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EVALUATION AND CHARACTERISATION OF REACTIVITY METRICS

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EXECUTIVE SUMMARY

This report describes the evaluation and characterisation of reactivity metrics to support the United States Environmental Protection Agency's efforts to update its reactivity policy for the attainment of ozone air quality standards. The review is based on three detailed computer modelling studies which taken together have made a significant contribution to basic understanding of the likely role that reactivity considerations could play in ozone control strategies. Reactivity-based policies should work efficiently on both the urban and regional scales by reducing episodic peak ozone levels and by reducing exceedances of the ozone air quality standards. Two preferred metrics have been selected as the most promising for policy development and these are the EKMA and Regional or 3-D Maximum Incremental Reactivity metrics. 3-D Eulerian regional air quality models have been demonstrated to be ideal tools for the visualisation of the ozone impacts of reactivity-based VOC substitution strategies across central California, the south-western and south-eastern United States of America. The choice of chemical mechanism, together with its adequacy and completeness, are crucial to the estimation of reactivity metrics and the compilation of reactivity scales.

If the potential value of reactivity-based VOC control strategies is to become accepted by policy-makers for the attainment of ozone air quality standards, then two basic tools will be required. The first is an evaluated reactivity scale that expresses our best understanding of the relative importance of each of upwards of 100 to 200 VOCs in photochemical ozone formation under given environmental conditions. The second is a 3-D Eulerian regional air quality model to provide the best possible visualisation of the urban and regional scale ozone impacts of candidate reactivity-based VOC control strategies.

1. Introduction

Sunlight-driven photochemical reactions in the atmospheric boundary layer involving volatile organic compounds (VOCs) and nitrogen oxides (NO_x) result in the formation of ozone and fine particles. Each VOC has widely differing reaction rates and shows differing propensities to form ozone. Each VOC will therefore make a different contribution to the elevated ozone concentrations found in each pollution episode in each situation. Basic understanding of these different reaction rates and reaction pathways for each VOC has increased steadily in recent years to the extent that, the United States Environmental Protection Agency is considering whether it is possible to use this increased understanding to develop more efficient, accurate and cost-effective control strategies for meeting the ozone air quality standards.

The focus of controls on the emissions of ozone precursors has been largely on the reductions in mass emissions of VOCs without regard to their different contributions to photochemical ozone production (Dimitriades, 1999). However, included in the policy framework has been the provision for the exclusion from the emission control regulations of those compounds that are considered to be of negligible reactivity. Inherent in this approach is the view that selective control of VOC emissions is more cost-effective than the indiscriminate mass control approach.

The contribution made by any individual VOC to photochemical ozone formation depends crucially on environmental conditions. However, the contributions made by one VOC relative to another, or pairs or groups of VOCs relative to each other, are much less variable. Ethane is thus relatively unreactive compared with most VOCs and isoprene is relatively more highly reactive, under most conditions. The relative rankings of VOCs in a quantitative table is termed a reactivity scale and the most frequently quoted such scale is the Maximum Incremental Reactivity (MIR) scale (Carter, 1994). The MIR scale is the most appropriate scale to quantify VOC reactivity under photochemical ozone formation conditions most sensitive to VOC emissions under the highest NO_x conditions associated with intense ozone source regions in the Los Angeles basin. It has been adopted in the state of California for the purpose of implementing reactivity-based regulations (CARB, 1993).

The Reactivity Research Working Group (RRWG, 1999) coordinates policy-relevant research related to VOC reactivity and has overseen three studies performed by Carter et al. (2003), Arunachalam et al. (2003) and Hakami et al. (2003, 2004). Taken together, these three studies have made a significant contribution to basic understanding of the likely role that reactivity considerations could play in ozone control strategies. These studies have shown that reactivity-based policies should work efficiently on both the urban and regional scales by reducing episodic peak ozone levels and by reducing the exceedances of the ozone air quality standards.

