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National Volatile Organic Compound Emission

Standards for Aerosol Coatings

Peer Review Report of

Reactivity Research Working Group (RRWG) Modeling Studies

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1. Background

Volatile organic compounds (VOCs) are a precursor to the formation of ground-level ozone in the atmosphere and their control is needed to attain ozone air quality standards in conjunction of control of nitrogen oxides (NO_x). Traditionally VOC control strategies to reduce ozone have focused on reducing the total mass of VOC emissions but it is well known that not all VOCs are equal in the amount of ozone formation they cause (e.g., Dimitriades, 1999). Control strategies that take into account these differences in "reactivities" of VOCs should provide a means for additional ozone reduction that could supplement mass-based controls. Examples of such control strategies include conversion of motor vehicles to alternative fuels in the California Low Vehicle Emission and Clean Fuel (LEV/CF) regulation (CARB, 1993) and reactivity-based emission limits contained in the California Aerosol Coatings Regulation (CARB, 2000).

Both regulations were adopted by the California Air Resources Board (CARB) on the basis of a reactivity scale, developed by Dr. William Carter at the University of California, Riverside, in the early 90s (Carter, 1994). The scale adopted was the maximum Incremental Reactivity (MIR) scale, derived from a series of highly simplified physical model (box model) simulations under conditions where ozone formation is most sensitive to VOC emissions. However, the MIR scale does not represent all conditions, e.g., multi-day transport or stagnation, where ground-level ozone is a problem, especially where ozone reduction is less sensitive to VOC controls. To address these concerns, the United States Environmental Protection Agency (U.S. EPA) participated in initiating the establishment of the Reactivity Research Working Group (RRWG, 1999; Hales, 2007) to coordinate policy-relevant research related to VOC reactivity.

Since 1999, the RRWG had developed and funded three major reactivity modeling research projects to address the effectiveness of reactivity-based controls and substitutions on multiple scales. The three studies, with the assumption that strong correlation between independent findings of the different groups would lend confidence to the overall conclusions, were conducted and documented individually by Carter et al. (2003), Hakami et al. (2003, 2004a, 2004b), and Arunachalam et al. (2003), and further peer reviewed (Derwent, 2004). All the three studies employed Eulerian grid models and chemical mechanisms for major regions of the eastern US and their primary tasks are the development and evaluation of reactivity metrics and the effectiveness of reactivity-based substitution scenarios. Together with a similar study conducted earlier in California (Martien et al., 2002), the three studies and the peer review have enhanced our basic understanding of the role that reactivity consideration could play in ozone control strategies and found that there is a good correlation between different relative metrics calculated with photochemical airshed models, regardless of the choice of model, model domain, scenario, or averaging time. Although these studies were not specifically intended to test the robustness of the box-model derived MIR metrics, the results suggest that the MIR metric is robust because of a good correlation between the scales calculated with photochemical airshed models and the box model derived MIR metric and a good "effective" range it represents.

Addition analysis was conducted by the U.S. EPA (ERG, 2007) to examine the differences between reactivity metrics and the findings were similar to the previous studies, i.e., the box-model derived MIR metric is reasonably correlated with the other 3-dimentional model derived metrics. Given the results described above and the practical limitations associated with the 183(e) rulemaking requirements and schedule, the U.S. EPA has concluded that it is reasonable to adopt the MIR-based limits developed by CARB in a national regulatory application (i.e., aerosol spray paints) since these limits are the most stringent in this source category (ERG, 2007).

The main objectives of this report are to review the above three modeling studies performed by Carter et al. (2003), Hakami et al, (2003, 2004a, 2004b), Arunachalam et al. (2003), and a peer review on the three studies by Derwent (2004), and to evaluate the U.S. EPA's conclusion that the box-model derived MIR is sufficiently robust for a national regulatory application. Specifically, this report responds to a number of conclusions/questions, provided by U.S. EPA (ERG, 2007), including the General Conclusions drawn in these studies and the specific conclusions drawn from each study.

2. Review and Assessment of the "General Conclusions"

The U.S. EPA has reviewed these reports and provided four General Conclusions related to EPA's intention to use the reactivity-based emission limits by CARB for aerosol spray paints, with a specific focus on the robustness of the MIR scale for regulatory applications (ERG, 2007). As mentioned earlier, although all these studies were not specifically intended to address these questions, some of the results are relevant and can be used to support the General Conclusions listed below.

