Assessing aromatic compound impacts on photochemical ozone generation utilizing an updated Perth airshed model

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EXTENDED ABSTRACT

Atmospheric processing of aromatic compounds, which are known pollutants in urban air occurring predominantly from road transport sources, are a major contributor to photochemical oxidant formation as evidenced by the formation of ozone. It is believed that urban atmospheres contain a mixture of in excess of 100 speciated aromatic volatile organic compounds (VOC). Recent studies in understanding the degradation mechanisms of aromatic species have resulted in a significant update of the chemical mechanisms for the atmospheric degradation of aromatic compounds. The elucidation of new detailed and more accurate chemical mechanisms has targeted specifically the aromatic group of volatile organic compounds (VOC). These updates have been incorporated in the MCM methodology and made available on the MCM website (MCMv3.1 October 2003). In this work a highly detailed airshed model appropriate to Western Australia has been further developed and updated to not only encompass the aromatic mechanism developments of the MCM, but also the most recent emission inventory data for the region.

Initial studies using the updated model have been in the determination of differences in ozone formation from individual aromatic VOC, which will depend on the Perth geographic location, local meteorological conditions, and local emissions. Perth currently experiences relatively few high ozone days, however there are still ozone exceedances recorded every year with the ozone concentration reaching levels in excess of the NEPM standard and world recognized health standards (Figure 1). With the continuing economic growth and development in the region and the projected increase in use of road transport vehicles comes the potential for worsening air quality. Only through detailed airshed modeling is it possible to assess the impact of individual VOC and changes in their emissions scenarios.

The meteorological conditions in Perth, Western Australia that give rise to high ozone episodes are generally a result of light morning easterly winds which pass over the populated urban area and pick up pollutants in the morning. The air mass then passes off shore where the photochemical processing develops. The air parcel is brought back over land early in the afternoon, where it receives further emissions from the afternoon rush hour peak. These conditions are very different to the multi-day high ozone development in Europe, hence reactivity indicators for aromatic compounds, appropriate to Perth are determined for the first time.
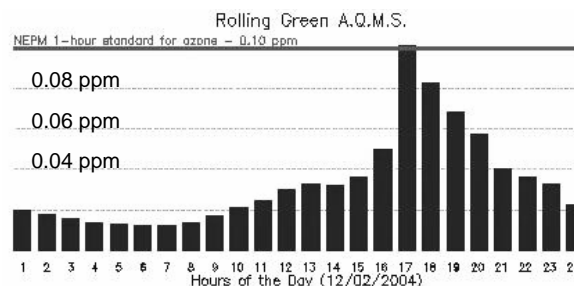
Figure 1. Ozone monitoring from Perth, showing exceedance of NEPM standard for ozone: Source (http://aqmpweb.environ.wa.gov.au/air_quality/Current_Air_Quality/Ambient_Monitoring_Data/Perth

The study is the first determination of the sensitivity of ozone levels to individual aromatic VOC emissions using the latest development in the aromatic degradation schemes of the MCM v3.1. The results are compared with data generated using the earlier Perth airshed model. The work is aimed towards gaining a detailed understanding of the sensitivities of photochemical ozone formation under widely varying conditions.

Results are discussed in terms of the impact of changes to the emission inventories and potential future emission reduction strategies.

1. INTRODUCTION

Tropospheric chemical models are designed to accurately simulate observed species profiles, and provide information on key components. Through the use of such models, aromatic compounds have been shown to make a greater contribution to ozone formation than any other class of emitted organic compound in Europe (Derwent et al. 1996) with toluene identified as the largest contributor. Emissions inventories are broadly similar for all large cities in industrialized nations (e.g. for Melbourne, AEPA (1998), which also indicates that aromatic compounds are a major contributor in Perth. Indeed the available Perth air monitoring data (DEP (2000) shows the major contribution from aromatic compounds, with toluene and benzene being the principal components of all the air samples taken. This assessment is made despite uncertainties in the emissions (Duffy et al. 1998) and mechanisms of degradation (e.g. Calvert et al. 2001 and references therein). Further, a recent study reported in Nature (Lewis et al. 2000) showed evidence to suggest that conventional air sampling analysis leads to a significant under estimation of aromatic components present in urban air.