This report describes the evaluation and characterisation of reactivity metrics to support the United States Environmental Protection Agency's efforts to update its reactivity

policy for the attainment of ozone air quality standards. The review is based on the above three studies performed by Carter et al. (2003), Arunachalam et al. (2003) and Hakami et al. (2003, 2004) and on the existing VOC reactivity literature, as appropriate.

2. Review and Assessment of VOC Reactivity Metric Studies

The incremental reactivity of a VOC species is estimated from the incremental increases in ozone exposure levels caused by the incremental increases in the emissions of particular VOCs. A ranked table of incremental reactivities for a series of VOCs comprises a reactivity scale. Because ozone exposure levels can be represented in a number of ways, these different representations or metrics can be used to define a number of reactivity scales.

Since reactivity-based policies are ultimately about achieving ambient air quality standards for ozone, the most appropriate quantification of ozone exposure levels is to use the 1-hour and 8-hour air quality standards. In addition, however, there may be many alternative methodologies for the integration of the ozone impacts across the model domains and over each episode day. Only a subset of the many possibilities have been considered here in the studies by Carter et al. (2003) and Hakami et al. (2003, 2004).

Before reactivities and reactivity scales can be quantified, it is necessary to specify the time period being studied, the model domains that are being analysed, the methods used to quantify ozone exposure levels in a given cell and the methodologies used to derive a single reactivity metric for the entire model domain.

Question 1. What are the attributes of the reactivity metrics that influence their suitability for use in large-scale policy applications ?

The main attribute of the reactivity metrics that influences their suitability for policy applications is robustness across model domains and between episode days. It is crucial that the relative positions of the VOCs or groups of VOCs in a reactivity scale, estimated for a given reactivity metric, do not shift significantly or change or reverse between different domains and episode days. An important issue is whether a reactivity scale that works in New York, with its high population density will also work in Atlanta with its large biogenic VOC emissions (Hakami et al. 2004).

A further important characteristic of a reactivity scale and hence an important attribute of a reactivity metric, from a policy perspective is its effective range (Carter et al. 2003). The effective range of a reactivity scale is the range of reactivity values generated between the most reactive VOC and an unreactive VOC such as ethane. If a reactivity scale is used with too low an effective range then there would be insufficient incentive for the consideration of reactivity-based policies. A reactivity scale with an unreasonably

high an effective range may lead to unacceptable ozone impacts with some large substitutions of low reactivity VOCs.

Hakami et al. (2004) consider six properties of reactivity scales and metrics that are relevant for air quality management purposes. These include spatial robustness, uncertainty, risk of being inaccurate, population weighting, fairness and regionally representivity. Ease of calculation is not considered to be an important attribute for a reactivity metric. Whilst spatial robustness is the most important property of a reactivity scale, the other five properties are best evaluated when candidate reactivity-based strategies have been visualized in a 3-D Eulerian air quality model.

Question 2. What are the most suitable reactivity metrics from both scientific and practical application perspectives for potential development of VOC control strategies based on VOC reactivity ?

Carter et al. (2003) describe how they have employed the CAMx model to study reactivity metrics across the eastern United States. The study period chosen was the NARSTO-NE episode which covered four days during July 1995. The model employed the Carbon Bond 4 (CB4) mechanism and was run at 4 km x 4 km, 12 km x 12 km and 36 km x 36 km scales. Reactivity metrics were estimated using the direct decoupled method (DDM) for 7 methods, 4 episode days, 3 grid resolutions and two ozone standards. In each case, a reactivity scale was produced comprising the following nine VOC species: OLE, formaldehyde, acetaldehyde, ethane, xylenes, ethanol, PAR, ethane and TOL.

