Development and Preliminary Results of an Explicit West Australian Tropospheric Photochemical Model

S. M. Saunders and Y. Ma

Disciplines of Chemistry and Geography, University of Western Australia, Perth 6009, Western Australia.

Abstract: An important area of study to assist in the understanding of the complex factors controlling air pollution is by the development of tropospheric photochemical models utilizing detailed chemical mechanisms. Conditions leading to photochemical pollution episodes (high ozone) vary depending on geographic location. To date highly explicit chemical models have been developed only for the UK, Europe and the US. In this work a highly detailed model appropriate to Western Australia has been developed. The elucidation of new detailed and more accurate chemical mechanisms has targeted specifically on volatile organic compounds (VOC) appropriate to the Australian environment, by identifying differences in emissions inventory data of the UK and USA. Preliminary application of the model has been in the determination of speciated VOC reactivities, for the first time under conditions appropriate to Western Australia providing a comparison with currently available reactivity scales. The model is being applied to the investigation of speciated VOC impacts on local pollution episodes aimed at aiding in the further understanding of the causes of local pollution episodes, and how to target reduction of these events

Keywords: *VOC oxidation; tropospheric ozone; Air quality modelling*

1. INTRODUCTION

Volatile organic compounds (VOC) are found throughout the planetary boundary layer and contribute significantly to the generation of both photochemical oxidants (including ozone) and fine aerosols. These have direct effects on health, through respiratory and eye irritations, and on climate change by modifying radiative budgets. Anthropogenic activity represents a major component of the global carbon load and as a result any future changes in emissions will continue to be a key consideration in air quality policy and climate change. Tropospheric models are pre-requisite in gaining a detailed understanding of the controlling processes and causes of poor air quality in different geographic locations and to predict future behaviour, in order to develop abatement policies that are based on strong scientific foundations.

There are many hundreds of emitted gas phase VOC, both anthropogenic and biogenic. They cover a vast range of volatilities, chemical functionalities and reactivity, which defines their participation in photochemical processes that contribute to air pollution. Each VOC reacts at a different rate, by a different chemical oxidation mechanism, and produces a differing contribution to ozone generation. A practical means of quantifying these differences is essential for the development of cost-effective ozone control policies, and this has been possible through the development of so called 'reactivity scales'. These give an indication of the contribution individual VOC make to photochemical ozone formation. However there is no widely accepted reactivity scale that applies under all conditions and in all locations, because the reactivity value of a VOC depends not only on its chemical properties, but also on the environmental conditions under which the compound reacts.

This paper describes the development of highly detailed photochemical model under conditions appropriate to Western Australia. To date highly explicit chemical models have been developed only for the UK, Europe and the US, and comparisons made between the UK POCP (Derwent et al. 1998, 2001) and US MIR (Carter 1994), reactivity scales. Preliminary application of the model has been in the determination of speciated VOC reactivities to determine differences in ozone formation, which depend on the Perth geographic location, local meteorological conditions, and local emissions. The study extends the determination of POCP values to the Southern hemisphere, and works towards gaining a detailed understanding of the sensitivities of photochemical ozone formation under widely varying conditions.

2. W.A. PHOTOCHEMICAL MODEL

A highly detailed photochemical model to simulate the development of ozone and other photooxidants in the Perth airshed has been developed, based upon local meteorology and emissions conditions that are known to give rise to elevated ozone observations (Rye, 1996). The air parcel to encompass the regions emissions extends to the top of the boundary layer and horizontally to a 10 x 10 km grid. The depth of the model boundary layer starts at 300m at 06:00 hrs and rises at a constant rate of increase throughout the morning reaching a height of 1800m by 14:00 hrs. The air parcel is followed through one photochemical day, as it passes over the more densely populated urban area, picking up pollutants during the morning, passing over the ocean where the photochemical processing develops to be brought back over land later in the afternoon. The model input meteorological conditions, emissions, aloft and initial concentration data for known high ozone episodes in the Perth region are taken from the PPSS (Perth Photochemical Smog Study) (Cope and Ischtwan 1995). Solar declination and latitude are set at -19.60 and -31.95026^{o} respectively appropriate for average summer time conditions in Perth. Initial concentrations were set for NOx at 10ppb, CO at 150ppb, CH_4 at 1700ppb, HCHO at 2ppb and O_3 at 25 ppb. The initial concentrations for the remaining VOC were adapted from the information of the Perth airshed given in Cope and Ischtwan 1995. For those VOC not speciated in the reactive organic compound emissions, but included in the model, initial concentrations were set to a baseline level of 1ppb.