The degradation of each emitted species occurs by a unique mechanism (because of differences in reactivity and structure), such that the relative contribution of each species to ozone formation varies from one compound to another (e.g. Carter and Atkinson, 1987, and Derwent and Jenkin, 1991). The W.A. photochemical model (Saunders and Ma, 2003) was initially developed using the master chemical mechanism (MCM) framework, which is the most comprehensive VOC degradation mechanism protocol available (Jenkin et al. 1997, 2003, and Saunders et al. 2003). The present study has been to update and extend this model to encompass the most current aromatic degradation mechanism available (MCMv3.1). Further updates to recently evaluated kinetic data and the emissions inventory for the region are described. The changes also include a more accurate representation of the emission profiles within the model.

The meteorological conditions and emissions in Perth that give rise to smog episodes are very different to the multi-day development in Europe, so initial studies using the updated model have been on the determination of aromatic VOC reactivities in Perth, WA for the first time.

2. UPDATES TO THE W.A. PHOTOCHEMICL MODEL

The initial development of a highly explicit photochemical model to simulate the development of ozone and other photooxidants in the Perth airshed has been described earlier (Saunders and Ma, 2003), and is based upon local meteorology and emission conditions that are known to give rise to elevated ozone observations (Rye, 1996). The framework of the model remains as described previously, being essentially a box model to encompass the regions emissions, however significant updates have been made to both the chemical degradation mechanism employed and the representation of the emissions data. 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. It then passes over the ocean where the photochemical processing develops to be brought back over land later in the afternoon. The model inputs, meteorological conditions, emissions, aloft and initial concentration data for known high ozone episodes in the Perth region are taken from the Australian Bureau of Meteorology (Kowald, BOM 2005) and the West Australian Department of the Environment (DEP 2000b, 2002). Solar declination and latitude are set at -19.60 and -31.95026° respectively, appropriate for average summer time conditions in Perth. Initial concentrations were set for NOx at 10 ppb, CO at 150 ppb, CH_4 at 1700 ppb, HCHO at 2 ppb and O_3 at 25 ppb. The initial concentrations for the remaining VOC were adapted from the information of the Perth airshed given by DEP (2002). 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, Saunders and Ma, 2003) and to date there has been no reassessment of aromatic sensitivities based on earlier aromatic chemical degradation mechanisms. This study provides the first investigation of the latest and most accurate aromatic degradation chemistry for assessing their impacts on high 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, as described previously (Derwent et al. 1998, 2001). The system includes 4644 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, MCMv3.1 (Oct 2003) comprising 4644 chemical species, 46 inorganic reactions and 13523 organic reactions. It can be viewed and downloaded via the world wide web at http://www.chem.leeds.ac.uk/Atmospheric/MCM/ mcmproj.html

2.1. Improvements to the Model Emissions Representation

Since the initial development of the highly explicit W.A. photochemical model (Saunders and Ma, 2003), more detailed emission reporting has become available, and this has enabled all the emissions representation in the model to be updated to the Perth airshed inventory of 1998-1999 (DEP, 2002). The original model used a simple step function to input an hourly emission term representing higher VOC and NOx early in the day decreasing in the afternoon and evening. The latest emissions data enables a more accurate representation of these hourly emission rates in a bimodal format shown in Figures 2 and 3, which is a reflection of increased emissions in both the early morning and afternoon peak periods.
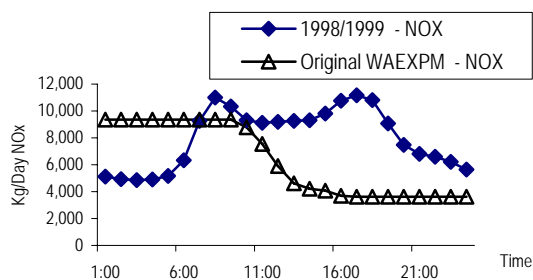

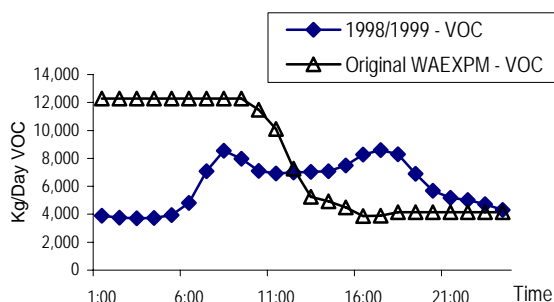**Figure 2.** Changes in NOx emissions data and model representation.

 Figure 3. Changes in VOC emissions data and model representation.