Table 1 summarises the evaluation of each of the reactivity metrics over the different episode days, model domains and grid resolutions based on Carter et al. (2003). Carter et al. (2003) comment that the differences between the different reactivity metrics for the same species were less than the differences between the species for the same metric. Hence, in each case, a usable reactivity scale could be constructed from the available results. In general, the use of the 8-hour or 1-hour ozone standards made little difference to the reactivity metrics and the use of cut-offs in the ozone levels of up to 80 ppb also did not significantly change the reactivity metrics. Significant differences were seen between the 4 km x 4 km grid resolutions and the 12 km x 12 km and 36 km x 36 km resolutions because of the better representation at the 4 km x 4 km resolution of urban source regions which are more VOC-sensitive.

In summarizing their results, Carter et al. (2003) noted that for most model species the EKMA reactivity metrics were surprisingly close to the regional model relative reactivity metrics. The three 3-D grid model reactivity metrics that were favoured were: Regional MIR, Regional MIR to MOIR and Minimum Substitution Error – Method 1. The EKMA and Regional MIR reactivity scales showed the largest effective ranges, whilst those of the Regional MIR to MOIR and Minimum Substitution Error – Method 1, showed reduced effective ranges.

Table 1. The evaluation of the reactivity metrics over the different episode days, model domains and grid resolutions described by Carter et al. (2003).

Reactivity metric	Evaluation
Regional Average Ozone[a]	Disadvantage is that this metric includes many low ozone cells that are the least VOC-sensitive
Regional Maximum Ozone[b]	Disadvantage is that it is highly variable between episode days and model domains and sometimes the absolute peak ozone is insensitive to VOC emissions
Regional Average Ozone Over Standard[c]	This is a robust metric that shows little variability and gives the best estimates for regions in exceedance of standards
Minimum Substitution Error – Method 1[d]	Disadvantage that this method does not work well for low and negative reactivity species but weights heavily VOC-sensitive cells
Minimum Substitution Error – Method 2[e]	Disadvantage that this method is sometimes unreliable for some species
Regional Maximum Incremental Reactivity[f]	This is a robust metric because all the cells used have similar VOC-sensitivities and negative NO_x sensitivities. Disadvantage is that this is not a truly global metric
Regional MIR to MOIR[g]	This is a robust metric that shows little variability because all the cells used have similar VOC sensitivities and are where NO_x controls would be counter-productive

Notes:
   a. the average incremental reactivity over the entire model domain.
   b. the incremental reactivity in the cell with the domain-wide peak concentration.
   c. the average incremental reactivity for all grid cells exceeding the standard.
   d. the incremental reactivity that minimizes the sum of squares of ozone changes in all cells caused by substituting a VOC by the base ROG.
   e. the incremental reactivity that minimizes the sum of squares of ozone changes in all cells caused by substituting the base ROG by a VOC.
   f. The incremental reactivities in the cells with the highest base ROG sensitivity.
   g. The incremental reactivities for all grid cells with negative NO_x-sensitivity.

Table 2. The evaluation of the reactivity metrics over the different episode days, model domains and grid resolutions described by Hakami et al. (2004).

Reactivity metric	Evaluation
3-D Maximum Incremental Reactivity MIR-3D	Consistent across model domains and days and protective of urban populations with high NO_x levels
3-D Peak Ozone Incremental Reactivity[a] POIR-3D or 3-D Maximum Ozone Incremental Reactivity MOIR-3D	Based on the relative reactivity at one point and perhaps relatively rare conditions of most NO_x-limited, less typical of population centres, least VOC-sensitive
Least Square Relative Reactivity LS - RR	Consistent across model domains and episode days
Regional Average Ozone AVG	Showed considerable inter-domain variability
Regional Average Ozone Above Standard AVS	Showed considerable inter-domain variability
3-D Maximum Incremental Reactivity to Maximum Ozone Incremental Reactivity M2M	Showed greatest inter-domain consistency, little variability between episode days

Notes:
a. for the conditions where the sensitivity of the maximum ozone to the initial NO_x is zero.