Question 1: Given the current state of knowledge, is it reasonable to use a box model-based MIR metric (following Carter 1994) to compare the contribution to ozone formation of aerosol coatings that differ in the mass and composition of VOC emitted?

It is well known now that different VOCs contribute to ozone formation to different degrees in a given scenario because of their different reaction rates and mechanisms to form ozone. Significant efforts on quantifying VOC reactivity with respect to ozone formation have been made for 20 years and our understanding of VOC reactivity science has been significantly improved since. The first MIR-based regulation was developed by CARB in its LEV/CF program (CARB, 1993), and subsequently, the MIR scale was used to establish VOC emission limits contained in the California Aerosol Coatings Regulation (CARB, 2000). Concerns were raised on the reactivity quantification methodology since the MIR metric is derived from a box model, which lacks physical details such as transport and meteorology. To address these concerns, the above three studies (Carter et al., 2003; Hakami et al., 2003, 2004a, 2004b; Arunachalam et al., 2003) were initiated and, as the Derwent's review (2004) concurred, concluded that reactivity-based control strategies should work efficiently on the urban and regional scale by reducing episodic peak ozone levels as well as exceedances of the ozone air quality standards.

Regional air quality 3-D models are the ideal platforms to visualize the likely impacts of VOC-based control strategies on the attainment of ozone standards. However, it is not presently practical to calculate reactivity for over 600 chemicals or mixtures contained in the California Aerosol Coatings Regulation due to limitations on computational efficiency. Although the three studies were not intended to assess the robustness of the MIR metric for scientific and regulatory applications, both the Carter et al. report (2003) and the Hakami et al. report (2003, 2004b) found that the most robust metrics derived from regional airshed models are MIR-3D, LS-RR, and M2M, which are correlated well with the EKMA MIR for studied VOCs, suggesting the MIR metric could be as effective as other regional reactivity metrics in assessing contribution of different aerosol coatings to ozone formation. Although some discrepancy was found for certain chemicals, the overall conclusion is reasonably sound. Thus, it is reasonable to compare the contribution to ozone formation of different aerosol coatings VOCs, especially in VOC sensitive areas.

Question 2: Is it reasonable to use this metric in nationwide regulatory applications?

Although the reactivity-based VOC emission limits for aerosol coatings was specifically developed for California as most of the California's regions are VOC sensitive with respect to ozone formation, the emission limits can be extended to other regions based on the above three studies. The model domain of these three studies (Carter et al., 2003; Hakami et al., 2003, 2004a, 2004b; Arunachalam et al., 2003) and the California study (Martien et al., 2002) covers a good portion of the U.S. continent, including northeast US (Carter et al, 2003), eastern US and southeast (Arunchalam et al, 2003), eastern US (Hakami et al., 2003, 2004a, 2004b), and South Coast and Central California (Martien et al, 2002). The Hakami et al. (2004b) study also included nine sub-domain analyses, i.e., urban areas, non-urban areas, as well as different geophysical sectors while the Carter et al. (2003) study addressed the question of VOC vs. NO_x limitation. The results indicate that the 3-D reactivity metrics are generally robust over different environmental conditions, domains, and sub-domains, and the M2M, MIR-3D, LS-RR metrics exhibited the best consistency. In general, the domains or sub-domains whose emissions are dominated by anthropogenic sources showed more consistency among different metrics although the sub-domains with large biogenic emissions exhibited greater variability. Based on the good consistent correlations between the EKMA MIR and the M2M, IR-3D, and LS-RR metrics, it is reasonable to expect that the MIR metric can be used in nationwide regulatory applications.

Question 3: Is it reasonable to use this metric across all seasons?

Most of the modeling simulations carried out in the above three studies focused on summer episodes, where high ozone concentrations were predicted and observed, while the Hakami's study (2003, 2004a, 2004b) were also carried out for a different season, i.e., spring (May), when meteorology and emission profiles are expected to differ from summer (July). The results indicate a good correlation between two seasonal episodes (May and July in 1995 and 2010) for different metrics. Slope larger than one was attributed to the May episode being radical limited (lower biogenic emissions). Although more investigations, especially simulations in other seasons such as fall and winter are desirable, these are less policy relevant since exceedances of the ozone standards tend to occur in hot summers and reactivity-based control strategies are intended to reduce ozone peak concentrations on the attainment of ozone standards. Ozone reduction is expected to occur in other seasons in VOC sensitive areas as the result of implementing reactivity-based VOC control strategies. Thus, it is reasonable to use the MIR metric across all seasons.

