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*

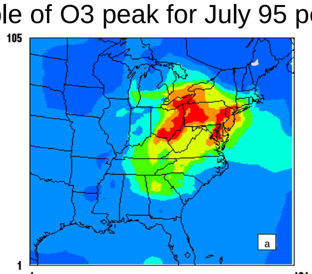
- URM-SAPRC99
- Two multiday episodes
  - May 95 (average ozone period)
  - July 95 (high ozone period)
  - Future cast to May 2010 and July 2010
- Multiscale model – Grids 24km^2 to 192 km^2
- Emissions – Gridded stationary, mobile and point sources and biogenics
- AQ and Met data from AIRS, NARSTO-NE 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	PPM (Colella and Woodward, 1984)
Emissions	processed using EMS-95
total number of emitted species	39

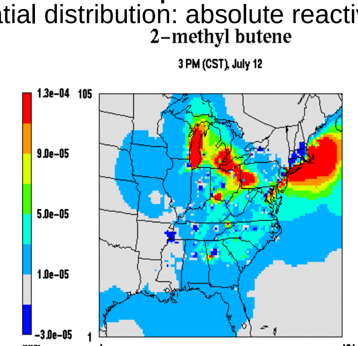
GIT Initial Output of Model Runs

- [Ozone] in all cells for all time periods
- Example of O3 peak for July 95 period

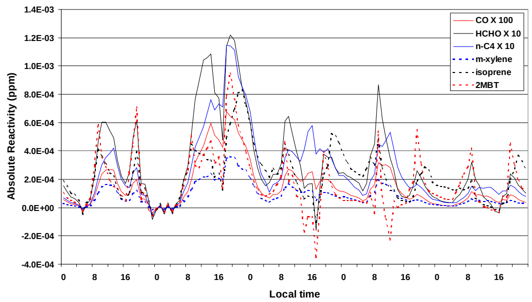


GIT Initial Output of Model Runs

Spatial distribution: absolute reactivities



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

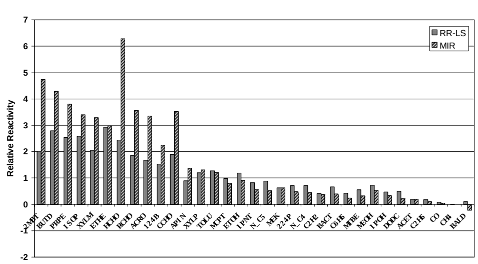
GIT	UCR	MCNC
MOIR – 3D 1-Hr and 8-Hr	Regional Maximum O3	Max Daily 1-h and 8-h Ozone
MIR-3D 1-Hr and 8-Hr	Regional MIR	Air Quality Index (AQI)
LS-RR	Min. Subst Error RR	Persistence
	MIR to MOIR	Severity
	Regional Average O3	Photochemical Indicator Ratios
	Reg. Ave. O3 over Std	

Metrics - Performance Evaluations

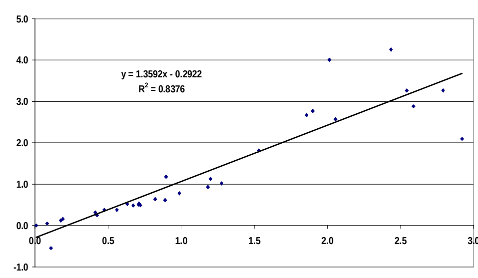
- Comparisons to Box Model MIRs
- Pattern of Metrics for each of four episodes (95 and 2010)
  - Comparison of California and East Coast
  - Comparison between episodes – May vs July
  - Comparison of present and future

Metrics to box models

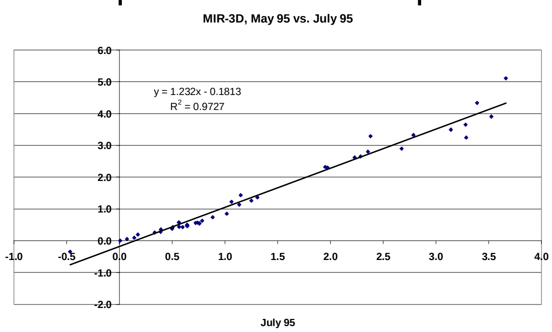
Box Model MIR and LS-RR for July 95 Episode
(From revised draft report)



California and Eastern US LS-RR 1hr



Comparison between Episodes



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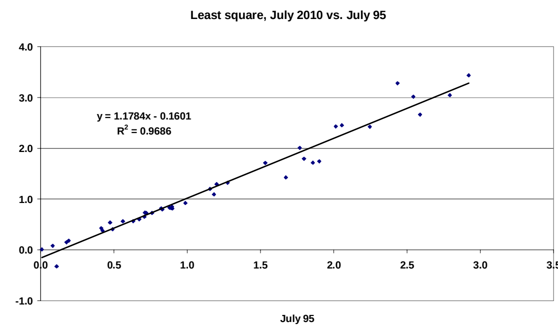
Metrics 1995 vs 2010 LS-RR



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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 the their potential effect on ambient ozone concentration.