Hakami et al. (2003, 2004) describe how they have used the Urban-to-Regional Multi-scale (URM) and MAQSIP 3-D models to estimate reactivity metrics over the Eastern United States and in central California. The NARSTO-NE episodes during May and July 1995 were used for the former domain and the SARMAP episode for the latter. The models were applied at a spatial resolution of 24 km x 24 km with other grid sizes up to 48 km, 96 km and 192 km and used the SAPRC 99 chemical mechanism. This mechanism represented 42 explicit VOC species of which 9 were lumped VOC species. Reactivity metrics using 6 different methodologies were calculated using the direct decoupled method.

In summarizing their results, Hakami et al. (2003) observed that the Peak or Maximum Ozone Incremental Reactivity POIR-3D or MOIR-3D reactivity metric was not adequately robust across the episode days and model domains. The Maximum Incremental Reactivity MIR-3D metric gave the best agreement with the box model reactivity scales for all episodes. The Least Square – Relative Reactivity LS – RR metric showed the best spatial consistency over the model domains. Reactivity metrics based on the 1-hour and 8-hour ozone standards behaved similarly and there was little difference between the metrics calculated with 80 ppb and 60 ppb ozone cut-offs. There were also

little differences between the reactivity metrics calculated with the different model emission inventories. However, the reactivities of aldehydes in the 3-D model were generally lower than those reported from box model studies due to the more efficient carry over of radical sources in the 3-D model. Reactivities of α-pinene and the trimethylbenzenes were lower than box model values and that of methanol was higher in the 3-D model.

Table 2 summarises the evaluation of the different reactivity metrics put forward by Hakami et al. (2004) covering the different models, episodes and domains. The three 3-D reactivity metrics that show the required consistency between the different model domains and episode days were reported as: Least Square Relative Reactivity LS – RR, Regional Maximum Incremental Reactivity to Maximum Ozone Incremental Reactivity M2M and Maximum Incremental Reactivity MIR-3D.

Question 3. What are the two or three most promising metrics from the science and policy perspective for use in developing reactivity-based control policies ?

Taking together the Carter et al. (2003) and the Hakami et al. (2003, 2004) studies, the most promising metrics for the development of reactivity policies are:
- EKMA-MIR, Regional MIR or MIR-3D,
- Regional MIR to MOIR or M2M and
- Minimum Substitution Error – Method 1 or Least Square Relative Reactivity.

However, there is an important requirement to develop reactivity metrics that generate reactivity scales with the widest effective ranges consistent with our understanding of the atmospheric chemistry of VOCs. **On this basis, the most promising reactivity metrics are EKMA-MIR and Regional MIR or MIR-3D.**

3. Review and assessment of the ozone impacts of reactivity-based policies for VOC controls

Based on the detailed studies performed by Arunachalam et al. (2003), Carter et al. (2003) and Hakami et al. (2003, 2004) a number of basic questions can be answered about the likely efficacy of reactivity-based strategies for VOC emission control policies.

Arunachalam et al. (2003) have used the Multi-scale Air Quality Simulation Platform (MAQSIP) model to investigate the impact of reactivity-based VOC emission control policies on the attainment of ozone air quality standards. The MAQSIP model was run for the August-September 2000 period of the Texas AQS campaign and for a period during June 1996 over the eastern United States. For the Texas study, the model resolutions were 5 km x 5 km, 15 km x 15 km and 45 km x 45 km whereas for the eastern United States study, they were set at 12 km x 12 km and 36 km x 36 km. Two different

chemical mechanisms were employed, namely Carbon Bond CB4 and RADM-2 (Stockwell et al. 1990) and 7 different ozone exposure metrics were calculated. The reactivity-based substitution scenarios evaluated were: a 15% reduction in man-made VOC emissions, substitution of 15% of all man-made VOC emissions with butanone and the substitution of non-mobile xylene emissions with 2-butoxyethanol.