Question 4: Is it reasonable to use this metric for other VOC emission source categories?

As mentioned earlier, CARB has adopted two MIR-based VOC regulations, i.e., the California LEV/CF program and the California Aerosol Coatings Regulation. These reactivity-based control strategies, in replacement of the traditional mass-based control programs, are intended to reduce more reactive VOCs, and subsequently to reduce peak ozone, and are expected to work for other emission source categories. Substitution analyses by Carter et al. (2003) and Arunachalam et al. (2003) included a number of substitution scenarios with different anthropogenic VOC emissions. The key finding by Arunachalam et al. (2003) was that the reactivity-based VOC substitution strategies resulted in reduced ozone levels, particularly in source regions and in areas downwind of major urban and industrial centers and appeared to work better on peak ozone levels and reducing exceedances of the ozone standards. Small increases were observed in some ozone metrics, in some model domains and on some days because the majority of the grid-cells fell within the NO_x-limited regime. The Carter et al. (2003) study indicates that reducing all anthropogenic VOC emissions resulted in modest ozone reductions although reductions in peak ozone are somewhat higher.

More recent studies by Derwent et al. (2007a, 2007b) indicate that the different VOC emission source categories show vastly different propensities for forming photochemical ozone as indexed by their photochemical ozone creation potential (POCPc), a concept similar to MIR. These studies conclude that across-the-board mass-based VOC emission reductions would necessarily underestimate the ozone benefits from controlling those stationary source categories that contribute most to photochemical ozone formation. In other words, VOC substitution strategies (substituting high reactive VOCs with lower reactive VOCs) for the stationary sources would offer significant ozone benefits compared with simple across-the-board mass emission reduction strategies. A similar reactivity-based control strategy is used in the Houston/Galveston/Brazoria area to control highly reactive VOCs emitted from point sources (Highly Reactive Volatile Organic Compounds (HRVOC) Emissions Cap and Trade Program) (TCEQ, 2003) and modeling simulations (Wang et al., 2007a, 2007b) suggest that this program could be effective in improving air quality in the area. At present, CARB is examining the feasibility in developing reactivity-based control strategies in other source categories such as consumer products and architectural coatings. The Hong Kong Environmental Protection Department (HKEPD, 2006) is also considering such strategies to combat ground-level ozone problem in Hong Kong.

3. Review of "Conclusions of particular interest to EPA" derived from each report

In addition to the General Conclusions, the U. S. EPA provides specific conclusions of interest to EPA, which are listed below for each of the six reports, and requests that these conclusions be reviewed and commented (ERG, 2007). Listed below are these conclusions, followed by my responses to them in italic.

1. Carter, W.P.L., G. Tonnesen, and G. Yarwood (2003) Investigation of VOC Reactivity Effects Using Existing Regional Air Quality Models, Report to American Chemistry Council, Contract SC-20.0-UCR-VOC-RRWG, April 17, 2003.

Conclusions of particular interest to EPA are:

- Except for the CB4 TOL model species, whose relative O3 impacts are much more sensitive to NOx conditions than comparable model species in other mechanisms, the ordering of reactivity rankings are generally preserved regardless of which region of the domain or quantification method are employed.
- The relative reactivities derived from regional model results were generally consistent with the results using the EKMA scenarios when derived using comparable metrics.
- Using 8-hour vs. 1-hour ozone averaging time does not significantly affect relative reactivity scales.
- Replacing all anthropogenic VOCs (AVOCs) with equal mass or moles of ethane resulted in ozone reductions comparable to, but somewhat less than, removing all AVOCs. If ethane was added back to replace the AVOCs on a "reactivity neutral" basis, ozone tended to increase in the non-urban regions but decrease in VOC sensitive areas dominated by urban emissions.