There is a significant difference in the total emissions reported between the periods on 1992-93 and 1998-99, resulting in a downwards trend of around 17% in total reported VOC and an upward

trend of around 28% in the total reported NOx emissions. The impact of these changes to potential ozone development in the Perth airshed is discussed in section 4.

2.2. Updates to the Chemical Mechanism

Changes to the chemical mechanism have been made to update the evaluated kinetic data set relevant to the MCM from IUPAC (2005). This data is available at http://www.iupac-kinetic.ch.cam.ac.uk/. Aromatic chemistry updates incorporate the EXACT project (Pilling et al. 2003) and related work available in the literature to June 2003, as described by Johnson et al. (2004). These changes have extended the aromatic chemical degradation scheme by 176 species and 825 reactions. It is important to represent the degradations as accurately as possible, as assessing the contribution that aromatic compounds make to urban air pollution is an integral part of developing emission reduction strategies.

3. 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 (Saunders and Ma, 2003), which gives confidence in the description of the degradation schemes of the VOC and the associated ozone production.
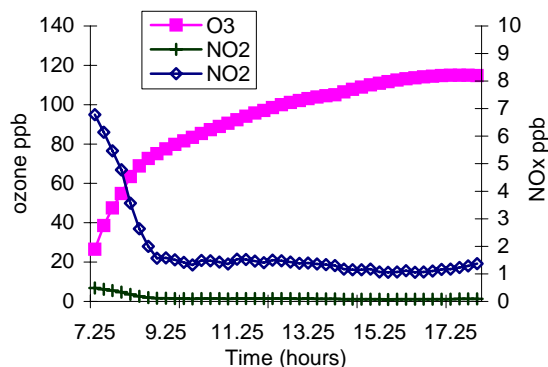

Figure 4. Base case model O_3 and NOx profiles

The ozone development in the base case model simulation (Figure 4) can be compared with the high ozone levels measured in Perth (Figure 1). The peak model ozone concentration is in close agreement with observation. 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 and NOx 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 e.g. Figure 1 from the 12 February 2004 at the Rolling Green monitoring station.
(http://aqmpweb.environ.wa.gov.au/air_quality/Current_Air_Quality/Ambient_Monitoring_Data/Perth)

4. RESULTS AND DISCUSSION

4.1. Base case model results

Updates to the model were made in a sequential manner, testing the ozone and NOx (NO and NO_2) output profiles as each update area (e.g. chemistry, emissions, and kinetics) was made. The stepwise changes did not have a large impact on the profiles. The greatest difference in ozone concentration throughout the daily profile was no larger that 8 ppb, and by 18:00 hours the difference had reduced to just over 2 ppb. However as these differences had been noted along the profile this suggested that the improved emissions representation was having a noticeable impact. To investigate further a model was setup, based on all the 2005 updates, but now reverting to the simplified step function representation of the emissions. Model runs were carried out to make an assessment of the contribution that an individual aromatic species makes to the overall ozone production. Hence, the two models differed only in their representation of the emissions profile; here again base case runs differed in ozone profile by a few ppb. As the focus of the study is on transport related VOC sources and that the major contributor is toluene, further model runs were carried out by incrementing the toluene emission. The increment 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. Ethene is often used as a reference compound in determining impacts on ozone generation, (Derwent at al. 1998, 2001) as it is regarded as a reactive species, which accounts for a significant (2-3%) amount of the total VOC emission. The same mass increment resulted in significantly different ozone changes. With the original emission representation, the toluene increment generated an increase in ozone production by the end of the photochemical day of little more than 0.5 ppb, whilst the same increment in the updated representation gave the increase at the end of the photochemical day as nearly 5 ppb. A similar result was also obtained carrying out a

check with incrementing the ethene emission in an analogous manner. These model runs suggest that the more realistic representation of the emission profiles is giving a heightened sensitivity to the ozone production, and that the second rise in VOC and NOx levels later in the day are inducing a higher potential ozone formation in the same air mass model. In terms of rank order of potential ozone formation there may be little difference, but the impact on ozone generation can influence the control measure employed to bring about future reductions

