RRWG Task 1579.1 Objectives and Modeling Results

Don Fox  January 8, 2003

- Goal
- To evaluate various approaches to represent and evaluate chemical reactivity in ozone formation; using existing tools, mechanisms and databases
- Three projects - GIT, MCNC and UCR

PC Modeling - Specific Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- To compare various platforms for tasks
- To investigate large geographical domains with multiday episodes
- To compare different chemical mechanisms
- To test impact of substitutions

Regional, Three-Dimensional Reactivity Assessment of Organic Compounds in Eastern US  GIT

- URM-SAPRC99
- Two multiday episodes
  - May 95 (average ozone period)
  - July 95 (high ozone period)
  - Future cast to May 2010 and July 2010
- Multiscale model – Grids 24km² to 192 km²
- Emissions – Gridded stationary, mobile and point sources and biogenics
- AQ and Met data from AIRS, NARSTO-NE and RAMS databases

URM Specifications

- Table 1 URM-1ATM specifications
  - Chemistry SAPRC-99
  - total number of species 109
  - steady state species 7
  - explicit VOCs 42
  - total number of reactions 252
  - number of photolytic reactions 31
  - chemical solver hybrid (Young and Boris, 1977)
  - Horizontal Transport finite element scheme
  - advection scheme RPM (Colella and Woodward, 1984)
  - Emissions processed using EMS-95
  - total number of emitted species 39

GIT Initial Output of Model Runs

- [Ozone] in all cells for all time periods
- Example of O3 peak for July 95 period
GIT Temporal Variation in Absolute Reactivities - Chicago

Underlying Reactivity Contributions to Ozone Formation - Approach

- GIT and UCR Evaluated Relative Reactivity Metrics; MCNC evaluated performance metrics
- Characteristics of Metrics
  - Extremes – a) Comparisons of metrics for cells containing maximum ozone value, b) highest sensitivity to VOC
  - Averages – a) average all information for cells containing Ozone maximum in domain
  - Intermediate – a) select cells with O3 above a threshold b) weight cells by relative contribution to ozone formation
- Requires common base mixture (or base case) for comparison

Metrics Terminology

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Metrics - Performance Evaluations

- Comparisons to Box Model MIRs
- Pattern of Metrics for each of four episodes (95 and 2010)
  - Comparison of California and East Coast
  - Comparison between episodes – May vs July
  - Comparison of present and future

Metrics to box models

Box Model MIR and LS-RR for July 95 Episode
(From revised draft report)

California and Eastern US LS-RR 1hr

y = 1.3592x - 0.2922
R² = 0.8376
January 8-9, 2003 Fox Summary of Preliminary Modeling Projects

GIT Summary

- 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.

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April 30, 2010 MCNC}

APPROACHES CONSIDERED FOR DERIVING REGIONAL REACTIVITY SCALES

1. REGIONAL MAXIMUM OZONE
   - Use reactivities at the time and location of the highest domain-wide daily maximum O3.
   - Addresses need to reduce peak O3.
   - Not a true global metric because it reflects impacts only at one location.

2. REGIONAL MAXIMUM INCREMENtal REACTIVITY
   - Use reactivities at the cell with the highest sensitivity of the daily maximum O3 to VOCs.
   - Represents impacts on regions where O3 is most sensitive to VOCs.
   - Comparable to the widely-used MIR scale.
   - Not a true global metric because it reflects impacts at only one location.
3. REGIONAL MIR-MOR
USE EFFECTS ON AVERAGE DAILY MAXIMUM \(O_3\) IN CELLS WHERE \(O_3\) HAS NEGATIVE SENSITIVITY TO NOx
- REPRESENTS IMPACTS NEAR SOURCE AREAS WHERE ONLY VOC CONTROLS WILL REDUCE \(O_3\)
- REPRESENTS CONDITIONS USED TO DERIVE \(MIR\) TO \(MOR\) SCALES
- REPRESENTS 4% OF AREA IN FULL DOMAIN