This study (Carter et al., 2003) describes how the CAMx grid model is used to assess the ozone impacts of Carbon Bond (CB4) VOC species, CO, and ethane across the eastern United States using DDM sensitivity analysis. A number of reactivity metrics were derived using the July 12-15 NARSTO-NE episode on the regional scale on daily maximum 1-hour averages as well as daily maximum 8-hour averages throughout the modeling domain. General conclusions derived from this study include insignificant difference on reactivity metrics between the use of the 8-

hour or 1-hour standards and consistent results between the use of the EKMA scenarios and 3-D regional model.

A detailed chemical mechanism such as SAPRC99 would be the most appropriate and crucial in reactivity assessment in both the EKMA and regional 3-D simulations. The shortcoming of the project is the use of an out-of-date, highly condensed chemical mechanism (CB4) due to limited budget although this study was not intended to develop actual reactivity scales for regulatory applications. For this reason, the reactivity metrics derived for some VOCs such as CB4 model species TOL were more variable because of its high sensitivity to NOx emissions. Nevertheless, the ranking of other species' reactivity metrics are reasonably consistent regardless of which method, domain, or mechanism is used.

In addition to the various reactivity metrics derived from the formal sensitivity calculations, substitution studies were performed. Because VOC contributions from biogenic sources dominated total eastern U.S. VOC emissions in the studied scenarios, ozone sensitivity to anthropogenic VOCs (AVOCs) was moderate in terms of ozone reduction. For example, replacing all AVOCs with ethane or eliminating all AVOCs resulted in comparable, moderate ozone reduction. Ozone tended to increase in the non-urban regions but decrease in VOC sensitive areas dominated by urban emissions if ethane replaced the AVOCs on a "reactivity neutral" basis. This is expected since reactivity-based control strategies are intended to work best in VOC limited areas. This is also important since exceedances of the ozone standards tend to occur in urban areas and non-urban regions are less policy relevant.

Overall, the report is well written and includes a comprehensive assessment of all the reactivity metrics studied. The conclusions derived are reasonably sound, justifiable and valuable for scientific communities and policy-makers.

2. Hakami, A., M.S. Bergin, and A.G. Russell (2003) Assessment of the Ozone and Aerosol Formation Potentials (Reactivities) of Organic Compounds over the Eastern United States, Final Report, Prepared for California Air Resources Board; Contract No. 00-339, January 2003.

Conclusions of particular interest to EPA are:

- None

See responses provided for report 3.

3. Hakami, A., M.S. Bergin, and A.G. Russell (2004a) Ozone Formation Potential of Organic Compounds in the Eastern United States: A Comparison of Episodes, Inventories, and Domains, Environ. Sci. Technol. 2004, 38, 6748-6759.

Conclusions of particular interest to EPA are:

- The metrics compare reasonably well (for most species) among different episodes, different emissions scenarios, different domains, and different averaging times.

- The results suggest that relative reactivity scales present a fairly robust method for ranking organic species based on their potential effect on ambient ozone concentration.
- The results here suggest that the use of reactivity scales is robust across domains, given the consistency found between this study, and similar ones conducted for southern and central California. On the other hand, the box model MIR scale appears to over-emphasize the differences between organic reactivities, particularly for the higher end of the spectrum and radical sources.

Both the Hakami et al. (2003) and Hakami et al. (2004a) reports are based on the same study and present the same results with the report 2 (Hakami et al., 2003) being more comprehensive. Report 3 (Hakami et al., 2004a) is a peer-reviewed journal article, derived from report 2 (Hakami et al., 2003). This study used the Urban-to-Regional Multiscale (URM) model coupled with a derailed chemical mechanism (SAPRC99) to calculate the reactivity of 32 explicit and 9 lumped compounds over the eastern U.S. and compare results to those derived from a similar study conducted in central California (Martien et al, 2003). In addition to the development of various reactivity metrics, this study is unique in the sense that it uses two episodes in two different seasons (May and July) as well as future scenarios, i.e., 2010, so that they can be used to test if the reactivity metrics can hold in different seasons, as stated in General Conclusion 3.