These initial conditions and emissions are notably different to those used in other related studies, (Derwent et al. 1998, 2001) and provides further investigation of elevated ozone episodes under very different regional conditions.

The chemical development of a defined species in the air parcel is described by a series of differential equations of the form

$$\frac{dCi}{dt} = P - L.Ci - \frac{VCi}{h} + \frac{Ei}{h} - (Ci - Bi)\,\frac{1dh}{h\,dt}$$

where Ci is the species concentration in the air parcel, P is the instantaneous production from photochemistry, L.Ci is the instantaneous loss rate by photochemistry, V is the species dependent dry deposition rate, h is the time-dependent boundary layer depth, Ei is the local emission rate from pollution sources, and Bi is the background concentration of species aloft (see Derwent et al. 1998, 2001). The system includes 4468 simultaneous stiff differential equations integrated using a variable order Gear's method of FACSIMILE (Curtis and Sweetenham, 1987). The tropospheric degradation of the emitted species is defined in a highly explicit chemical mechanism. This consists of the current master chemical mechanism, MCMv3, together with further expansion to include new species identified in the Australian emissions database (NPI 2000) and from the Perth baseline air toxics project (DEP, 2000). The new species are not part of the 124 base UK emissions inventory species that are currently implemented in MCMv3. The developments are described further in section 3. The current MCMv3 mechanism comprises 4353 chemical species and 12741 chemical reactions, it can be viewed and downloaded via the world wide web at http://chem.leeds.ac.uk:80 /Atmospheric/MCM/mcmproj.html

3. MCM DEVELOPMENTS

An assessment of the Australian NPI and Perth baseline air toxics project identified significant omissions in the treatment of emitted species in the MCMv3 reactions database. These include compounds from various group classifications, notably several halocarbon, oxygenate, aromatic and biogenic compounds. Further, at present the 124 primary emitted VOC included in MCMv3 account for ~70% of UK emissions (Derwent et al. 2003). Addressing not only the significant Australian omissions, but also other known emitted species that are not included in the primary VOC list of the MCM, represents an important part in its continued development. A large and ever changing number of VOC continue to be emitted. Development of the MCM to be appropriate in widening domains, further aids in establishing it as globally applicable mechanism.

Table 1. Halocarbons for which degradation schemes have been constructed. DEP (DEP 2000), NPI (NPI 2000) and NAEI (see http://www.naei.org.uk/, http://www.aeat.co.uk/ netcen/airqual/naei/annreport/annrep98/naei98.html)

VOC species	Australian Identification	UK emission inventory
Bromomethane	DEP,	NAEI
1,2-dibromoethane	DEP, NPI	
Chloroethane		NAEI
1,2-dichloroethane	DEP	NAEI
1,1-dichloroethane		NAEI
1,1,2,-trichloroethane	DEP	
1,1,2,2-tatrachloroethane	DEP	
1,2-dichloropropane	DEP	
1,1-dichloroethene		NAEI

Work to date has focused on the development of an explicit photochemical model appropriate to Western Australian conditions and initial testing. New degradation schemes have been constructed for the series of halocarbon compounds listed in Table 1. The reaction schemes have been developed using the MCM construction protocol (Jenkin et al. 1997 and Saunders et al. 2003).

This section of the mechanism consists of an additional 115 species and 292 reactions and for the first time includes degradation mechanisms for bromine containing compounds. The other significant primary VOC emissions, for which detailed mechanism construction is required, represent ongoing work.