The key finding presented by Arunachalam et al. (2003) was that reactivity-based VOC substitution strategies resulted in reduced ozone levels, particularly in source regions and in areas downwind of major urban and industrial centres. Noticeable changes in ozone were seen with the 15% substitution by butanone in a region dominated by natural biogenic emissions and not usually thought to be VOC-sensitive. The substitution of the highly reactive xylene with 2-butoxyethanol was beneficial in reducing exceedances of the ozone standards but small increases were noted in some ozone metrics, in some model domains and on some days. VOC substitution strategies appear to work better on peak ozone levels. Finally, gram-based VOC substitutions seem to produce more favourable ozone outcomes compared with mole or mol-C based strategies.

In addition to the studies of reactivity metrics discussed above, Carter et al. (2003) also performed some VOC substitution experiments with a view to evaluating the impact of the substitution of current VOC emissions with low reactivity or borderline exempt VOCs. Ethane was the chosen surrogate for these low reactivity VOCs. Varying amounts of ethane were added back to replace the entire man-made VOC emission inventory. This type of substitution led to almost as much ozone reduction as the complete curtailment of man-made VOC emissions. If enough of a low but positive reactivity VOC such as ethane was added, then ozone levels would eventually equal or exceed current levels. This level of substitution was found to involve replacing all man-made VOC emissions with about five times the mass of ethane.

Question 4. Is it possible to use incremental reactivities to develop more efficient control strategies for meeting the ozone air quality standards ?

Taken together, the studies by Carter et al. (2003), Arunachalam et al. (2003) and Hakami et al. (2003, 2004) have made a significant contribution to basic understanding of the likely role that reactivity considerations could play in ozone control policies. These studies have shown that reactivity-based policies should work efficiently on both the urban and regional scales by reducing episodic peak ozone levels and by reducing the exceedances of the ozone air quality standards. Regional air quality 3-D models have been shown to be ideal platforms with which to visualize the likely impacts of VOC-substitution strategies on the attainment of the ozone standards.

Question 5. What view should be taken on the increases in ozone found in some highly NO$_x$-sensitive regions with large substitutions of low reactivity VOC species ?

In principle, if the ozone increases in highly NO$_x$-sensitive regions, following large substitutions of low reactive VOC species, do not take ozone levels above the ozone standards then they are probably of little policy significance. However, they may still be of some scientific interest. Some form of process-analysis should be conducted to understand the mechanism of any such ozone increases found in 3-D Eulerian regional air quality models. An important issue is whether such ozone increases are likely to be a real feature of the atmospheric chemistry of the VOC substitution or an artifact of the cut-down representation of the oxidation of those VOCs with NO$_x$-sinks, together with free radical sources and sinks, in the chemical mechanisms adopted in 3-D models.

Question 6. Are reactivity-based controls ineffective or counter-productive in multi-day transport or stagnation scenarios ?

The studies by Carter et al. (2003), Arunachalam et al. (2003) and Hakami et al. (2003, 2004) certainly addressed multi-day ozone episodes but this is a long way from addressing multi-day transport or stagnation scenarios. This question therefore remains largely unanswered in the current studies evaluated above.

Further work will be required to address these issues in the North American context. This will entail developing an improved set of EKMA or trajectory scenarios so that box model reactivity scales can be estimated for multi-day and stagnation conditions. Although box models cannot represent the meteorological aspects of multi-day effects, they can represent the relevant issues of atmospheric chemistry. Stockwell et al. (2001) have shown that the EKMA-type models can be readily adapted to calculate multi-day effects and that the resulting reactivity scales generated are more representative of non-urban areas. 3-D Eulerian regional air quality models, in contrast, can fully represent the meteorological processes driving multi-day and stagnation effects. However, caution must be exercised in the representation of the oxidation of those VOCs with NO$_x$-sinks, together with free radical sources and sinks, in the cut-down chemical mechanisms employed in 3-D Eulerian models.