In general, this study suggests that these results support the use of reactivity-adjusted emissions regulations. Several conclusions drawn from this study can be evident to support the General Conclusions. The results indicate that the ozone reactivity metrics derived are fairly robust and consistent (for most species) among different episodes, different seasons, different emissions scenarios, different domains, and different averaging times. In particular, the regional 3-D metrics show fairly similar rankings for VOC reactivity when compared to the box model species although lower reactivity was observed for some of the more reactive radical-producing VOCs such as aldehydes. In other words, a good correlation between the box-model derived MIR metric and regional 3-D metrics suggests that the MIR-based control strategies could be as effective as those based on the regional 3-D metrics (General Conclusion 1). A good correlation between different domains (eastern US vs. central California) suggests that this metric could be used in nationwide VOC regulatory applications (General Conclusion 2). A good correlation between May and July episodes suggests that this metric could be used across other seasons although seasons other than summer are less policy relevant (General Conclusion 3). Further, a good correlation between different emission scenarios suggests that this metric could be used for other VOC source categories (General Conclusion 4).

Overall, this study is particularly useful in assessing the robustness of the MIR metric by examining the correlation between the EKMA MIR and regional reactivity metrics to support the General Conclusions provided by the U.S. EPA (ERG, 2007).

Additional research is needed to examine the behaviors of highly reactive radical-producing chemicals in the EKMA vs. regional conditions.

4. Hakami, A., M. Arhami, and A.G. Russell (2004b) Further Analysis of VOC Reactivity Metrics and Scales, Final Report to the U.S. EPA, Contract #4D-5751-NAEX, July 2004.

Conclusions of particular interest to EPA are:

- The LS-RR, M2M and MIR-3D scales best satisfy the desire for consistency. LS-RR, M2M and MIR-3D also led to similar scales, so the choice between them is not likely to lead to any significant differences. AVG, AVS and POIR-3D were found to have significant deficiencies.

This study is a follow-up project to the 2003 Hakami et al. study (Hakami, 2003) and its primary objectives are to examine additional metrics (i.e., AVG, AVS, and M2M) that can be compared with those developed by Carter et al. (2003), to assess the sub-domain variability of the reactivity scales, and to evaluate various reactivity metrics as candidates for regulatory applications. The results were similar to the previous study (Hakami et al., 2003) and are consistent for most species among different episodes, different seasons, different emissions scenarios, different domains, and different averaging times. Several criteria were proposed and examined in assessing the appropriateness of reactivity metrics for use in regulatory applications. Based on the criteria, the study concluded that the M2M and LS-RR appear to be the most robust metrics and the MIR-3D has also the desired consistency and can be viewed as protecting more populated areas. The sub-domain analysis indicates that more consistency was found for sub-domains whose emissions are dominated by anthropogenic sources among different metrics than sub-domains with large biogenic emissions. This provides additional support for the applicability of nationwide regulatory applications (General Conclusion 2).

5. Arunachalam S., R. Mathur, A. Holland, M.R. Lee, D. Olerud, Jr., and H. Jeffries (2003) Investigation of VOC Reactivity Assessment with Comprehensive Air Quality Modeling, Prepared for U.S. EPA, GSA Contract # GS-35F-0067K, Task Order ID: 4TCG68022755, June 2003.

Conclusions of particular interest to EPA are:

- Comparison of the metrics computed for the two different case studies, Eastern U.S. and Southeastern U.S., revealed mostly comparable trends in computed reactivities, with no significant outliers in either case.
- VOC substitution (replacing high reactivity compounds with low reactivity compounds) is beneficial in reducing both 1-h and 8-h ozone, with 1-h ozone showing greater ozone reduction than 8-h ozone in some cases.

- In some instances, small increases are seen in ozone, and it is possible that this type of substitution results in unique pollutant regimes and can vary from one region to the other.
- Metrics calculated using a higher ozone cutoff threshold showed better responses than those at lower threshold, indicating that VOC substitution strategies are more effective in reducing modeled peak ozone concentrations

The main focus of this study was on substitution analyses to assess the effectiveness of exemption strategy and high vs. low reactivity substitution strategy while the study also investigated a number of "indicators" to examine the distribution of VOC- and NOx-limited conditions. The Multi-scale Air Quality Simulation Platform (MAQSIP) was used for the August-September 2002 period of the Texas AQS campaign and a June 2006 period over the eastern US, respectively, to investigate the impact of reactivity-based VOC emission control policies on the attainment of ozone air quality standards. Two chemical mechanisms, i.e., CB4 and RADM-2 (Stockwell et al., 2000) were employed and seven different ozone exposure metrics were calculated.