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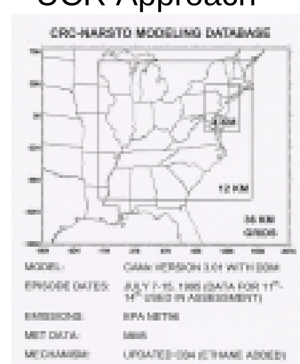
UCR Approach



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Metrics Terminology

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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 O_3

- ADDRESSES NEED TO REDUCE PEAK O_3
- NOT A TRUE GLOBAL METRIC BECAUSE IT REFLECTS IMPACTS ONLY AT ONE LOCATION

<u>**GIT**</u>

MOIR-3D

2. REGIONAL MAXIMUM INCREMENTAL REACTIVITY

USE REACTIVITIES AT THE CELL WITH THE HIGHEST SENSITIVITY OF THE DAILY MAXIMUM O_3 TO AVOCs

- REPRESENTS IMPACTS ON REGIONS WHERE O_3 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

MIR-3D

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APPROACHES CONSIDERED FOR DERIVING REGIONAL REACTIVITY SCALES

3. REGIONAL MIR-MOIR

USE EFFECTS ON AVERAGE DAILY MAXIMUM O_3 IN CELLS WHERE O_3 HAS NEGATIVE SENSITIVITY TO NO_x

- REPRESENTS IMPACTS NEAR SOURCE AREAS WHERE ONLY VOC CONTROLS WILL REDUCE O_3
- REPRESENTS CONDITIONS USED TO DERIVE MIR TO MOIR SCALES
- REPRESENTS 4-7% 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 WEIGHED EQUALLY AS EFFECTS ON AREAS WHERE O_3 IS A REGULATORY CONCERN
- GIVES URBAN IMPACTS LEAST WEIGHT OF ALL THE METHODS CONSIDERED

Approaches Considered for Deriving Regional Reactivity Scales

GIT LS-RR

5. REGIONAL AVERAGE OZONE OVER STANDARD

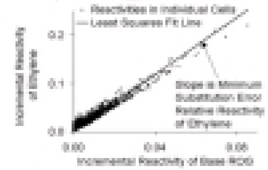
USE EFFECTS ON AVERAGE O_3 IN CELLS WHERE OZONE EXCEEDS U.S. AIR QUALITY STANDARDS

- 0.12 PPM CUTOFF FOR 1-HOUR SCALES, 0.08 PPM CUTOFF FOR 8-HOUR SCALES
- GLOBAL METRIC FOR REGIONS WHERE O_3 AIR QUALITY STANDARDS ARE NOT MET
- BUT DOES NOT ADDRESS IMPACTS IN AREAS WHERE SLIGHT O_3 INCREASES MAY RESULT IN EXCEEDENCES.

6. MINIMUM SUBSTITUTION ERROR

RELATIVE REACTIVITY THAT MINIMIZES THE SUM-OF-SQUARES CHANGE IN O_3 IN A NULL TEST SUBSTITUTION OF THE BASE ROG FOR THE VOC

- A "NULL TEST" IS A SUBSTITUTION THAT THE SCALE PREDICTS WILL NOT CHANGE O_3
- SAME AS SLOPE OF LINE, FORCED THROUGH ZERO, OF SPECIES vs BASE ROG REACTIVITIES

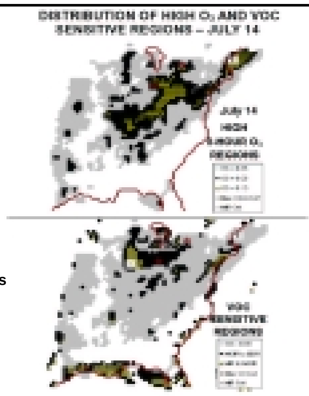


- WEIGHS EFFECTS ON HIGHEST O_3 AND MOST VOC-SENSITIVE AREAS MORE HIGHLY WHILE TAKING EFFECTS ON ALL AREAS INTO ACCOUNT

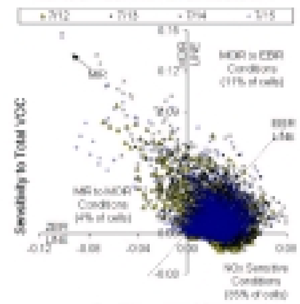
DISTRIBUTION OF HIGH O_3 AND VOC SENSITIVE REGIONS – JULY 14

Maximum Ozone Cell Distribution

Distribution of Cells VOC Sensitivity

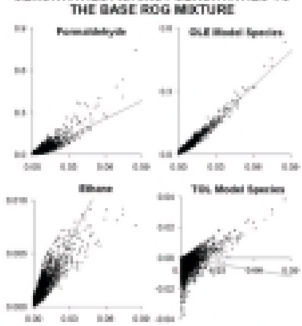


SENSITIVITIES OF MAXIMUM 1-HOUR AVERAGE O_3 TO TOTAL VOC AND NO_x



EACH POINT REPRESENTS ONE GRID CELL FOR EACH EPISODE DAY IN THE 36K DOMAIN

PLOTS OF MAXIMUM 1-HOUR AVERAGE O_3 SENSITIVITIES AGAINST SENSITIVITIES TO THE BASE ROG MIXTURE



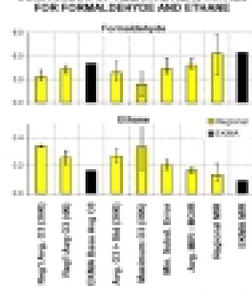
SLOPE OF LINE FORCED THROUGH ZERO IS MINIMUM SUBSTITUTION ERROR REACTIVITY

LS-RR / MSE Metric
For 4 types of species
•Initiators
•Reactive
•Non Reactive
•Most variable – TOL