In Europe, long-range transboundary transport and multi-day formation are paramount and reactivity scales already fully take these issues into account (Derwent et al. 1998). Multi-day reactivity refers to the process by which emitted VOCs contribute to ozone formation on time scales beyond the day during which they were emitted. All VOCs, including the most reactive alkenes and carbonyls, have a capacity to produce ozone during the day following their emission and multi-day ozone formation is driven by the carry-over of unreacted parent VOC, of organic nitrogen compounds and by the step-wise formation and destruction of carbonyl compounds (Derwent et al. 2004). The cut-down chemical mechanisms used in 3-D Eulerian air quality models may not fully represent all

these processes and so they consequently underestimate the extent of multi-day ozone formation with the reactive alkenes and carbonyls.

4. Discussion of the major issues involved in estimating reactivity metrics

Question 7. How important is the choice of chemical mechanism in estimating reactivity metrics ?

The choice of chemical mechanism, together with its adequacy and completeness, are crucial to the estimation of reactivity metrics and the compilation of reactivity scales. The main task in the development of a reactivity scale is the distillation of all that is known concerning the kinetics and mechanism of the oxidation of individual VOCs into the one single number for each VOC in the reactivity scale.

The three reactivity studies employed three distinctly different chemical mechanisms: CB4, SAPRC 99 and RADM-2. These are all widely used mechanisms, each with its own strengths and weaknesses. It is a relatively straightforward task to evaluate them against each other under particular environmental conditions. Such an evaluation would not significantly help with the evaluation of reactivity metrics because the above three mechanisms have been designed largely to represent photochemical ozone formation in the base case environment. To develop a reactivity scale, we need chemical mechanisms for each of the many hundreds of VOCs that may not necessarily be explicitly represented in the base case but are an essential component of the perturbed cases in which incremental reactivities are being estimated.

To illustrate this point, it is useful to examine the three reactivity studies considered above. An explicit mechanism for ethane photo-oxidation had to be added to the CB4 mechanism to represent the contribution to photochemical ozone formation from a VOC which is exempt because of its low reactivity. Explicit mechanisms for 2-butoxyethanol and butanone were also added to CB4. RADM-2 has no explicit representation of butanone (Stockwell et al. 1990) and so it was assumed to behave in the same manner as the lumped species, KET, which represents all ketones of all carbon chain lengths. An explicit mechanism for 2-butoxyethanol was also added to RADM-2. **How are such extensions and assumptions to be adequately and robustly evaluated ?**

For a reactivity scale to be a practical and policy-relevant tool, it will need to address upwards of 100 to 200 VOCs. Detailed explicit chemical mechanisms will be required that can address accurately, the fate and behaviour of a large number of VOCs. Without access to these detailed and explicit chemical mechanisms, it will not be possible to check out the simplifications, assumptions and extensions made when additional VOCs are added to the simplified chemical mechanisms that are employed in 3-D Eulerian regional air quality models.

Additional laboratory, field and smog chamber experimental data may be required to construct and validate the detailed and explicit chemical mechanisms for individual VOCs. There are still many uncertainties in the explicit chemical mechanisms for the aromatics and other important classes of VOCs.

Question 8. What is the appropriate modelling framework, 3-D or box model, for the development of reactivity scales ?

Calculating reactivity scales using 3-D Eulerian air quality models is a significant undertaking, as the three studies discussed above have shown. It has been possible to calculate reactivities for up to 42 VOCs in the URM model (Hakami et al. 2003, 2004) but this is a long way off the number that would be required for the development of a practical and policy-relevant reactivity scale. A significant effort will be required in the preparation of accurate but simplified representations of the fates and behaviour of each VOC so that computer run times do not become inordinately long. It is not clear whether such simplifications will necessarily be available for all candidate VOCs.

A more practical alternative is the development of an improved set of EKMA-type box model or trajectory model scenarios that can be used to evaluate reactivities. Although box models cannot represent specific episodes in detail, they permit the use of fully detailed and explicit chemical mechanisms. They can represent the major conditions that control VOC reactivity (Carter, 1994) and they can represent the atmospheric chemistry issues relevant to multi-day and stagnation conditions (Derwent et al. 2004).

