lower ozone mixing ratios than

all other chemical mechanisms.

The VOC degradation described in CRI v2, a lumped-intermediate chemical mechanism, produced the most similar amounts of O_x to the MCM v3.2 for each VOC. On the other hand, the degradation of VOC in all other reduced chemical mechanisms led to differences in O_x production with the largest differences occurring after the first day of simulations. The degradation of aromatic VOC in the reduced chemical mechanisms led to the largest differences in O_x production from the MCM v3.2.

Many VOC are broken down into smaller-sized degradation products faster on the first day in reduced chemical mechanisms than the MCM v3.2. The faster breakdown of VOC leads to lower amounts of larger-sized degradation products that can further degrade and produce O_x in the reduced chemical mechanisms. Thus, many VOC in reduced chemical mechanisms produce a lower maximum of O_x than the MCM v3.2 resulting in lower ozone mixing ratios from the reduced chemical mechanisms compared to the MCM v3.2.

Reactive VOC, such as alkenes and aromatic VOC, produce maximum O_x on the first day of the simulations. Alkenes produce similar amounts of O_x on the first day between chemical mechanisms; differences in O_x production arise when mechanism species are used to represent individual VOC. Large inter-mechanism differences in O_x production result from the degradation of aromatic VOC on the first day due to the faster break down of the mechanism species representing aromatic VOC in reduced chemical mechanisms. The less-reactive alkanes produce peak O_x on the second day of simulations and this peak is lower in each reduced chemical mechanism than the MCM v3.2 due to the faster break down of alkanes into smaller sized degradation products on the first day.

3.2 Paper II: Variation of the NMVOC Speciation in the Solvent Sector and the Sensitivity of Modelled Tropospheric Ozone

Published: E. von Schneidemesser, J. Coates, A. J. H. Visschedijk, H. A. C. Denier van der Gon, and T. M. Butler. Variation of the NMVOC speciation in the solvent sector and the sensitivity of modelled tropospheric ozone. *Atmospheric Environment*, Submitted for Publication, 2016.

The second publication compared ozone production when using different emission inventories (EIs) of NMVOC emissions for the solvent sector within a box

model. The MCM v3.2, MOZART-4 and RADM2 chemical mechanisms were used to ascertain whether the representation of tropospheric chemistry affected the differences in ozone production when using the different emission inventories. Simulations using the tagged approach of Sect. 3.1 were performed to allocate O_x production to the emitted NMVOC specified by each EI.

A maximum difference in peak ozone mixing ratios ranged between 11 and 15 ppbv using different EIs with a single chemical mechanism. When using the same EI, a maximum difference of 7 ppbv in ozone mixing ratios was determined between simulations with different chemical mechanisms. Thus both the choice of chemical mechanism and EI influenced the amount of ozone produced.

Further simulations using emissions from all other non-solvent sectors while varying the emissions from the solvent sector produced a lower maximum difference in ozone mixing ratio (6 – 9 ppbv) for each chemical mechanism. Including emissions from biogenic sources further reduced the maximum differences in ozone mixing ratios even further (5 – 8 ppbv) with each chemical mechanism.

Reactive VOC, such as alkenes and aromatic VOC, contributed the most to O_x production on the first day. While less-reactive VOC, such as alkanes and oxygenated VOC, contributed the most to the cumulative O_x production after seven days. A positive correlation between O_x production and the contribution of alkane species by the EIs was determined while a negative correlation was determined between cumulative O_x production and the contribution of oxygenated species by the EIs. No correlation was found between the specification of aromatic species by EIs and O_x production and not all EIs specify alkene emissions thus no correlation was made between alkene emissions and O_x production.

3.3 Paper III: The Influence of Temperature on Ozone Production under varying NO_x Conditions – a modelling study

Published: J. Coates, K. A. Mar, and T. M. Butler. The influence of temperature on ozone production under varying NO_x conditions – a modelling study. *Atmospheric Chemistry and Physics Discussions*, In preparation, 2016.

The final publication looked at the ozone-temperature relationship with different NO_x conditions simulated by a box model. A series of box model simulations varying the temperature and NO conditions were performed using NMVOC emissions

representative of central Europe, first using a temperature-independent source of isoprene emissions followed by simulations using a temperature-dependent source of isoprene emissions. All simulations were repeated using the MCM v3.2, CRI v2, MOZART-4, RADM2 and CB05 chemical mechanisms.

A non-linear relationship between ozone, temperature and NO_x was produced using each chemical mechanism. This non-linear relationship was similar to that previously reported from observational studies. With each chemical mechanism, the absolute increase in ozone with temperature was greater for temperature-dependent chemistry than the increase ozone with temperature due to isoprene emissions. The largest increases in ozone mixing ratios were obtained in High- NO_x conditions and the lowest increase in ozone mixing ratios was achieved using Low- NO_x conditions.

The O_x production normalised by the total loss rate of emitted NMVOC was constant with temperature showing that the production of O_x with temperature was controlled by the loss rate of VOCs. The increased loss rate of VOCs with temperature was mainly due to the increase of OH with temperature. Net production of O_x increased with temperature in all NO_x conditions due the temperature dependent chemistry of RO_2NO_2 species, such as PAN. At higher temperatures the equilibrium of RO_2NO_2 (??) shifts towards decomposition to RO_2 and NO_2 thus at higher temperatures more RO_2 is available for O_x production via (??).

The box model results were also compared to observational data and output from the 3-D model WRF-Chem. The rate of increase of ozone with temperature from the box model was about half the rate of increase of ozone with temperature using observational and WRF-Chem output. Observational data and the output of 3-D models such as WRF-Chem include additional effects of temperature on ozone, such as stagnant conditions, where low wind speeds lead to the accumulation of oxidants promoting ozone production. Box model simulations were performed without mixing to approximate stagnant conditions and in these box model simulations the increase in ozone with temperature was faster than the box model simulations including mixing. The differences in the rate of increase of ozone with temperature between mixing simulations and chemical mechanisms indicated a higher sensitivity to mixing than the choice of chemical mechanism.