The key finding of interest is that reactivity-based substitutions result in ozone reductions but the response is moderate since the domains modeled are dominated by biogenic VOCs. The substitution of low reactive species for high reactivity species is beneficial in reducing both 1-hour and 8-hour ozone, with the 1-hour ozone reduction being greater. Small increases in ozone concentration were observed in some instances where ozone formation is NOx-sensitive. In addition, the results indicate that the metrics derived with a higher ozone cutoff threshold responded better than low threshold, suggesting that the VOC substitution strategies could be more effective in reducing peak ozone levels, as intended.

This study suggests that the reactivity-based control strategies should be beneficial in reducing peak ozone on the attainment of ozone standards. Some recent modeling studies (Wang et al, 2007a, 2007b) also demonstrate that the reactivity-based control program, i.e., the Texas highly reactive emission cap and trade program (TCEQ, 2002), can be effective in improving air quality.

6. Derwent, R.G. (2004) Evaluation and Characterization of Reactivity Metrics, Final Draft, Report to the U.S. EPA, Order No. 4D-5844-NATX, November 2004.

Conclusions of particular interest to EPA are:

- 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.
- The main attribute of the reactivity metrics that influences their suitability for policy applications is robustness across model domains and between episode days. … 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. On this basis, the most promising reactivity metrics are EKMA-MIR and Regional MIR or MIR-3D.

- 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 effectiveness of reactivity-based controls in multi-day transport or stagnation scenarios remains largely unanswered in the current studies evaluated.
- EPA is also interested in comments on the next steps proposed for the development of reactivity-based policies for VOC controls.

This Derwent report (2004) reviewed the three modeling studies, i.e., Carter et al. (2003), Hakami et al. (2003, 2004a, and 2004b), and Arunachalam et al. (2003), assessed the regulatory applications of reactivity scales and provided recommendations for further development. The report's discussion is framed in the context of the eight questions, provided by RRWG (Hales, 2007). The report, along with some recent works of his (Derwent et al., 2007a, 2007b), suggests that the reactivity-based control strategies should work on both the urban and regional scales by reducing peak ozone levels as well as exceedances of the ozone air quality standards. A detailed chemical mechanism was recommended in deriving reactivity metrics. Although the report did not specify which mechanism was preferred, both SAPRC99 and MCM mechanisms seem to be the logical choice. Two main attributes of the reactivity metrics, i.e., robustness and effective range, were discussed in the report. On this basis, the most promising reactivity metrics were determined to be the EKMA-MIR and MIR-3D for regulatory applications. This is consistent with the existing applications, e.g., MIR-based regulations for the California LEV/CL and aerosol coatings programs, and the MIR-3D was one of the metrics, recommended by Carter et al., (2003) and Hakami et al. (2004b) for regulatory applications. Note: whether the EKMA-MIR is appropriate for regulatory applications was not evaluated in either Carter et al. or Hakami et al. studies.

The Derwent report (2004) contends that the three studies did not address the effectiveness of reactivity-based controls in multi-day transport or stagnation scenarios although the multi-day scenarios were included in these studies. It is suspected that the author was asking for regional model simulations for all the chemicals (there are over 600 chemicals or mixtures contained in the California Aerosol Coatings Regulations), not just for dozens of studied chemicals since the author recommends developing an improved set of EKMA or trajectory scenarios so that box model derived scales can be estimated for multi-day and stagnation conditions. The advantage of using improved EKMA scenarios is that a detailed chemical mechanism can be used to estimate reactivity for 600 plus chemicals, which 3-D models cannot accomplish at this time due to limitations on computational efficiency.