To exploit fully the potential of reactivity-based strategies in the future, both box and 3-D Eulerian regional air quality models will be required. Indeed, one of the important conclusions of the Carter et al. (2003) study addressed the concern as to whether reactivity scales generated using EKMA-type box models could represent reactivity issues over the regional scale. The close similarity between the EKMA-type box model scales and the corresponding 3-D regional MIR scale on the 4 km x 4 km model domain, shows that, indeed, both box models and 3-D Eulerian models are capturing the same important features of regional scale photochemical ozone formation (Carter et al. 2003).

This viewpoint necessarily represents, at first sight, a departure from that set out by the Reactivity Research Working Group (RRWG, 1999) which considered that 3-D Eulerian regional scale air quality models are the only tools that can realistically capture the long-range impacts of VOCs.

Hakami et al. (2003, 2004) describe how 3-D Eulerian models account for the carry-over of species that provide a source of free radicals into the next day's chemistry and how this feature accounts for the lower reactivities for aldehydes compared with box models. It may well also account for the lower reactivity found for α-pinene and the higher reactivity found for methanol. This is an important observation and it strongly supports the viewpoint that only 3-D Eulerian models can realistically simulate the long-range

impacts of VOCs. However, there is a potential danger here if the carry-over of radical source species were not a real feature of VOC chemistry but an artifact of the simplifications and non-stoichiometric factors introduced in the cut-down representations of VOC chemistry in the 3-D models. If the carry-over of radical sources were an artifact of the chemical mechanism then its importance would have been considerably overstated by the 3-D Eulerian models and this would have led to the estimation of biased reactivities.

Whatever results are generated by 3-D Eulerian models, they are only as reliable as the simplified chemical mechanisms employed in them. Without access to box models, there will be no route by which the situation envisaged by the Reactivity Research Working Group can be reached and 3-D Eulerian regional scale air quality models become the only reliable tools that can realistically simulate the long range impacts of VOCs.

5. Next steps in the development of reactivity-based policies for VOC controls

If the potential value of reactivity-based VOC control strategies become accepted by policymakers for the attainment of ozone air quality standards, then a number of steps will need to be taken to underpin their development. These steps are laid out in the following paragraphs.

Two sets of basic tools will be required, as follows:

- An evaluated reactivity scale containing evaluated reactivity values for upwards of 100 to 200 VOCs, and
- 3-D Eulerian regional air quality models to visualise the impacts of potential reactivity-based strategies on the attainment of ozone air quality standards.

The basic principles being that the evaluated reactivity scale expresses our best understanding of the relative importance of each VOC in photochemical ozone formation under given environmental conditions and that the 3-D Eulerian regional air quality models provide the best possible visualization of the urban and regional scale impacts of potential reactivity-based strategies.

Step 1: Development of an interim reactivity scale

There are currently two independent methodologies for estimating reactivity values for upwards of a 100 VOCs under North American conditions. The first methodology has led to the production of the MIR scale and is based on the SAPRC family of chemical mechanisms (Carter, 1994). The second has led to the POCP scale and is based on the Master Chemical Mechanism (Derwent et al., 2001). Both adopt EKMA-like box models and both employ the same input data based on Baugues (1990).

The general level of agreement between the MIR and POCP values is excellent for a wide range of VOCs and VOC classes. The remaining differences need to be resolved where they exist. The two reactivity scales should then be reviewed and a combined interim reactivity scale should be constructed.

Step 2: Development of candidate reactivity-based strategies

Using the interim reactivity scale, all stake-holders should be encouraged to develop candidate reactivity-based strategies. In this way policy-makers can obtain some understanding of the types of substitutions and their geographic scales, that are being contemplated.