4. REGIONAL AVERAGE OZONE
USE EFFECTS ON AVERAGE OR TOTAL DAILY MAX.
GROUND-LEVEL \(O_3\) THROUGHOUT THE DOMAIN
- GLOBAL METRIC THAT WEIGHTS \(O_3\) SENSITIVITIES AT EACH LOCATION EQUALLY
- EFFECTS ON THE WIDESPREAD LOW \(O_3\) AREAS
WEIGHTED EQUALLY AS EFFECTS ON AREAS WHERE \(O_3\) IS A REGULATORY CONCERN
- GIVES URBAN IMPACTS LEAST WEIGHT OF ALL
THE METHODS CONSIDERED

Maximum Ozone Cell Distribution

Distribution of Cells VOC Sensitivity

LS-RR / MSE Metric
For 4 types of species
-Initiators
-Reactive
-Non Reactive – TOL
-Spread \(\Rightarrow\) Variability over domain
-In general consistency for majority of species, also agrees with Russell
Effect of Averaging Time on MSE Metric

Carter and Russell
Each conclude that
Averaging time not
Significant variable for
Reactivity Metrics

Metrics show
consistency with EKMA
approach
Result supported by
Carter and Russell Results

Development of a Scale from Metric derived
from Regional Modeling – From Bill Carter

- Classification of Reactivity Metrics by Effective
  Range.
- Consider upper and lower bounds for a scale
  Select Ethane for lower bound
  Select reactive species for upper bound OLE
- Ratio OLE/Ethane for various metrics to
  compare characteristics

Scales weighting
impacts throughout
large regions more
equally give the lowest
effective ranges (down
to ~20)

Scales dominated by
Urban or VOC-
sensitive regions give
highest effective
ranges (up to ~60 on
carbon basis)

UCR Conclusions
- Regional and EKMA models directionally consistent
  reactivity rankings by most metrics for the major types of
  reactive VOCs
- Incremental reactivity analysis can give fair estimates of very
  large scale substitutions
- Averaging time for daily maximum O3 does not significantly
  affect relative reactivities
- The effective range provides a useful means to classify
  relative reactivity scales
  reflects predicted maximum benefit of reactivity-based
  substitutions
correlated to relative reactivities of most species
Effective ranges of scales can vary by up to a factor of ~3 depend on how impacts in different types of regions are weighted
- EKMA and regional model scales give similar results for
  similar regions and metrics
**MCNC Project**

- Use 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 analyses.

**MCNC Approach**

- MAQSIP with CB4 and RADM2
- Two Multiday Eastern US episodes
  - Mid Atlantic June 96 – RADM2
  - Texas Gulf Coast Aug Sept 2000 – CB4
- SMOKE Emissions Processor
- MM5 Meteorology
- EPA 96 NET Emissions

**MCNC Episode Domains**

- MAQSIP Domain for 78x Project (500 km)
- MAQSIP Modeling Domain for Texas Air 2000 (555 km)

**MCNC Substitution Scenarios**

- Across-the-board 15% reduction of all pt and area anthropogenic VOC sources
- Substitutions
  - 15% of all pt/area VOCs Substituted by MEK
  - High vs low reactivity substitution. Xylene with glycol ether surrogate
  - Substitutions by gram, mole and mol C

**MCNC Outcome Metrics (comparison of base case with substitution)**

- Daily Maximum 1-h and 8-h Ozone
- Air Quality Index (AQI) Counts
- Persistence - Grid-hr
- Severity -- Grid-hr-ppm (Conc Weighted persistence)
- Photochemical Indicator Ratios (Used to ID VOC and NOx sensitive regions)

**MCNC Conclusions**

- “Persistence” and “severity” metrics are very comparable in most cases
- Overall, more sensitivity seen in the Eastern US domain (M1), than in the South central US domain (M2) BUT both are dominated by biogenics
- Gram-based substitution yields relatively more sensitivity than mole-based or mol C-based substitution
MCNC Conclusions

- Substituting highly reactive compounds with low reactive compounds does have an effect on ambient O₃
  - Mostly restricted to areas of high XYL in base case
- VOC substitution strategy gives same directional sense as a VOC reduction based strategy in improving Air Quality
- MEK substitution not as conclusive as anticipated for testing exemption threshold