4.2. VOC and NOx sensitivity

It is important to try to quantify if the Perth air mass is in the VOC or NOx limited regime or in transition between the two. This was investigated using a VOC and NOx sensitivity indicator, (Sillman et al. 1997) by returning to the base case 2005 model, and determining the O_3 to NOz ratio (where NOz is defined as the sum of the concentrations of HNO3, PAN, PANS and nitrate aerosol) at the end of the photochemical day. This result can also be compared with further model runs implementing a 25% reduction, first the NOx and then the VOC emissions. The O_3 to NOz ratio was found to be 22, indicating an increased sensitivity to NOx. The model run with the 25% reduction in VOC resulted in a 0.2 ppb reduction in ozone concentration, whilst an equivalent reduction in NOx reduced the ozone by 8 ppb. The overall results indicate that Perth is currently NOx limited, and implies the importance of NOx control. However if road transport and other VOC sources increase significantly, this can alter the balance

4.3. Aromatic VOC impacts

Working with the current scenario, it is also possible to look at the current emissions and ranking of aromatic VOC, by determining the contribution each aromatic species makes to the ozone production. This was carried out by performing repeated model runs and in each run a specific aromatic VOC species emission was set to zero. The sum of the differences in ozone concentration between the base case and the run with the VOC emission set to zero would then be an indication of the contribution that particular VOC makes to the ozone formation over the photochemical day. The emissions of the other VOC were not adjusted by the switching off of a particular aromatic VOC. The results are presented in table 1. Aromatic VOC contribute 28% of the total transport related VOC emissions in Perth (DEP, 2002), with toluene and xylenes ranked the highest, however the model runs clearly show that

it is the trimethyl benzenes that have the largest impact on ozone generation. Keeping the total emission unchanged shows that the loss of one species emission can indeed lead to increased ozone (negative values in table 1) formation, as the reactivity of the remaining VOC adjust the overall chemical development of the air parcel in a highly non-linear fashion.

Table 1. Comparison of aromatic VOC contribution to ozone production. Values represent the ozone increase (-ve) or decrease (+ve) with respect to the base case model

Aromatic VOC species	% mass transport emission source (DEP, 2002)	Sum O$_3$ formation contribution (ppb) Base case emission	Sum O$_3$ formation contribution (ppb) 2*VOC emission
benzene	4.0	-0.5	-3.1
toluene	8.0	-0.6	-5.4
ethyl benzene	1.4	-0.2	55.0
xylenes	7.5	1.2	5.4
trimethyl - benzenes	2.1	4.2	26.0
ethyl toluene	2.4	0.04	-3.0
Other aromatics	2.6	–	–

This initial investigation was concluded considering a possible future scenario whereby NOx control to maintain current levels have been implemented, however VOC controls have not. The question then is how do these changes impact on overall ozone generation over a photochemical day, and does this impact on the O$_3$ to NOz ratio. This model was set up with NOx at the current levels, and double the VOC emissions. To attribute the increased VOC emission to road transport sources, the distribution of the VOC emissions was changed so that the doubling of the VOC was reflected only by an increase in the aromatic species. Overall this model resulted in an increase in ozone production at the end of the photochemical day of 3 ppb. The O$_3$ to NOz ratio gave a value of 23, close to the base case model, but despite the air mass still being more amenable to NOx control, the individual aromatic VOC species show an enhanced contribution to ozone formation. Now removing the trimethyl benzenes emission reduces the ozone generation as much as

26 ppb, and 55 ppb for ethyl benzene, over the photochemical day.

The study further demonstrates the need to consider all aspects of ground level ozone generation. The models can indicate the most significant control measure, determining if the air mass is VOC or NOx limited, but in addition the study also indicates that in implementing NOx control further reductions in ozone generation can also be achieved by targeting specific VOC species. In this model scenario, reducing the trimethyl and ethyl benzene VOC components, even though they are not the major ranking aromatic species, will have a significant impact on the ozone generation.

5. CONCLUSIONS

The aim of this study has been the further development and update of a highly detailed West Australian Tropospheric Photochemical Model. Initial investigations of the sensitivity of ozone production from the aromatic compounds included have enabled the first determination of scenario impact changes in the Perth airshed using the new MCMv3.1 aromatic chemistry degradation mechanisms.

This investigation of aromatic VOC impacts on tropospheric ozone generation in Perth provides useful information in assessing their overall impact on air quality. The results provide further confirmation that choice of policy focus needs to be continually assessed as airshed emissions change over time.

The model will continue to be developed and applied to the investigation of speciated VOC impacts and scenario modeling of possible future changes to the local emission inventory data, and to investigate the impact of these changes on local pollution episodes. Further work is continuing towards making an assessment of the airshed model results to compare with single VOC environmental chamber studies, on which the development of detailed chemical airshed models is highly dependent.

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