



**REACTIVITY  
RESEARCH  
WORKING  
GROUP**

**DRAFT**

**Summary of the Reactivity Research Working Group Meeting for January 8-9, 2003 Research Triangle Park, NC.**

**Wednesday January 8, 2003**

Attendees: Bob Avery, Dan Baker, Rick Brown, Bill Carter, Ed Casserly, Andy Collantes, John Dege, Basil Dimitriadis, Susan Eastridge, Don Fox, Barbara Francis, Doug Fratz, Bob Hamilton, Tom Helms, Bob Hinrichs, Andrew Jaques, Bill Johnson, Jon Kurland, Deborah Luecken, Dongmin Luo, Paul Makar, Bruce Moore, Dave Morgott, Bob Nelson, Bill Rawson, Doug Raymond, Ted Russell, Bob Stallings, David Sanders, Stan Tong, Robert Wendoll, Jeff West,

*I. Welcome and Introductions. Review of Agenda*

At 1:00 PM, Don Fox, RRWG Chair called the meeting to order and introduced the agenda. Attendees introduced themselves. The primary focus of this meeting was a review of the Task 1579.1 objectives and modeling results and discussion of subsequent research questions.

*II. Task 1579.1 Objectives and Research Results - Don Fox*

A review of Task 1579.1 objectives and research results was presented by Don Fox. (Appendix A. Task 1579.1 Summary of Modeling Results). Task 1579.1 is comprised of the three modeling studies which were carried out under contract by three different research organizations: Georgia Institute of Technology (GIT), University of California at Riverside (UCR), and MCNC from Research Triangle Park, NC (now part of the UNC Carolina Environmental Program). Don Fox summarized the overall objectives of the modeling studies which were to develop reactivity metrics,

to investigate large geographical domains with multiday episodes, to compare different chemical mechanisms and to test the impact of substitutions. Don said that GIT and UCR evaluated relative reactivity metrics while MCNC evaluated performance metrics. Don Fox gave a summary of each of the research projects.

The GIT study used URM-SAPRC99 for two multiday episodes. A multiscale model with grids of 24 km<sup>2</sup> to 192 km<sup>2</sup> was used. Among findings of the study is that the relative reactivities are consistent with each other, independent of which metric is chosen; MIR-3D, MOIR-3D, or LS-RR, and for different averaging periods. The metrics compare reasonably well (for most species) among different episodes, different emissions scenarios and different domains. 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 for the test conditions in each study.

The UCR approach used a CAMx version 3.01 with DDM. Several different approaches were considered for deriving regional reactivity scales including regional maximum ozone, regional maximum incremental reactivity, regional MIR-MOIR, and regional average ozone. These metrics varied in how representative they were of the modeling domain. The first two reflected impacts only at one location, the Regional MIR-MOIR scales represents 4-7% of area in the full domain. The regional average ozone gives urban impacts the least weight of all the metrics considered. The study compared nine different metrics in regard to how wide the spread was between lowest reactive compound and highest reactive compounds. The results varied by a factor of three depending on which scale was used. This is a significant finding in that the scale chosen for regulatory purposes would influence how much credit was given for solvent substitutions. This study showed that scales derived from urban air shed models did not differ greatly from scales derived from more simple EKMA modeling, indicating that easier to use EKMA modeling might be valid to use in the future. This study also indicated that the position of individual chemicals in the various scales did not change a great deal from scale to scale. There was occasionally some shifting of a chemical by a few positions, but highly reactive chemicals remained highly reactive in all scales and low reactive chemical remained of low reactivity. Another significant finding was the averaging time for daily O<sub>3</sub> (i.e. 1-hour or 8-hour) does not significantly

affect relative reactivities.

The MCNC project used state-of-the-art modeling systems like SMOKE-MAQSIP over diverse chemical regimes and geographical regions to design and perform various VOC substitution scenarios and their subsequent analysis. MCNC studied several substitution scenarios using high versus low reactivity substitutions. They did substitutions by gram, mole and mol C. Among the MCNC conclusions was that, overall, more sensitivity was seen in the Eastern US domain than in the South central US domain, but both are dominated by biogenics. Gram-based substitutions yield relatively more sensitivity than mole-based or mol C-based substitution. Substituting highly reactive compounds with low reactive compounds does have an effect on ambient O<sub>3</sub>. VOC substitution strategy gives the same directional sense as a VOC reduction based strategy in improving air quality.

Tom Helms summarized what he had heard by saying he saw several things which we should take from this meeting. These include:

1. averaging time (1-hour or 8-hour) doesn't seem to matter in devising scales.
2. the spread between the lowest and highest reactive compounds can vary considerably depending on the scale used.
3. both removal and substitution of VOC are good ways of controlling ozone.
4. the ranking order of compounds on scales seems to hold up using different scales.

In response to item 4, Ted Russell said that there are exceptions in that a compound may switch three or four places on scale, compared to a different scale. Bill Rawson said we should not let the perfect be the enemy of the good in devising scales. Bill Carter said that the reactivity scale values have a  $\pm 30\%$  variability, so if policy can't stand that there is a problem. Tom Helms summarized by saying that relative position may change a little, but not much. If substitution is used, it should be among compounds that are far apart of the scale, not right next to each other.