Meeting Modeling Project Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- To compare various platforms for tasks
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Task 1579.1 - Specific Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- To compare various platforms for tasks
- To investigate large geographical domains with multiday episodes
- To compare different chemical mechanisms
- To test impact of substitutions

Meeting Modeling Project Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- Develop Metrics - Two types
  - Relative Reactivity Metrics (GIT and UCR)
    - GIT (3) and UCR (3 + 3)
  - Performance Metrics (MCNC)
    - MCNC (4)
Meeting Modeling Project Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- Sensitivity
  - Absolute and relative reactivities vary in space and time due to different environmental conditions and the individual metrics vary accordingly BUT in general remain consistent as a group (GIT/UCR)
  - Reactivity metrics have different effective ranges based on how they are derived (UCR)
- Models appear to be sensitive to substitutions based on reactivity (MCNC/UCR)

Meeting Modeling Project Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- Reactivity based substitutions appear to be in the right direction (MCNC)
- Null test results are variable depending on VOC or NOx sensitive regions (MCNC/UCR)

What Next
RRWG January 8-9, 2003
Session II – Milestone Review

RRWG Milestone Review

• Task 1579.1
  – Finalize Draft Reports for NARSTO Posting
  – Follow-up and New Research (To be developed)
  – Auxiliary to EPA OAQPS Process

• Task 3 Fate and Availability
  – SENES Ltd Finalizing Initial Model Project
    • Draft Report by end of January 2003
  – Second Effort to test model with surrogate species
    with range of physical and chemical parameters
RRWG Milestone Review

• Task 8  Emissions Processing Module
  – ACC Contracting with MCNC

• Other Tasks
  – Task 2 Classification of VOC/NOx Sensitive Regions
    - Some results coming out of 1579.1
  – Task 6 Existing Modeling Assessments and Task 10
    Existing Chamber Databases – Completed
  – Task 4 – Evaluating Emissions Suitable for
    – Reactivity-based Controls Suitable Chemicals for
      Reactivity —
      Some results from Task 3 and 1579.1
Session III – RRWG List of Possible Research Projects

Project 1

- **Task:** Complete review of current regional modeling draft reports
- **Approach:** Small Group (~4) RRWG Members review and provide single comments to PIs by January 24. PIs finalize reports and submit in 3 weeks.
- **Product:** Results of Regional Modeling in Public Domain – NARSTO Site or other suitable link.
Project 2

• **Task:** Analyze May and July 95 episodes with additional metrics utilizing SAPRC mechanism
• **Approach:** Re-analysis of output files from GIT regional modeling to derive additional metrics in UCR investigation
• **Product:** More robust set of metrics with detailed mechanism for subsequent evaluation

Project 3

• **Task:** Evaluate metrics to determine Pros and Cons
• **Approach:** Investigate parameters such as
  – effective range,
  – area (e.g., urban vs. rural, VOC or NOx sensitive, interurban corridor),
  – mechanistic role or chemical class (initiators, radical or NOx sinks, low reactive, high reactive);
  – underlying size of data set (one cell, VOC sensitive cells, above a threshold);
• **Product:** Results from which to select candidate metrics for future investigation and analysis
Project 4

• **Task:** Select two candidate reactivity metrics and conduct additional evaluation
• **Approach:** RRWG recommend (??) of two metrics. Further evaluation with respect to:
  - Underlying information set upon which they are based (one cell, all cells etc);
  - degree of consistency of species behavior (reversal in ranks, variably);
  - anomalies (species, behavior with localized substitutions etc).
• **Product:** Detailed characterization of two metrics testing next steps in the process (*work up to this point is based on regional modeling approach with 39 species*).

Directions and Options –

• 1. Work on how to consider much larger number of VOCs; guidelines for determining relative reactivities for placement on the metric based scale with an effective range (EKMA, fixed regional modeling scenario, chamber data, etc).
• 2. Error Analysis - Meaningful substitutions (gap between groups) vs. all substitutions (side by side)
• 3. Uncertainty analysis and reduction