•Spread ➔Variability over domain

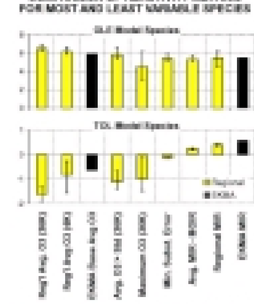
•In general consistency for majority of species, also agrees with Russell

COMPARISON OF RELATIVE REACTIVITIES FOR FORMALDEHYDE AND ETHANE



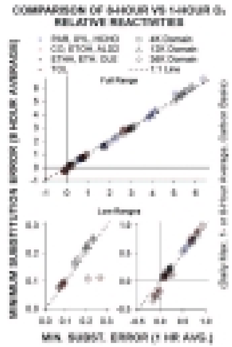
AVERAGES OF EFFECTS ON DAILY MAXIMUM 1-HOUR O_3 FOR 4 EPISODE DAYS ARE SHOWN. ERROR BARS SHOW RANGE BETWEEN MINIMUM AND MAXIMUM

COMPARISON OF REACTIVITY METRICS FOR MOST AND LEAST VARIABLE SPECIES

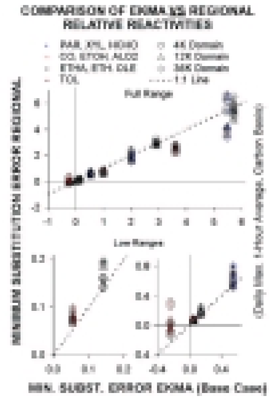


AVERAGES OF EFFECTS ON DAILY MAXIMUM 1-HOUR O_3 FOR 4 EPISODE DAYS ARE SHOWN. ERROR BARS SHOW RANGE BETWEEN MINIMUM AND MAXIMUM

Effect of Averaging Time on MSE Metric

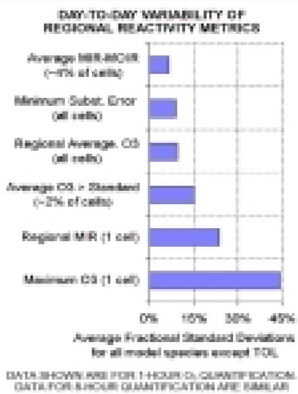


Carter and Russell Each conclude that Averaging time not Significant variable for Reactivity Metrics



Metrics show consistency with EKMA approach

Result supported by Carter and Russell Results



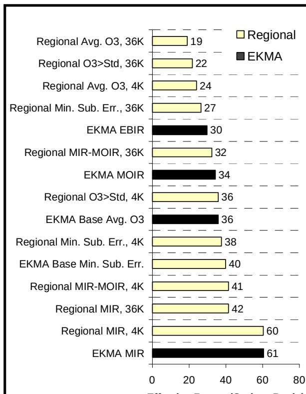
GIT
LS-RR

MIR-3D

MOIR-3D

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

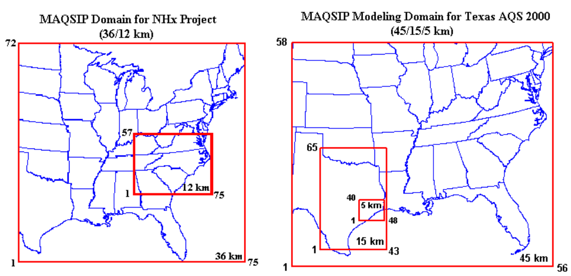
MCNC Project

- 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



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 O_3
  - 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

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 compare various platforms for tasks
  - URM, CAMx, MAQSIP
- To investigate large geographical domains with multiday episodes
  - EASTERN US 1995 July (GIT)
  - EASTERN US 1995 July (UCR)
  - EASTERN US 1995 May (GIT)
  - EASTERN US 1996 June (MCNC Southeast)
  - EASTERN US 2000 Aug-Sep (MCNC South central)
- To compare different chemical mechanisms
  - SAPRC 99 and CB4
  - RADM2 and CB4
- To test VOC substitutions
  - By UCR and MCNC

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)

Metrics Terminology

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Meeting Modeling Project Objectives

- To develop and assess reactivity metrics w.r.t. consistency, sensitivity, and directionality
- Consistency
  - Reactivity Metrics across episodes (GIT)
  - Reactivity Metrics across mechanisms (GIT/UCR)
  - Reactivity Metrics across chemical species (High reactive to low reactive)
  - Metrics across averaging times (GIT/UCR/MCNC)

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 base 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