Step 3: Development of the SMOKE emissions processing system

It is likely that some changes will be required to the SMOKE emissions processing system in CMAQ so that the candidate reactivity-based strategies can be visualized in CMAQ and other 3-D Eulerian regional air quality models.

Step 4: Development of EKMA-type scenarios

The input data employed in the construction of the MIR and POCP scales were taken from Baugues (1990) and represent 39 urban areas at some point in time in the past when peak ozone concentrations were far greater than currently observed (Carter et al., 2003). There is a case for the development of an updated set of EKMA-type scenarios for intense urban ozone episodes and for those conditions responsible for multi-day transport and stagnation. Once these scenarios are available, it would be a straightforward task to generate MIR and POCP scales and to produce an updated and evaluated reactivity scale. The proposal would be to generate up to 100 of these updated scenarios from 3-D Eulerian regional air quality model simulations for a range of different air basins and ozone episodes, using present and future emission levels.

Step 5: Development of an evaluated reactivity scale

Whilst reactivity scales and the reactivity values that populate them are not basic geophysical constants, they are derived from them. In this context, basic geophysical constants include reaction rate coefficients, quantum yields and absorption cross-sections. There is a case for extending the work of the JPL and IUPAC chemical kinetic data

evaluation panels to the review of the chemical kinetic data for the reactions of OH, NO_3 and O_3 with VOCs and of the reactions of the alkyl, oxy, peroxy and peroxyacyl radicals produced by them. Such a panel could also review quantum yield and absorption cross-section data for the VOCs and their degradation products.

Evaluated chemical kinetic data could then be fed into the SAPRC mechanisms and Master Chemical Mechanism as they become available. These mechanisms would then be used with the updated EKMA-scenarios to develop an evaluated reactivity scale which would replace the interim scale for the development of candidate reactivity-based strategies.

Step 6: Assemble a 3-D Eulerian regional air quality model with an explicit mechanism

There is a case for taking a 3-D regional air quality model and adding an explicit chemical mechanism for each candidate VOC species and performing a 'gold standard' visualisation of one reactivity-based strategy in one air basin. This model run would then be used to bench-mark cut-down chemical mechanisms for that VOC species.

Step 7: Establish cut-down representations of VOC oxidation for 3-D Eulerian regional air quality models

The SAPRC and Master Chemical Mechanisms provide a framework within which cut-down representations of VOC oxidation could be developed for 3-D Eulerian regional air quality models. Protocol would need to be laid out, setting out the basic principles to be adhered to in mechanism simplification and the accuracy to be achieved in the representation of the production of ozone, temporary NO_x reservoirs, free radical sources and sinks and major oxidation products. Cut-down representations could then be tested against the 'gold standard' visualisation produced in step 6 above, on a VOC-by-VOC basis.

Step 8: Visualisation of the impacts of reactivity-based VOC controls on the attainment of ozone standards

Using the evaluated reactivity scale, potential reactivity-based VOC control strategies could be generated for ozone non-attainment areas. Cut-down representations of the oxidation mechanisms of the VOCs involved would then be added to the 3-D Eulerian regional air quality models, together with the required speciated VOC emission inventories generated using SMOKE. The 3-D Eulerian regional air quality models would

then be able to visualize the impacts of the reactivity-based strategies on ozone non-attainment. The model results would also show up any areas where ozone concentrations had increased and any impacts of meteorological and transport processes that cannot be allowed for in simple box models.

In this context, it is useful if the evaluated reactivity scale has the largest effective range that is consistent with our understanding of the atmospheric chemistry of VOCs. In this way, there would be maximum incentive given to the consideration of reactivity-based policies. The reactivity scale would then give an upper limit to the magnitude of the substitutions of low reactivity VOCs for highly reactive VOCs. Visualisation with 3-D Eulerian models would then provide a vital check that there were no unacceptable ozone increases, exactly as envisaged by Carter et al. (2003), Hakami et al. (2003, 2004) and Arunachalam et al. (2003).

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