4. MODEL VALIDATION AND COMPARISON WITH OZONE OBSERVATIONS

Rigorous testing of the model and detailed chemistry has not been carried out in the time frame of the current project. However, related work and testing of sub-parts of the mechanism has been shown to be entirely satisfactory, as discussed previously (e.g. Carslaw et al., 1999, Hayman and Jenkin 1999, Derwent et al., 2001, 2003), which give confidence in the description of the degradation schemes of the VOC and the associated ozone production.

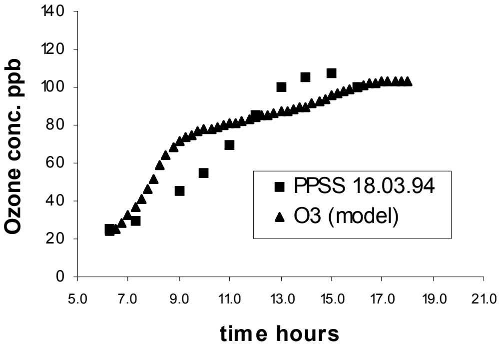

Figure 1 Time development of ozone concentrations in the base case model compared with the Perth Photochemical Smog Study (PPSS) on the 18.03.94 (from Cope and Ischtwan, 1995)

A comparison of the ozone development in the base case model simulation with the levels determined on a high ozone event day of the PPSS (Cope and Ischtwan, 1995), is given in Figure 1. This work provided the base case scenario conditions for the model setup. The peak model ozone concentration (103 ppb) is in close agreement with that observed at Cullacabardee on that day (110 ppb). This is also in comparable agreement with earlier studies where the model peak ozone concentrations are within a few ppb of available measurements and it is this measure that is used to determine the sensitivities to the VOC emissions. The shift of the model peak ozone to later in the afternoon is consistent with observations of elevated ozone levels in the Perth monitoring network, and is dependent on the monitoring location site and prevailing meteorological conditions. Data can be viewed on the DEP website at http://aqmpweb.environ.wa.gov.au:8000/ air_quality, e.g. on the 23.02.03 at the Rolling Green monitoring station.

5. REACTIVITIES UNDER PERTH CONDITIONS

Previous studies have shown that the peak model ozone concentrations are highly sensitive to the VOC emissions (Derwent at al. 2001), and provide a means for determining a relative indication of the reactivity of each VOC on the overall level of ozone generated. This was achieved by introducing an additional mass emission of an individual VOC above the base case scenario, and following the ozone concentration profile out to 18:00 hrs in separate model runs. The additional mass emission was given the same time of day dependence as the VOC emission, and was equivalent to the mass of ethene injected in the base case. It was identical on a mass basis for each of the individual VOC studied. The additional ozone generated over the base case was used in the calculation of a Photochemical Ozone Creation Potential (POCP) value as follows:

$$\mathrm{POCP}i = \frac{\text{ozone increment with the } i\text{th VOC}}{\text{ozone increment with ethene}} \times 100$$

with the value for ethene being 100 by definition.

6. INITIAL TESTING AND COMPARISONS OF POCP VALUES DETERMINED IN THE UK, US AND WEST AUSTRALIA

In order to provide some test of the model output, initially POCP calculations were made for the group of chlorocarbon compounds included as primary emitted VOC species in MCMv3, and also for cis-but-2-ene, a much more reactive VOC. Table 2 gives a comparison of POCP values determined in this study, with those previously studied under the very different conditions of north west Europe and north America. The results of this study showed similar trends to those determined previously. Giving confidence in the model simulations.

Table 2. POCP values determined in this study, West Australian conditions, and those reported in the literature (Derwent et al. 2001, and Saunders et al. 2003). Figures are used to illustrate the differences between values. Their accuracy should be taken as +/-5 units for POCP's below 20 and +/-20% otherwise.