Further, the report includes eight recommended steps toward implementation of reactivity-based regulatory applications, which presents a good compromise between the EKMA-MIR and regional metrics for the above reason. The steps include development of EKMA-type scenarios (step 4), designed for intensive urban ozone episodes and multi-day transport and stagnation (Stockwell, 2001). The current 39 city scenarios (Baugues, 1990) used to derive EKMA reactivity metrics were developed in the late 80s when peak ozone concentrations were far greater than currently observed, thus are out of date. Although step 5 focuses on development of an evaluated reactivity scale by reviewing chemical kinetic data for the reactions of OH, NO_3, and O_3 with VOC and of the reactions of the alkyl, oxy, peroxy, and peroxyacyl radicals produced by them and incorporating the data into the SAPRC or MCM mechanisms, additional chamber experiments specifically intended for assessing some problematic aspects of the mechanisms such as aromatics are highly desired. A detailed and evaluated chemical mechanism is most crucial to derive robust reactivity scales in both the EKMA and regional model simulations so an improved mechanism should be a high priority when assessing VOC reactivity.

4. Conclusions and Recommendations

This report evaluates the three detailed computer modeling reactivity studies and associated reports and their relevance to the U.S. EPA's intention to use the MIR-based emission limits established by CARB as the basis for a national emission standard for aerosol spray paints. In particular, the report addresses a number of questions/ conclusions drawn from these studies, based on the collective findings from these studies and any additional information found in literature. In general, these three modeling studies are well documented and the conclusions derived from each study are scientifically sound. Although the objectives of these studies were to develop 3-D reactivity metrics and to assess the effectiveness of reactivity-based chemical substitutions, and were not intended to assess the robustness of the EKMA MIR for reactivity-based control strategies, useful information can be drawn from these studies to support that the EKMA MIR metric is appropriate for scientific and regulatory applications.

Both Carter et al. and Hakami et al. studies found a good correlation between the most robust reactivity metrics derived from the regional airshed models, and the EKMA MIR, suggesting that the use of the MIR metric could be as effective as other regional metrics in reactivity-based control strategies. The domain, sub-domain, and VOC vs. NO_x grid cell analyses by three studies have a good spatial and temporal coverage and suggest that the reactivity-based chemical substitutions should be efficient in reducing peak ozone levels nationwide. The MIR metric should be robust across all seasons although other seasons are less policy relevant since exceedances of the ozone standards tend to occur in hot summers. This metric can be used for other VOC emission categories for control strategies. The recommended eight steps by Derwent (2004) represent a good compromise since they address the shortcomings contained in the EKMA and regional model simulations.

Although this report concludes that the MIR metric is reasonably sound for its use in a national VOC rule, several aspects of the MIR metric should be further improved. First, a state-of-the-art mechanism is most crucial in developing this metric. Although the SAPRC99 was considered the state-of-the-art, it must be updated on a regular basis since the science of atmospheric chemistry is evolving (Carter et al., 2007). For instance, recent studies (Carter et al., 2004, 2005) indicate that an improved mechanism for the aromatics is needed. In addition, the base ROG mixture used in reactivity chamber experiments needs to be re-evaluated since its reactivity is much higher than observed in the atmosphere. Second, the 39 city scenarios used in calculating MIR values were taken from Baugues (1990) and need to be updated since ozone levels in those scenarios are far greater than currently observed. Third, to visualize the impact of reactivity-based control strategies on the attainment of ozone standards nationwide, a global model that can cover the entire U.S. continent is desired. Fourth, a monitoring and verification program should be designed to ensure the success of the reactivity-based emission reduction strategies. In addition to ozone impacts, other environmental impacts such as secondary organic aerosol, multimedia impact, health effects, ozone depleting potential, and global warming potential should be considered when assessing chemical substitutions, as suggested by CARB (2006).

5. References

Arunachalam S., Mathur R., Holland A., Lee M.R., Olerud D., and Jeffries, H. (2003) Investigation of VOC reactivity Assessment with comprehensive air quality modeling, Final report to the U.S. EPA, Carolina Environmental Program, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Baugues, K. (1990) Preliminary planning information for updating the ozone regulatory impact analysis version of EKMA, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

CARB (1993) Proposed regulations for low-emission vehicles and clean fuels. California Air Resources Board, Mobile Source Control Division, El Monte, California.

CARB (2000) Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, "Determination of Volatile Organic Compounds in Consumer Products", California Air Resources Board, Stationary Source Division, Sacramento, California, May 5.

CARB (2006) Environmental Impact Assessment of tert-Butyl Acetate, California Air Resources Board, Research Division, Sacramento, California.

Carter W.P.L. (1994) Development of ozone reactivity scales for volatile organic compounds, Journal of Air and Waste Management Association 44, 881-889.