One interesting discussion occurred after someone said that lowering mass of VOC could sometimes lead to more ozone formation

because the solvents in the reformulated low VOC product may be chemicals of much higher reactivity than the original solvents. This could lead to more ozone being formed. They said that lowering reactivity would never lead to more ozone. Deborah Luecken replied that there are circumstances where switching to a lower reactive solvent can lead to more ozone, if more of the lower reactive solvent is used after the substitution. This could occur when the solvent is transported over several days in an air mass. There is experimental evidence that the MIR values of two compounds which are wide apart in reactivity can become closer in reactivity over a several day reaction period. If there is more of the low reactive solvent than the originally high reactive one, the reactivity of the low reactive one may approach that of the high reactive solvent and make more ozone. Bill Carter concurred that this could happen in some situations.

#### **Thursday January 9, 2003**

Don Fox called the meeting to order at 8:00 AM.

#### *II RRWG Milestone Review – Don Fox (See Appendix B Milestone Review)*

Don Fox initiated a review of the status of projects being sponsored by the RRWG other than task 1579.1. Jon Kurland gave an update of the SENES, Ltd. effort to develop a model to predict environmental fate of chemicals and then to test the model on several chemicals. Dave Morgott said that Task 8 which is development of the SMOKE emissions pre-processor is on track. There was a discussion of Task 4 and whether the name of that task, i.e. "suitable source categories" or "suitable chemicals for reactivity," may be misleading. [Post meeting review of Task 4 history reveals the effort to focus on evaluating emissions suitable for reactivity-based controls]

Paul Makar described a Canadian project (funded at ~\$200,000 US) in which a graduate student was looking at partitioning of organic chemical between water and air. This work is being done in connection with Marion Diamond who is doing ambient air modeling and Paul Makar who is doing regional modeling.

Dan Baker said that another outcome of Task 2 is to determine if the

episodes we are using to model are typical of all episodes. He said we would determine this by looking at a larger number of episodes.

*Session IV. List of Additional Research Tasks  
Discussion by Group  
(See Appendix C.)*

Don Fox discussed follow up work. He proposed that RRWG have a team to review the three modeling reports and give comments. We need to have a date to finalize the reports for placing them on the internet. Bill Carter had a question about whether posting the larger reports on the NARSTO website would interfere with the authors publishing a summary article in scientific journal. Jeff West said that was not the past experience.

Don Fox said that comments on the three reports should be received within 5 weeks. Bill Carter said that after incorporating these comments the reports should be considered final reports. Don Fox suggested a team of four individuals to review the reports and to coordinate collecting comments from others. These individuals are:

Dan Baker  
Deborah Luecken  
Jon Kurland  
Bob Stallings

After discussion, Dongmin Luo's name was added to the list of reviewers to represent CARB which had funded the GIT study. We should not post the GIT report on the NARSTO web page until CARB has reviewed this.

There was a discussion of what further work we might get contractors to do. These are project that were listed.

1. Re-analyze the GIT output file to derive new metrics similar to those developed by the Carter report.
2. Evaluate the metrics and pick possibly two metrics to focus future efforts on. Dr. Carter said some of the metrics could possibly

be eliminated for scientific reasons, but that for most of them the decision on which to keep would be a policy decision. He recommended a one or two day workshop to focus on this issue and make decisions.

3. Robert Wendell said that he is interested in identifying uncertainties related to low NO<sub>x</sub> conditions. He said at 20 to 25 ppb low NO<sub>x</sub> conditions many compounds have low or even negative incremental reactivities. Dr. Carter said that low NO<sub>x</sub> conditions are one of the things that the new UCR smog chamber is slated to be used for.

4. Deborah Luecken wanted to fund a project on transport down wind to see what impact changes in reactivity in one location have on down wind areas. There was widespread agreement that this question should be put to rest by doing this type of modeling study. Deborah suggested Dr. Carter do this. Dave Morgott suggested that Dr. Russell also do this type of study using SAPRC.

At one point in the meeting, it was requested that the scientists in the room who expected that they might try to get contracts for future RRWG studies leave the room as the group was going to discuss funding and other specific aspects of projects. Some people did leave, notably Bill Carter and Ted Russell.

The question was asked, how is RRWG going to fund this new work? EPA representatives said that EPA currently has adequate budget to fund this work. The question is how to get the money contractually to the people whom RRWG thinks are most competent to do the work. EPA seemed to think that this might be worked out through existing contracts.

It was emphasized that we need to fund this new research as it would be an imposition to ask the current researchers to do more without further funding. The feeling was that RRWG had already gotten quite a bit from the current contractors for the amount of money already spent.

There was a discussion of the timing of future funding. If EPA takes 6 weeks to get the money out, it will be March 1 to start new work. If

the contractors do the work in 60 days, it will be late May or early June before results of the new work are available.

David Sanders suggested that we stay in frequent telephone contact with each other so as not to let momentum slide.

A tentative date of May 21 and 22 was suggested for the next RRWG meeting. There was some mention of possibly having the next meeting in Riverside, California so that everyone could tour the new UCR smog chamber. Initially at the formation of RRWG, there had been discussion that some RRWG meetings would be held on the West coast to accommodate members from the West. However, it appeared that the next meeting will be scheduled for Research Triangle Park, NC.

The meeting adjourned at 11:55 AM. There had been 37 people in attendance during all or part of the meeting.

### **Adjournment**

The meeting adjourned at 11:55 AM.

### Appendices

- A. Task 1579.1 Summary of Modeling Results –Fox
- B. January 9 03 RRWG Milestone Review
- C. List of Additional Research Projects Jan 09 03