VOC species	**POCP Europe**	**POCP North America**	**POCP West Australia**
Chloromethane	0.4	1	0.5
Dichloromethane	3.5	4	0.8
Trichloromethane	2.4	1	0.5
1,1,1-trichloro-ethane	-1.6	0	0.5
Trichloroethene	31.6	13	11.6
Tertachloroethene	2.7	0	1.1
Cis-1,2-dichloro-ethene	44.0	22	19.0
Trans-1,2-dichloro-ethene	42.5	21	17.2
Cis-but-2-ene	109.1	131	104.7
Bromomethane			0.1
1,2-dibromoethane			1.0
Chloroethane			3.5
1,2-dichloroethane			0.0
1,1-dichloroethane			3.5
1,1,2,-trichloroethane			3.4
1,1,2,2-tatrachloroethane			3.7
1,2 dichloropropane			0.7
1,1-dichloroethene			34.8

Further model experiments were performed for the additional halocarbon species, and the results are also given in Table 2. These are the first POCP determinations for this group of VOC and notably the first determination of POCP values for bromine species. The halocarbon alkane species all have low POCP values (< 5 +/- 5) with the bromine compounds also exhibiting small ozone forming potentials like their chlorine counterparts. The halocarbon alkene species have significantly larger POCP values. Under the single day high ozone development conditions of Western Australia 1,1-dichloroethene has the highest determined POCP value of 34.8. Figure 2. is a plot of POCP values determined under North American conditions against those determined in Europe and Western Australia. The trend lines are close to 2:1 and 1:1 correspondence respectively. This suggests that under the European multi-day conditions 1,1-dichloroethene is expected to exhibit a POCP value around 70. Which places it much higher in the overall ozone formation potential ranking than the other halocarbon species. These data are providing further insights into the assessment of speciated halocarbons in air quality policy.

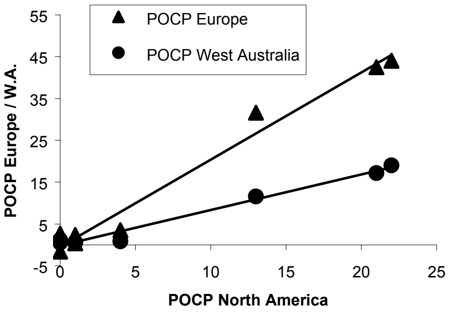

Figure 2 Scatter plot of halocarbon POCP values determined under West Australian and European conditions against those determined under North American conditions.

Even though many of these compounds are not highly reactive as indicated by their relatively low POCP values, they represent an important group in air quality models. Emissions of halocarbons are of considerable importance and many have significant global warming potentials (GWP) (see http://www.grida.no/climate/ipcc/emission). Therefore a detailed investigation of their speciated VOC impacts on tropospheric ozone generation also provides useful information in assessing their overall impact on air quality and climate change. The results provide further confirmation that choice of policy focus between single–day and multi-day conditions is important in establishing a quantitative reactivity scale particularly for such less reactive VOC. The close correspondence between the POCP values determined in Western Australia and those in North America clearly demonstrate how the single-day high ozone events effect POCP determination even though the North American conditions are much more highly polluted in terms of the initial O_3 (70ppb) and NOx (90ppb).

7. CONCLUSIONS

This study describes the development and preliminary testing of a highly detailed West Australian Tropospheric Photochemical Model. Initial calculations of POCP values for a series of halocarbon compounds have provided a comparison with previous studies under the very different conditions of north west Europe and north America. The work required the construction of degradation schemes for an additional group of halocarbons including for the first time 2 bromine containing species. These additional primary emitted VOC were identified as being significant in Western Australia and other industrialized nations, but prior to this study, not been treated explicitly in any photochemical model. The model simulations for this group of compounds under West Australian conditions enabled the first determination of POCP values for these VOC.

The model will continue to be developed with the addition of further significant compounds, which are currently not included in the primary emitted VOC listing of the MCM, together with an update of emissions to the latest data available for Perth (http://www.npi.gov.au/). The model will then be applied to the investigation of speciated VOC impacts on local pollution episodes.

8. ACKNOWLEDGEMENTS

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