Carter W.P.L. (2004) Development and evaluation of a gas-phase atmospheric reaction mechanism for low NOx conditions, Final report to California Air Resources Board, University of California, Riverside, Contract number 01-305, May 5.

Carter W.P.L. (2005) Evaluation of atmospheric impacts of selected coatings VOC emissions, Final report to California Air Resources Board, University of California, Riverside, Contract number 00-333, March 25.

Carter W.P.L. (2007) Updated chemical mechanisms for airshed model applications, Final report to California Air Resources Board, University of California, Riverside, Contract number 03-317, in preparation.

Carter W.P.L., Tonnesen G., and Yarwood, G. (2003) Investigation of VOC reactivity effects using existing regional air quality models, Final report to the Reactivity Research Working Group, Center for Environmental Research and Technology, University of California, Riverside, California.

Derwent R.G., Jenkin M.E., Saunders S.M., Pilling M.J., and Passant, N.R. (2005) Multiday ozone formation for alkenes and carbonyls investigated with a Master Chemical Mechanism under European conditions. Atmospheric Environment, 39, Pages: 627 - 635.

Derwent R.G., Jenkin M.E., Passant N.R., and Pilling M.J. (2007) Photochemical ozone creation potentials (POCPs) for different emission source of organic compounds under European conditions estimated with a master Chemical mechanism. Atmospheric Environment 41, 2570-2579.

Derwent R.G., Jenkin M.E., Passant N.R., and Pilling M.J. (2007) Reactivity-based strategies for photochemical ozone control in Europe. Environmental Science & Policy, in press.

Dimitriades B. (1999) Scientific basis of an improved EPA policy on control of organic emissions for ambient ozone reduction. Journal of Air and Waste Management Association 49, 831-838.

ERG (2007) Peer review of the reactivity Research Working Group Modeling studies, Eastern Research Group, Agreement Number 0223.00.016/1.

Hakami A., Bergin M.S., and Russell A.S. (2003) Assessment of the ozone and aerosol formation potentials (reactivities) of organic compounds over the eastern United States, Final report to the Reactivity Research Working Group, Atlanta, Georgia.

Hakami A., Arhami M., and Russell A.G. (2004) Further analysis of VOC reactivity metrics and scales, Final report to the Reactivity Research Working Group, Atlanta, Georgia.

Hales J.M. (2007) The Reactivity Research Working Group: A chorological overview and evaluation, A report to NARSTO, February.

Hong Kong Environmental Protection Department (2006) Personal communication.

Martien P., Harley R., Milford J., Hakami, A., and Russell A. (2002) Development of reactivity scales via 3-D grid modeling of California ozone episodes, Final report to California Air Resources Board, Contract number 98-309, May.

RRWG (1999) VOC reactivity science assessment: Executive Summary, Reactivity Research Working Group. http://www.cgenv.com/narsto/reactinfo.html.

Stockwell W.R., Middleton P., Chang J.S., and Tang X. (1990) The second generation regional acid deposition model chemical mechanism for regional air quality modeling, J. Geophys. Res. 95, 16,343-16,367.

Stockwell W.R., Geiger H., and Becker K.-H. (2001). Estimation of incremental reactivities for multiple day scenarios: An application to ethane and dimethoxymethane, Atmospheric Environment 35, 929-939.

TCEQ (Texas Commission on Environmental Quality). (2002). Controlling Highly Reactive Volatile Organic Chemicals (HRVOCs), http://www.tceq.state.tx.us/implementation/air/sip/hrvoc.html, December 13.

Wang L., Thompson T., McDonald-Buller E.C., Webb A., and Allen D.T. (2007) Photochemical Modeling of Emissions Trading of Highly Reactive Volatile Organic Compounds in Houston, Texas. 1. Reactivity Based Trading and Potential for Ozone Hot Spot Formation, Environmental Science Technology, 41(7), 2095-2102.

Wang L., Thompson T., McDonald-Buller E.C., and Allen D.T. (2007). Photochemical Modeling of Emissions Trading of Highly Reactive Volatile Organic Compounds in Houston, Texas. 2. Incorporation of Chlorine Emissions, Environmental Science Technology, 41 (7), 2103 –2107.